MODIFICATION OF POLYPROPYLENE/HIGH DENSITY POLYETHYLENE BLEND USING NANOKAOLINITE CLAY AND E-GLASS FIBRE: PREPARATION, CHARACTERIZATION AND MICROMECHANICAL MODELLING

Thesis submitted to

Cochin University of Science and Technology

in partial fulfilment of the requirements

for the award of the degree of

Doctor of Philosophy

under the

Faculty of Technology

by

Anjana R

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Kochi- 682 022, Kerala, India

November 2014

Modification of Polypropylene/High Density Polyethylene Blend Using Nanokaolinite Clay and E-Glass Fibre: Preparation, Characterization and Micromechanical Modelling

Ph. D Thesis

Author

Anjana R
Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin- 682 022, Kerala, India
E-mail: anjan.nair@gmail.com

Supervising teacher

Dr. K.E. George
Retd. Professor
Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin- 682 022, Kerala, India

Principal
Albertian Institute of Science and Technology,
Archbishop Angel Mary Nagar,
Kochi, Kerala, India 682022
E-mail: principal@aisat.ac.in

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin- 682 022, Kerala, India

December 2014

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin- 682 022, Kerala, India

Dr. K.E. George
Retd. Professor

Phone: +91 9446447851
E mail: principal@aisat.ac.in

Date: December 2014

Certificate

This is to certify that the thesis entitled **"Modification of Polypropylene/ High Density Polyethylene Blend Using Nanokaolinite Clay and E-Glass Fibre: Preparation, Characterization and Micromechanical Modelling"** is a report of the bonafide research work carried out by Ms. Anjana R under my supervision and guidance in the Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-682 022, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral committee have been incorporated in the thesis.

Dr. K.E George
(Supervising Teacher)

Declaration

I hereby declare that the thesis entitled **"Modification of Polypropylene/ High Density Polyethylene Blend Using Nanokaolinite Clay and E-Glass Fibre: Preparation, Characterization and Micromechanical Modelling"** is based on the original research work carried out by me under the guidance and supervision of **Dr. K.E. George**, Retd. Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin-682 022 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

Cochin-22 **Anjana R**
December 2014.

Acknowledgements

I thank God Almighty for His abundant grace and blessings bestowed upon me to reach this milestone in my life.

It is a great pleasure for me to put on record my deep sense of gratitude for my guide, Dr. K. E. George. Principal, AISAT. (Retd. Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology), for his relentless support, constant encouragement and inspiration. His valuable suggestions and affectionate advice have been a source of constant inspiration for me throughout the tenure of my Ph.D work.

Prof. Dr. Sunil K. Narayanan Kutty, Head of the Department of Polymer science and Rubber Technology was kind enough to provide necessary facilities for the completion of my research work. I express my sincere thanks to him.

I am extremely thankful to Prof.Dr. Eby Thomas Thachil and Prof. Dr. Thomas Kurian, the former Heads of the department for rendering me necessary help and support. I also extend my thanks to all teaching, non teaching, office and library staff members of the PS&RT department for their valuable services, cooperation and support during the period of my research work.

My research committee members - Prof. Dr. Rani Joseph and Prof Dr Philip Kurian helped me in solving all the issues and hurdles in the course of my research. Rani teacher taught me the subject Polymer Science as part of the Ph.D course work and gave valuable suggestions in my research whenever I was struck in a cross road without knowing the direction. I am grateful to them.

I am thankful to Prof. Dr. Jacob Philip, former director, STIC and Prof. Dr. V.P.N Nampoothiri, Emiritus Professor, Department of Physics, for offering me the subject-Research Methodology, as part of my Ph.D course work.

I would like to express my heartfelt thanks to all my senior and co-researchers especially Dr. Bipin Pal P K, Dr. Jayalatha, Dr. Anna Dilfi, Dr. Saisy, Preetha K Nair, Dennymol, Dr. Ajalesh, Aiswarya, Abhilash, Sreejesh, Sona, Renju, Reshmi, Julie, Shadiya, Sreedevi, Jolly Sir and Newly teacher of the Department of Polymer Science and Rubber Technology for their help, cooperation and making my course of study a delightful experience. Me, Asha Krishnan and Tresa Sunitha George (my co-researchers at PS&RT Department) worked in a team and my research would not be successful without their help, wholehearted support and fruitful interactions. I am extremely grateful to Asha and Sunitha. I also thank all the project students especially Rohith and Anagha for their support.

I sincerely acknowledge the services rendered by staff of Sophisticated Testing and Instrument Calibration Centre STIC for testing my samples.

I gratefully acknowledge the support received from the staff members of Department of Chemical Engineering, Government Engineering College, Thrissur. Dr. Renjana Devi, Associate Professor, Department of Chemical Engineering introduced me into this field of research and I am grateful to her. I also acknowledge Dr. P A Soloman, Associate Professor, Department of Chemical Engineering, for introducing me into the field of DoE and Minitab. I highly appreciate my colleague-Ajeesh for his wholehearted willingness to help me to make attractive presentations and clarify all doubts during my research work. I am also grateful to Shameela teacher and I owe special thanks to my students Asha, Indira and Safeer for their help in completing my research.

I am thankful to the Government of Kerala, Department of Technical Education and Principal of Government Engineering College, Thrissur for granting me permission to do research. I feel privileged to place on record my sincere gratitude to Dr. K Vijayakumar, Principal, GEC, Thrissur and Dr. K Krishnakumar, Teqip Coordinator, for taking special pains for obtaining financial assistance for me to present paper in international conference at Dubai, from Teqip. I also acknowledge

Centre for Engineering Research and Development, CERD for providing me financial support as a research project.

Finally I express my deepest sense of gratitude to my beloved family members especially my husband, my children, my parents, my brothers and my maids for their help, encouragement and moral support which helped me a lot in completing this study.

Anjana R

Preface

The reinforcement with nanofillers greatly improves desirable properties of thermoplastics. The ability to develop and process nanocomposite materials into various products will be of critical importance in the development of polymer products in this era of life to meet the ever increasing demands. The need to promote organophilicity in place of the natural hydrophilic character in inorganic nanomaterials is a crucial prerequisite for the good performance of polymer-clay nanocomposites. When properly dispersed in polymer matrix, nanofiller can provide excellent reinforcement, even when present in very low filler loadings. Short fibre reinforced composites are finding ever increasing applications in engineering and consumer products. Short fibres are used in order to improve or modify certain thermo-mechanical properties of polymeric materials so as to meet specific application requirements or to reduce cost of the fabricated article. Short fibres can be directly incorporated into thermoplastics during processing along with other additives and the resulting composites are amenable to the standard processing steps and various type of moulding operations. But in most of the cases fibre reinforced composites require fairly high fibre loading to get the desired property. Higher fibre loading causes processing difficulty which increases the chance for the voids during manufacturing processes. This causes reduction in properties of short fibre reinforced composites. Hence a composite with low filler loading is always the optimum choice. Addition of small volumes of nanofillers into fibre composites can effectively improve the properties. This type of hybrid nanocomposites based thermoplastics are expected to possess attractive performance even at low filler loading. The main objective of the present study is to develop cost effective and highly versatile hybrid composite based on Polypropylene (PP)/High Density Polyethylene (HDPE) blends. To make the composite cost effective, surface modified kaolinite clay is used as the nanofiller while the proven glass fibre as the microfiller. The resultant nano and hybrid composites were characterized by analyzing thermal, mechanical, rheological and morphological behaviour. While many studies on nanocomposites focus on the importance of chemical surface modification and the use of compatibilizers, the role and importance of processing conditions are not extensively studied. Hence the optimization of processing conditions and filler loading is carried out using Box-Behnken method of Design of Experiments (DoE) and Minitab IV software. Further if the mechanical properties are not described by appropriate models, the application spectrum of the hybrid composite will be seriously restricted. Hence micromechanical modelling is performed in the last section to analyze the structure-property relationship and behaviour of the composites under applied load.

The thesis is divided into nine chapters as follows.

Chapter 1: Introduction

A review of earlier studies conducted on mechanical, thermal, rheological and morphological properties of nanoclay composites, short glass fibre composites and hybrid composites along with a review on design of experiments and micromechanical modelling is given in this chapter. The scope and objectives of the present work are also discussed.

Chapter 2: Experimental

A brief description of the materials and experimental procedures adopted for the preparation, analytical techniques and characterization methods used for the study of both nano and hybrid composites of PP/HDPE blend, nanokaolinite clay and E-glass fibre are presented in this chapter

Chapter 3: Preliminary experiments for selection of materials and range of experimentation

In this section the material system best suited to produce high performance nanocomposites and hybrid composites is selected and the range of melt compounding temperature is fixed by changing one factor at a time method. The results are organized in 4 sections.

In section 3.3.A, the effect of surface modification of nanoclay in improving the dispersion characteristics in polymer matrix is described. Five different commercially available surface modified nanoclays are added to the PP/HDPE blend and the mechanical, thermal and morphological properties are analyzed. Based on the results, amino silane modified nanoclay and unmodified nanoclay are selected to upgrade PP/HDPE blend.

Optimization of blend composition of PP/HDPE/nanokaolinite clay composites in the case of both unmodified and amino silane modified nanoclay is described in section 3.3.B. The mechanical properties are analyzed and 80 PP/20 HDPE blend is selected as the base polymer matrix.

Selecting the range of melt compounding temperature and glass fibre content suitable for the preparation of nano and hybrid composites are depicted in sections 3.3.C and 3.3.D respectively.

Effect of compatibilizers on the mechanical properties of PP/HDPE/ unmodified clay nanocomposites is illustrated in section 3.3.E.

Chapter 4: Mechanical properties of PP/HDPE/nanokaolinite clay composites.

In this part, the effect of modified and unmodified nanoclay on the mechanical properties of PP/HDPE matrix is described. Experiments are carried out according to the Box-Behnken design table and the contour and surface plots are drawn, which give a clear picture of response variation.

Model equations are developed to calculate the value of response at any combination of process variable within the experimental domain. The main effects plots are drawn to study the individual effect of each variable on the mechanical properties. The p (probability of occurrence) and ANOVA (Analysis of Variance) tests are carried out to investigate the relative effect of each process variable. Statistical evaluation is also carried out to check the adequacy of the model and the effect of process variables on the responses. The tensile strength, tensile modulus, flexural strength and flexural modulus increase on the addition of nanoclay where as the impact strength decreases.

Chapter 5: Characterization of PP/HDPE/nanokaolinte clay composites

The PP/HDPE/naokaolinite clay composites are characterized using thermogravimetric analysis(TGA), differential scanning calorimetry(DSC), dynamic mechanical analysis(DMA), dynamic rheological analysis(DRA), X-Ray diffraction(XRD), scanning electron microscopy(SEM) and transmission electron microscopy(TEM) in this section.

Chapter 6: Mechanical properties of PP/HDPE/nanokaolinite clay/E-glass fibre hybrid composites.

The mechanical properties of PP/HDPE/nanokaolinite clay/E-glass fibre hybrid composites are analysed in this section according to Box-Behnken experimental design. The synergistic effect of surface modified nano-micro filler suggests that organomodifed clay can act as a molecular bridge between the hydrophilic glass fibre and organophilic polymer matrix improving filler matrix adhesion and filler dispersion. This improves all the mechanical properties including impact strength. The model equations are developed, response surface, contour and main effects plots are drawn and statistical evaluation is carried out.

Chapter 7: Characterization of PP/HDPE/nanokaolinte clay/E-glass fibre hybrid composites.

The PP/HDPE/naokaolinite clay/E-glass fibre hybrid composites are characterized using TGA, DSC, DMA, DRA, XRD, SEM and TEM in this section.

Chapter 8: Micromechanical modelling of PP/HDPE/nanokaolinite clay composites and PP/HDPE/nanokaolinite clay/E glass fibre hybrid composites

Micromechanical modelling of both nano and hybrid composites is carried out to obtain a better understanding of the behaviour of composite under load bearing conditions. The experimental data on tensile modulus is compared with conventional composite theories & models like Halpin-Tsai model, Modified Halpin-Tsai model, Takayanagi model, Voigt rule of mixtures, Reuss inverse rule of mixtures and Ji's three phase model.

Chapter 9: Summary Conclusions

The summary and conclusions of the study are given in this section

Contents

Chapter 1

Chapter 2

Chapter 5

CHARACTERIZATION OF PP/HDPE/KAOLINITE CLAY NANOCOMPOSITES

Chapter 6

MECHANICAL PROPERTIES OF PP/HDPE /NANOKAOLINITE CLAY/E-GLASS FIBRE HYBRID COMPOSITES

Chapter 7

Chapter 8

Chapter 9

……

Chapter 1

INTRODUCTION

Contents

Introduction

History of mankind is classified into various ages as stone age, copper age, bronze age, iron age, plastics age, silicon age and finally composite age based on the most important material used. Polymers play a vital role in the development of composite materials. Polymers are widely used in engineering applications due to their ease of production, light weight, design flexibility and processability. However, polymers are of lower modulus and strength compared to metals and ceramics. One way to increase the applicability of polymeric materials is to reinforce with either micro or nano sized fillers

With the historic speech of Richard Feyynman, the concept of term ‘nano’ was first introduced to the scientific community. His historic statement “There is plenty of room at the bottom” was delivered to the American Physical Society in Pasadena in 1959. Later on, the nanoscale particles continue to fascinate materialists, physicists, biologists, chemists and scientists from all other disciplines. From then onwards, there was plenty of research with the nanomaterials, and the impact of these materials occurred in the field of composites materials also. The introduction of nanomaterials has created wonders in the performance and applicability of polymer composites Polymer nanocomposites (PNC) are being used for the manufacture of products ranging from day to day products to high end applications such as space research and development.

Increase in mechanical and thermal properties of the polymer matrix material is tremendous on the addition of even minute amount of nanofillers. The increase in properties is due to the enhanced filler-matrix adhesion and high aspect ratio of fillers. But nanofillers alone cannot give superior impact strength to composites. Incorporation of more than one type of filler into the same matrix will lead to the formation of hybrid composites. Hybrid composites made with both nano and micro sized fillers are now replacing the conventional polymer composites in all walks of life. In the case of conventional composites with micron sized fillers, filler content above 20% by volume is required to optimally impact mechanical properties. At these higher concentrations the filler can detrimentally affect other benefits of polymers such as processability and appearance. The micron sized filler loading can be significantly reduced by the combined addition of nano and micron sized fillers. Addition of both the type of fillers will synergistically modify all the polymer properties at a reduced filler loading, retaining low weight, processibility, durability and appearance.

The emerging importance of hybrid composites involving nanoscience and polymer technology affords unique opportunities to create novel materials with specific and useful properties. Such materials promise new applications by exploiting the unique synergisms between constituents that only occur when the constituents are present in the right proportions and processed with optimum operating conditions. Hybrid composites are at the peak of the pyramid in the hierarchy of structural materials due to their unique properties. They provide the designers with the unique freedom of tailoring composites and achieving properties that cannot be realized in binary systems containing one type of reinforcement dispersed in a matrix. Such systems have the potential of achieving a balanced pursuit of cost and performance through proper material design. Both nanocomposites and hybrid composites offer users significantly enhanced properties compared to conventional composites. To comprehend the property enhancement in both nano and hybrid composites, it is quite necessary to know more about the filler-matrix interaction and load bearing mechanism in these type of materials. In this study the optimization of processing and performance characteristics of polymer matrix composites with nano filler (polymer nanocomposites) and with both nano and micro filler (hybrid composites) are investigated in detail.

1.1 Composite materials

Composite materials combine with more than one material, most commonly a matrix material and a filler material comprising of high strength fibres or particulate matter. One of the earliest known composite materials is adobe brick in which straw (a fibrous material) is mixed with mud or clay. The straw allows the water in the clay to evaporate and distributes cracks in the clay uniformly, greatly improving the strength of this early building material. Later, in the twentieth century, when we speak of composite materials, or just "composites", we are referring to the highly engineered combinations of plastics/polymer resins and reinforcing materials such as high strength glass fibres. A fibre glass composite structure is a combination of glass fibres of various lengths with either thermosetting or thermoplastics. The term FRP is often used, meaning fibre reinforced plastic. FRP is a very general term for many different combinations of reinforcement materials and bonding resins. Thus, the term "composites" is used extremely broadly used to describe many materials with many different properties targeted at an even larger number of applications.

1.2 Classification of composites

Composites have been classified in different ways based on their occurrence, size, matrix system and on the type of filler used. They are classified as metal matrix, ceramic matrix and polymer matrix composites based on the matrix material that constitutes the composite. Depending on the size of filler material in the composite, they are classified as macro, micro and nanocomposites. Based on the type of reinforcement, they are classified as particulate reinforced, fibre reinforced, laminates and hybrid composites. Particulate fillers are used to improve high temperature performance, reduce friction, increase wear resistance and to reduce shrinkage. The particles share load with the matrix but, to a lesser extent than a fibre. Composites with greater tensile strength and stiffness are produced with fibrous reinforcements. A laminate is fabricated by stacking a number of laminae in the thickness direction. The incorporation of several different types of fillers, especially fibres and particulates into a single matrix, led to the development of hybrid composites. A balance in cost and performance is achieved through proper material design in the case of hybrid composites.

1.3 Polymer matrix composites

Global consumption scenario of polymers are increasing exponentially due to their low cost easy mouldability and light weight. One way to improve their mechanical properties is to reinforce them with particulate fillers like talc, mica, $CaCO_3$, kaolin, fumed silica or fibres like glass fibres, nylon fibres etc. Both thermosetting resins and thermoplastics are used to make polymer matrix composites. Polyolefins are a class of most widely used thermoplastics. Polyolefin based materials can be tailor made for a wide range of applications: from rigid thermoplastics to high performance elastomers. These vastly different properties are achieved by a variety of molecular structures, whose common features are low cost, excellent performance, long life cycle and ease of recycling[1-5]. Polyolefins make up approximately 50% of the plastics found in cars. Extensive use of polyolefins in automobiles not only helps to reduce weight and conserve fuel, but also provides added comfort and safety. Polypropylene (PP) and High density polyethylene (HDPE) are two important class of polyolefins that are used in various sectors like: automobiles parts, packaging industry, furniture, household articles, safety equipments, electric plugs, bottles, ropes, drum, pipes, lining of chemical vessels etc. Due to all these virtues, PP and HDPE are excellent candidates to be selected in this study as matrix material for polymer matrix composites

1.3.1 Polypropylene (PP)

Polypropylene is one of the most widely used commodity plastics, due to its superior properties like excellent processibility, commercial availability, comparatively low market price, weather, chemical, moisture and staining resistance etc. It is the lightest of common plastics (specific gravity of about 0.9), has a higher softening point, low shrinkage and immunity to stress cracking. PP has excellent and desirable physical, mechanical and thermal properties when used in room temperature applications. Isotactic PP has a melting point of about 165°C and has excellent electrical properties.

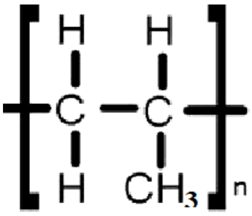


Figure 1.1 Chemical Structure of Polypropylene

1.3.2 High density polyethylene (HDPE)

High density polyethylene also ranks number one in world's consumption due to its special attributes like high strength to weight ratio, excellent chemical resistance and good processibility and recyclability. Moreover it has good impact resistance also. Melting point is about 130°C and density is in the range of 0.95-0.97 g/cm^3.

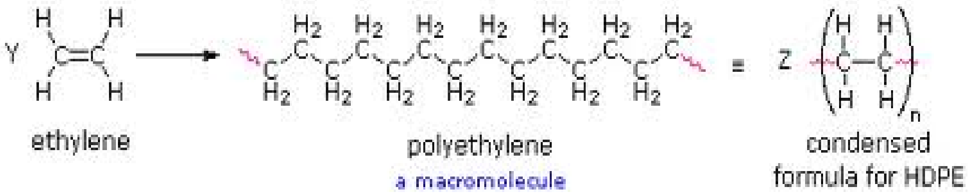


Figure 1.2 Chemical structure of high density polyethylene

Blending is the most attractive engineering method of producing new materials with tailor made properties. It has the advantages of both the materials. Hence Polypropylene/High density polyethylene blend is selected as the matrix material for up gradation. In order to improve the competitiveness of polyolefins in engineering applications, it is important to simultaneously increase stability, heat distortion temperature, stiffness, strength and impact resistance without sacrificing their processibility. Blending and modification of PP and HDPE by addition of nano/micro fillers as reinforcements can render them more flexible with a variety of other properties, and their competitiveness in structural and material applications can be greatly improved

1.4 Polymer nanocomposites

Nanofillers have now emerged as the ultimate reinforcing agents for polymers for improving their mechanical properties without affecting density, transparency and processibility[6-9]. Reinforcing polymers with nano sized clay particles yield materials with enhanced performance without recourse to expensive synthesis procedures[10-12]. Polymer nanocomposites (PNC) are a new class of materials that have attracted great interest in industry and academy.

Polymer nanocomposites are commonly defined as the combination of a polymer matrix and additives that have at least one dimension in the nanometer range (<100 nm). The additives can be one-dimensional (examples include nanotubes and fibres), two-dimensional (which include layered minerals like clay), or three-dimensional (including spherical particles)[13] as shown in figure 1.3.

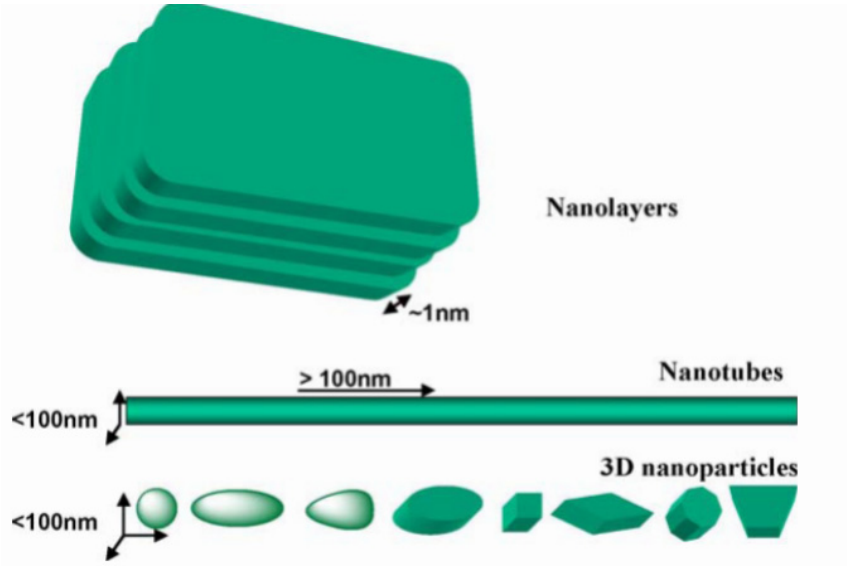


Figure 1.3 Types of nanoparticles[13]

Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of their nanometre sizes, nanocomposites with good filler dispersion exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability. Due to nanometer length scale which minimizes scattering of light, nanocomposites are usually transparent[14]. The main reason for these improved properties in nanocomposites is the nanometer scale of the dispersed fillers and the interfacial interaction between matrix and nanomaterial as opposed to conventional composites[15].

Global cost of nanofillers are demonstrated in figure 1.4. In particular, clay silicates (e.g. nanoclay) and carbon nanotubes are two most popular nanofillers under the wide investigation and commercialisation. Nanotubes show the superior electrical and thermal conductive properties to fabricate the multifunctional PNC, but confronted with limited usage owing to a much higher reported price as shown in figure 1.4.

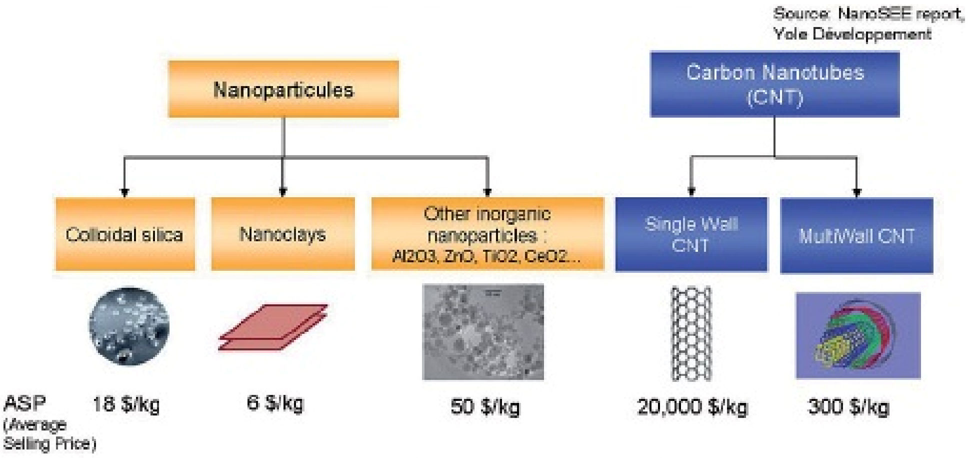


Figure 1.4 Comparison of cost of nanoparticles

In addition, the health hazards related to handling nanotubes are still uncertain though the laboratory-scaled techniques are available to prepare polymer/nanotube composites. Hence, much greater attention has been drawn to clay silicates since they are more cost-effective and eco-friendly with a reasonable price and have broad utility in reinforcing common thermoplastics like polypropylene (PP), high density polyethylene (HDPE), polystyrene (PS), polyethylene terephthalate (PET) and nylon. More remarkably, the addition of nanoclay helps to considerably enhance their mechanical, thermal, barrier and heat retardant properties. Clay and layered silicate fillers have been most widely investigated for this reason, and now there is a wide body of knowledge on their use in polymer composites[16-18].

1.5 Polymer/clay nanocomposites (PNC)

In the last few decades, inorganic clay minerals, such as montmorillonite, have been widely used as reinforcement materials for polymers due to their nanoscale size and intercalation/ exfoliation properties[19-21]. Nanoclays are less expensive than other nanomaterials (as carbon nanotubes), partly because they are produced in existing, full-scale production facilities and because the basic materials come from readily available natural sources[22].

Two major findings that have stimulated the revival of interest in these materials: first, the report from the Toyota research group of a Nylon-6/montmorillonite (MMT) nanocomposite[23], for which very small amounts of layered silicate loadings resulted in pronounced improvements of thermal and mechanical properties; and second, the observation by Vaia *et al.*[24] that it is possible to melt-mix polymers with layered silicates, without the use of organic solvents. Today, efforts are being conducted globally, using almost all types of polymer matrices. In order to make stiffer, light weight and high performance material products, polymer nanocomposites now play an emerging role in the era of material science

1.5.1 Structure and classification of nanoclays with special reference to nanokaolinite clay

Nanoclay is one of the most commonly used nanofillers of today. Clay minerals appear in various structural forms but most commonly used grades in nanocomposite production belong to the family of layered aluminium silicates. They consist of silicate platelets where SiO_4 tetrahedrons and AlO_6

octahedrons are organized in various combinations. When one octahedral sheet is bonded to one tetrahedral sheet, an 1:1 clay mineral results. The 2:1 clays are formed when two tetrahedral sheets bond with one octahedral sheet. The 2:1 clays for example montmorillonite etc. are inherently capable of intercalating or exfoliating in polymer matrix. Other clay materials such as 1:1 structures, 2:1 pyrophillites and mica are not commonly used in polymer nanocomposites because they do not have useful intercalation/ exfoliation characteristics and they are not easily separated into layers (the different types of clays and their composition are shown in Table 1.1). Due to the higher charge density on the layers they are strongly stacked together and the hydration of inter layer cations or intercalation of polymer chains between layers are difficult or not possible. To increase intercalation, surface modification of clay and proper processing conditions are necessary in case of 1:1 clays

Table1.1 Classification and example of clay minerals[8]

Structure	**Group**	**Mineral examples**	**Ideal composition**	**Basal spacing (Å)**
2 : l(TOT)	Smectite	Montmorillonite Hectorite Saponite	$[(Al_{3.5-2.8}Mg_{0.5-0.2})(Si_8)O_{20}(OH)_4]\ Ex_{0.5-0.2}$ $[(Mg_{5.5-4.8}\ Li_{0.5-1.2})(Si_8)\ O_{20}(OH)_4]\ Ex_{0.5-0.2}$ $[(Mg_6)(Si_{7.5-6.8}\ Al_{0.5-1.2}\ O_{20}(OH)_4]\ Ex_{0.5-0.2}$	12.4-17.0
2 : l(TOT)	Illite	Illite	$[(Al_4)\ (Si_{7.5-6.8}\ Al_{0.5-1.2})\ O_{20}(OH)_4]\ K_{0.5-1.5}$	10.0
2 : l(TOT)	Vermiculite	Vermiculite	$[(Al_4)\ (Si_{8.8-8.2}\ Al_{1.2-1.8})\ O_{20}(OH)_4]Ex_{1.2-1.8}$	9.3-14.0
1 : l(TOT)	Kaolin serpentine	Kaolinite dickite, nacrite	$Al_4Si_4O_{10}(OH)_8$	7.14

The idealized structure of the kaolinite mineral is that of a single sheet of hydroxyls octahedrally coordinated to aluminium cations linked to a single sheet of oxygen tetrahedra centred by silicon atoms. The combined layer has a unit cell thickness of 0.713 nm[25]. The structure of kaolinite is shown in figure 1.5. It neither swells when wet nor shrinks when dry, which makes it well suited for various applications. It has a relatively low cationic exchange capacity. Although kaolinite is cheaply and abundantly available and used industrially as filler in paints and varnishes, it is very difficult to disperse in its nano-form into the polymer matrix. This is due to its 1:1 structure, smaller interlayer spacing and hydrophilic nature. To improve miscibility with other polymer matrices, one must convert the normally hydrophilic silicate surface to organophilic, which makes intercalation possible with many engineering polymers.

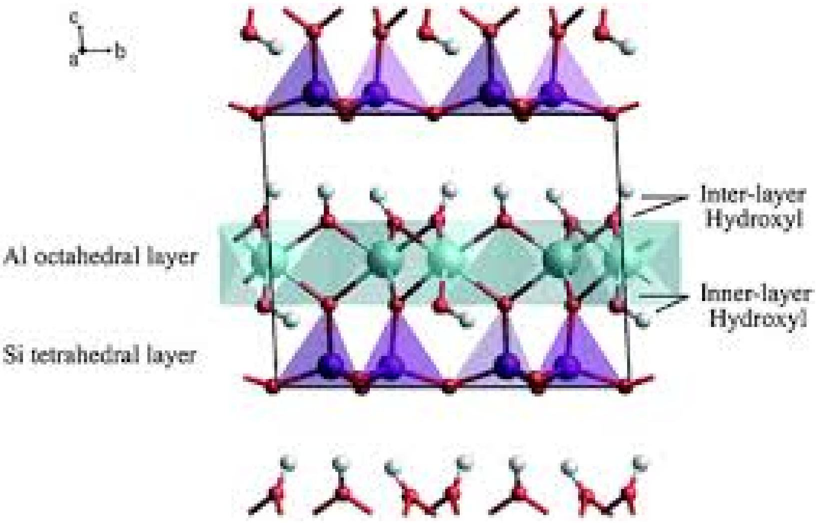


Figure 1.5 Structure of kaolinite clay

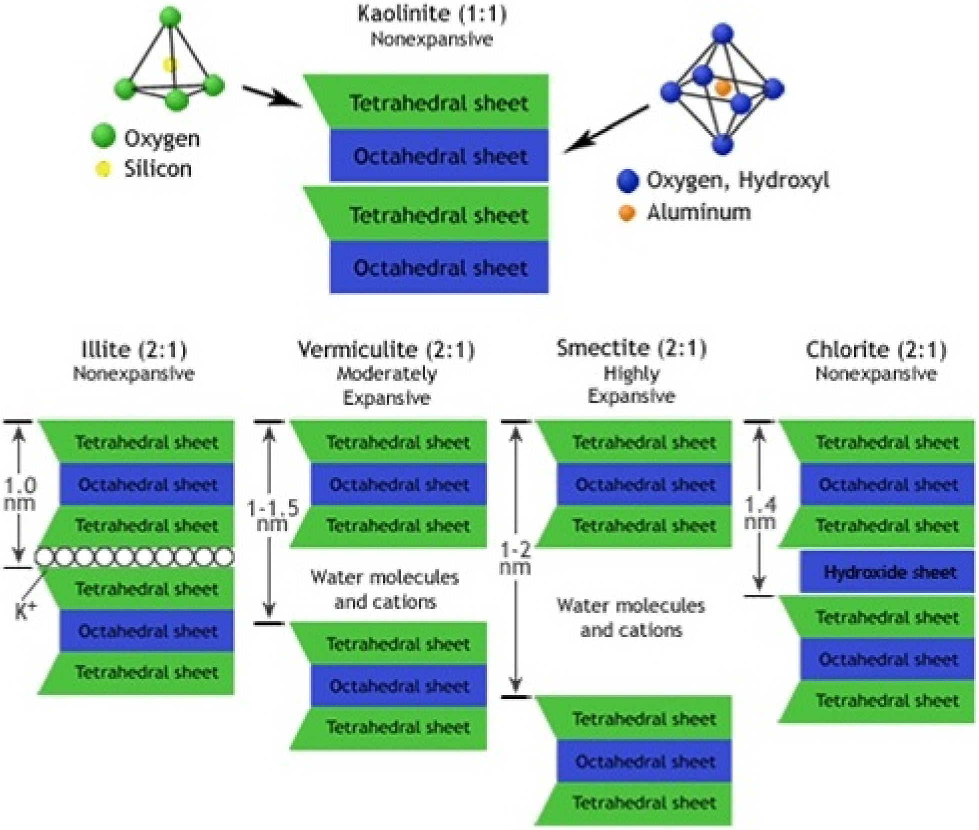


Figure 1.6 **Comparison of structure and interlayer spacing of kaolinite and other clays**

Although great amount of literature is available on polymer nanocomposites containing montmorillonite clay (MMT) as nanofiller, scarce amount of work has been done on abundantly available kaolinite clay. This is due to the 1:1 structure of nanokaoloinite clay which shows less dispersion characteristics compared to MMT[26]. To increase dispersion and filler matrix adhesion surface modified clays are used in polymer nanocomposites[23,27-35].

1.5.2 Surface modification

Two particular characteristics of layered silicates are generally considered for polymer nanocomposites. The first is the ability of the silicate particles to disperse into individual layers. The second characteristic is the ability to fine-tune their surface chemistry through ion exchange reactions or pre-intercalation by guest displacement method. The physical mixture of a polymer and layered silicate may not form a nanocomposite. This situation is analogous to polymer blends, and in most cases separation into discrete phases takes place. In immiscible systems, which typically correspond to the more conventionally filled polymers, the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the layered silicate in polymer nanocomposites lead to the organic and inorganic phases being dispersed at the nanometre level (exfoliated nanocomposite). As a result, nanocomposites exhibit unique properties not shared by their micro counterparts or conventionally filled polymers[23,27-35]. Obviously, in its pristine state, layered silicates are only miscible with hydrophilic polymers, such as poly ethylene oxide (PEO)[38], or poly vinyl alcohol (PVA)[39]. To render layered silicates miscible with other polymer matrices, one must convert the normally hydrophilic silicate surface to an organophilic one, making the intercalation of many engineering polymers possible. This process is termed as surface modification (figure 1.7). The usual procedure to achieve surface modification is either by ion-exchange or by intercalation and surface treatment through guest displacement method.

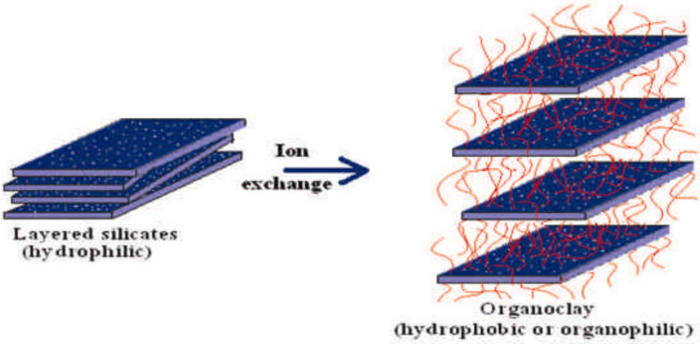


Figure 1.7 Mechanism of surface modification

The structure of kaolinite clay posses difficulty in undergoing surface modification by ion exchange method. Each layer bears no charge due to the absence of isomorphic situation in either octahedron or tetrahedron sheet. Thus, except for water molecules, neither cations nor anions occupy the space between the layers and the layers are held together by van der vaal's forces and hydrogen bonding between hydroxyl groups in the octahedral sheets and oxygen in the tetrahedral sheets of the adjacent layers[18,42]. Hence the surface modification is usually done by guest displacement method. It is also difficult to ensure higher degree of intercalated or exfoliated composites with nanokaolinite clay.

Kaolinite ($Al_2Si_2O_5(OH)_4$) is a layered aluminosilicate of the 1:1 type that is formed by two different types of interlayer surfaces. From one side, the lamellar face resembles the structure of gibbsite, with aluminum atoms coordinated octahedrally with oxygen and hydroxyl groups. The other face of the lamella resembles the structure of silica, where silicon atoms are coordinated tetrahedrally with oxygen atoms of the lattice[36,40-41]. Therefore, hydroxyl groups are exposed at one side of the lamella (the Al side), whereas the other is surrounded by oxygen atoms (the Si side). Adjacent layers are linked to one another by hydrogen bonds involving both Al and Si groups (Al–O–H· · ·· · ·O–Si). As a result of this close fitting, the tightly associated lattice of kaolinite is not accessible to intercalation compounds and this justifies its low susceptibility to chemical modification. The most common compounds used for direct intercalation are dimethylsulfoxide (DMSO) and N-methylformamide (NMF) as basal space expanders[37]. The intercalants are then hydrolysed and amino triethoxy silane is incorporated by guest displacement method to change virgin nanokaolinite to organoclay. Recently nanocomposites based on kaolinite clay were prepared by these pre-intercalated and surface modified nanokaolinite clay. In this study five different commercially available surface modified nanoclays are used to make composites with polymer matrix and are compared with the properties of pure matrix

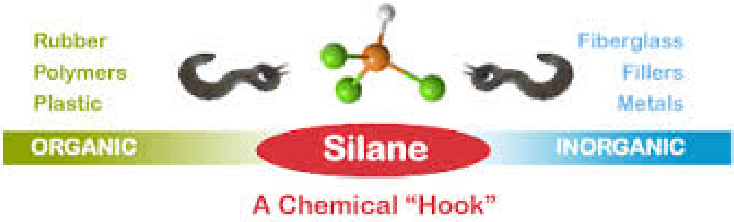


Figure1.8 Mechanism of surface modification by amino silane

1.5.3 Classification of polymer/clay nanocomposites

In general, layered silicates have layer thickness on the order of 1 nm and a very high aspect ratio (e.g. 10–1000). A few weight percent of layered silicates that are properly dispersed throughout the polymer matrix thus create much higher surface area for polymer/filler interaction as compared to conventional composites. Depending on the strength of interfacial interactions between the polymer matrix and layered silicate (modified or not), three different types of polymer nanocomposites are thermodynamically achievable (see fig 1.9):

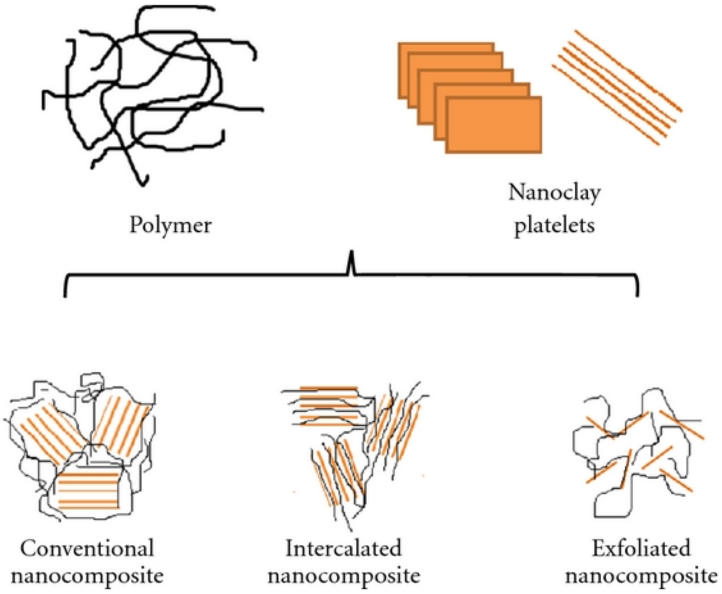


Figure 1.9 Types of nanocomposites[49]

a) Conventional nanocomposite: In this silicate layers were agglomerated and encircles by the polymer layers. The filler/matrix interaction is very weak and the properties are similar to the conventional microcomposite.

b) Intercalated nanocomposites: In intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer. Properties of the composites typically resemble those of ceramic materials.

c) Exfoliated nanocomposites: In an exfoliated nanocomposite, the individual clay layers are separated in a continuous polymer matrix by an average distances that depends on clay loading. Usually, the clay content of an exfoliated nanocomposite is much lower than that of an intercalated nanocomposite. These composites show excellent enhancement in properties.

1.5.4 Advantages of polymer/clay nanocomposites

- Enhanced mechanical properties even with low filler loadings (<5 wt%)
- High thermal stability and heat distortion temperature
- Excellent flame retardant, oxidative properties and reduced smoke emissions
- Chemical and corrosion resistant
- Better surface appearance, colourability and paintability
- Low electrical conductivity
- High optical clarity and transparency
- Good recyclability
- Less permeable to gas, oxygen, water, better barrier properties
- High strength to weight ratio
- Very good processibility.

1.5.5 The current global market trend for polymer/ clay nanocomposites

Global consumption of clay based nanocomposites was 46,044 metric tons with a value of $232.5 million in 2008 and the value increased to $893.6 million in 2011. By 2014, the consumption increased exponentially by 1181,094 metric tons with a value of $1856. The consumption is expected to increase with a compound annual growth rate of 32.4% and will reach a value of $2500 by 2016 (graphically represented in fg.1.10).

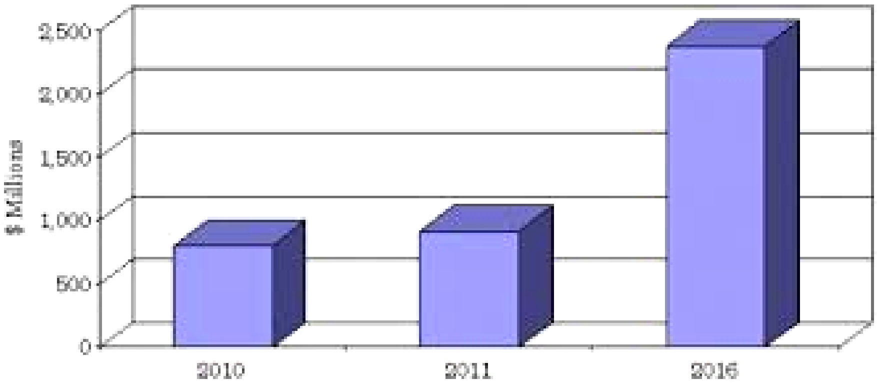


Figure 1.10 Worldwide consumption patterns of polymer/clay nanocomposites

1.5.6 Applications of polymer/clay nanocomposites

Polymer/clay nanocomposites represent a very exciting and promising alternative to highly filled conventional composites with the multifunctional material properties. Their wide range of applications have been achieved in recent years through the commercial development, involved with major automotive and packaging industries. It is very encouraging that the potential markets for polymer/clay nanocomposites might also expand in the near future to more versatile fields of building and construction, biomedical and bioengineering applications[43].

a) Automotive applications

With the increasing global demand on the fuel efficiency and low emissions for transportation and manufacturing, (PNC), as a novel class of reinforced polymeric materials, become very suitable to replace the metals in the automotive industry due to their low-cost, high-performance, light weight characteristics and superior mechanical, thermal and feasible processing properties. The key nanocomposite properties [44] for automotive application consist of (i) enhanced modulus and dimensional stability; (ii) higher heat distortion temperature; (iii) improved scratch and wear resistance and (iv) well balanced toughness and rheological properties, which most likely result from the good clay dispersion and strong compatibility between clay particles and the polymer matrix. The pioneering work was carried out by Toyota Motor Company to make the timing-belt cover using nylon 6/clay nanocomposites in early 1990's, which is known as the first commercial practical example for automotive application[43-44]. Good rigidity, excellent thermal stability and no wrap characteristics are demonstrated with the weight saving of 25%. Apart from nylon 6, polyolefin nanocomposites were employed by General Motors in moulding step assists on Safari and Chevrolet mid-size vans in 2002, Due to the small amount of additive clay materials (~2.5 wt%) in the polymer matrix, polyolefin nanocomposite parts cost about as much as those from neat polymer. Furthermore, conventional moulding tools do not need to be altered in order to fit the new product manufacturing lines. More recently, the usage of polyolefins further expanded to mould a variety of automotive parts including the vehicle trim, centre bridge, sail panel and box rail protector in 2005 General Motors Hummer H2 SUT cargo. The other successful story is the commercialisation of FORTE™ polypropylene (PP)/clay nanocomposites fabricated by Nobel Polymers in application for seat backs of the 2004 Acura TL[45-46]. From the aforementioned applications, there is no doubt that polymer/clay nanocomposites with versatile superior properties and cost-competitive feature can become the potential materials in various vehicles for making automotive exteriors and interiors such as dashpots, bumpers and mirror housings, etc. In addition, the weight advantage of nanocomposites also has a significant impact on the environmental protection and material recycling. The history of evolution of PNC is shown in fig.1.11.

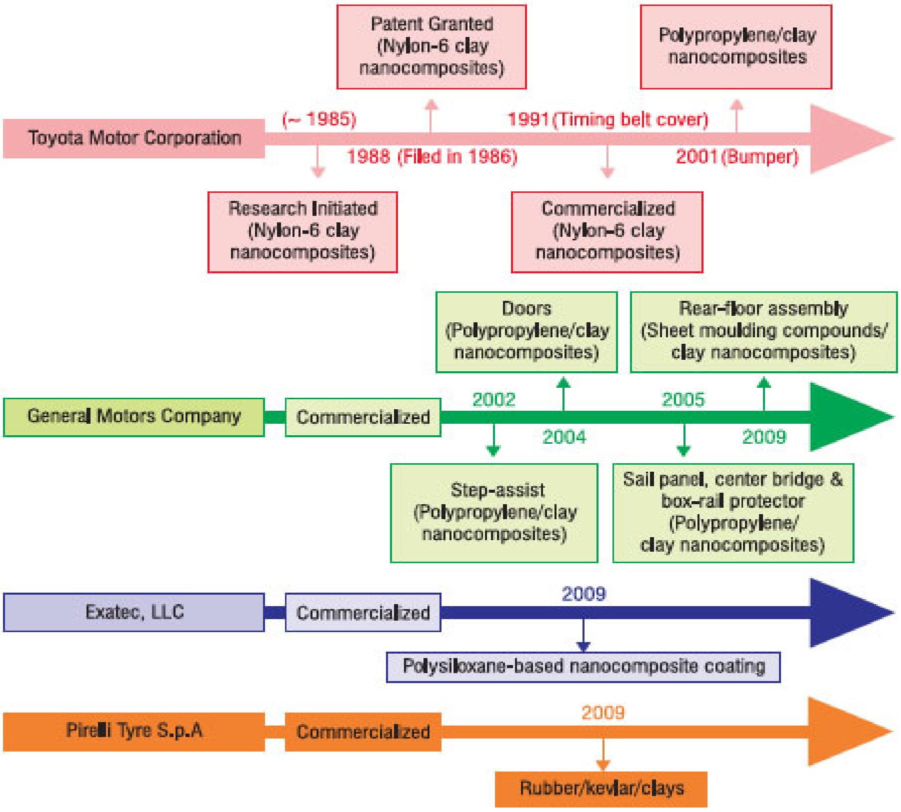


Figure 1.11 History of automotive applications of polymer/clay nanocomposites[46].

b) Packaging materials

The second major application of polymer/clay nanocomposites lies in food product packaging. A critical problem in packaging industry arises from the oxygen permeability that promotes the decay in beverages and dairy products stored in the plastic bottles and containers. The excellent barrier properties of nanocomposites result in the considerable enhancement of shelf-life and flavour preservation for many packed foods. The improvement of barrier properties are attributed to the fact that well exfoliated clay platelets work as obstacles to the gas/liquid molecular diffusion by creating a tortuous or zigzag extended pathway as opposed to a straight penetration for corresponding unfilled polymers Both Mitsubishi Gas Chemical and Honeywell used nylon/clay nanocomposites as barrier layers in multi-layered PET bottles and films for food packaging[45]. In particular, Honeywell's AegisTM nylon 6 nanocomposites more as the barrier layer provided a 26- week good shelf life. For handling toluene and light hydrocarbon fluids, LG Chem Ltd, South Korea, developed high-barrier, monolayer blow moulded containers using high density polyethylene (HDPE)/clay nanocomposites (clay content: 3-5 wt%), which achieved significant permeability reduction of hydrocarbon solvents by 40 to 200 times compared to neat HDPE[45].

c) Flame retardancy

Flame retardancy, from an engineering point of view, is another important issue to prevent the fire hazards caused by the ignition of materials. Extensive research work[47] at the National Institute of Standards and Technology (NIST), USA, has revealed that the rate of heat release would be reduced by 32% and 63% by adding 2 wt% and 5 wt% clay particles to nylon 6, respectively, which was experimentally validated in gasification tests.

d) Miscellaneous applications

Polymer/clay nanocomposites are not limited to the aforementioned areas, but can be implemented in the other broad areas such as coating and pigments, electro-magnetic materials, drug delivery and sensors and medical devices[43] which is illustrated in figure 1.12. Extensive applications for such nanocomposites are currently under thorough investigation to strengthen their economic benefits as the promising alternative of conventional composites.

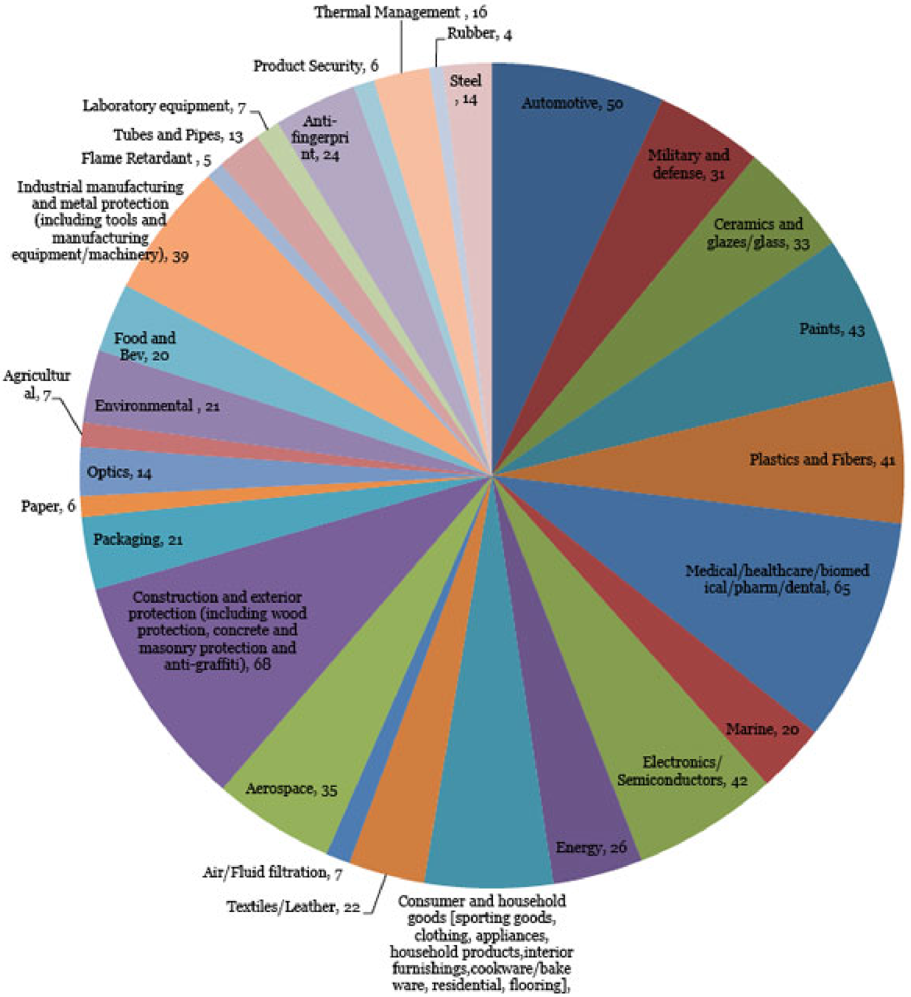
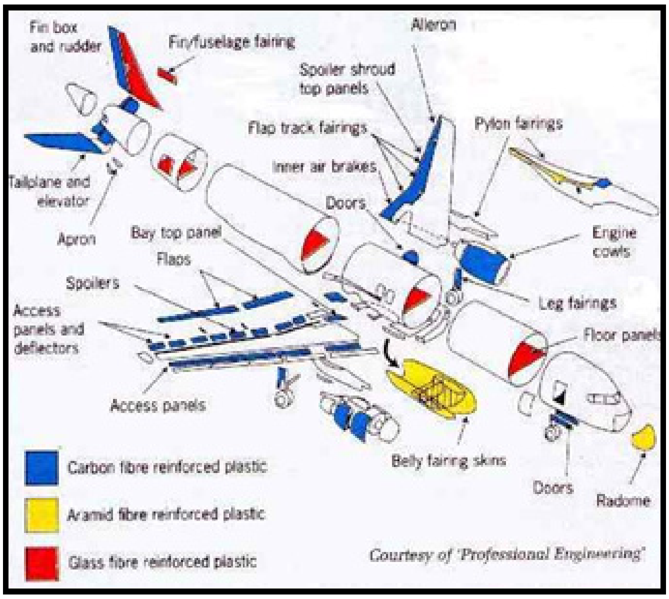


Figure 1.12 Applications of polymer/clay nanocomposites[43]

1.6 Hybrid composites

Hybrid composites are materials made by combining two or more different types of fillers in a common matrix. By hybridization it is possible to achieve a balance between performance properties and cost of composite, which would not be obtained by a single kind of reinforcement. Hence by careful selection of reinforcements and processing techniques, it is possible to engineer the hybrid material to better suit the various practical requirements with economic benefits.

Glass fibre – reinforced micro composites with polymer matrix has been widely used in automotive and aerospace industries for their high strength and light weight properties. Glass fibres (gf) demonstrate excellent thermal and impact resistance, high tensile strength, good chemical resistance and outstanding insulating properties. Therefore they are used in high performance applications in the industry as shown in figure 1.3.



Courtesy of 'Professional Engineering'

Figure1.13 Glass fibre reinforced plastic parts in aeroplane

1.6.1 E-glass fibre

Depending on the composition, various types of glass fibres are produced and supplied. They are available in various trade names as A,C,E,R and S. E-glass or electrical grade glass (alumina-borosilicate, low alkali composition glass) is selected for the present study as it can provide good strength, high stiffness, relatively low density, non flammable, resistant to heat, good chemical resistance, relatively insensitive to moisture, able to maintain strength properties over a wide range of conditions and good insulation property. It is easily available in different grades and is cost effective. Because of electrical resistance it is suited for applications where radio signal transparency is desired as in air craft radomes and antenna.

The concentration of reinforcing filler commonly used in glass fibre reinforced-polymer micro composites is 15% to 50% by weight. It is reported that addition of high concentration of fillers have drawbacks such as increased moulded part weight, brittleness, opacity and processing difficulty. At higher fibre loadings the long term durability of the polymer is decreased. To overcome these drawbacks, a hybrid composite with improved properties and low filler concentration is highly desirable.

The concept of combining nanocomposites as matrix material with fibre reinforcement in a new three-phase composite reinforcement (hybrid composites) has been shown to be very successful. Lighter, thinner, stronger, and cheaper structures are the goals of materials science and engineering applications nowadays. In addition to improving recyclability of the fibre reinforced composites, the improved properties of the nanocomposite matrix material may upgrade the properties of relatively low-cost composites up to the level of high performance composites and further increase the temperature resistance of existing high-performance composites. The added cost of the nano-filled matrix can be small due to the low amounts of filler necessary for a significant improvement.

Development of polymer/clay/glass fibre hybrid composites is one of the latest evolutionary steps in polymer technology. This have attracted great attention due to potentially large improvements in mechanical and physical properties that can be achieved by incorporating small amounts of clays (1-3wt%) into glass fibre/polymer composites. The simultaneous use of clay and fibre fillers, so called hybridization, leads in many cases to synergistic effects, improving properties such as impact strength, wear resistance, stiffness, fracture toughness and dynamic response. Structure of polymer-fibre-nanoclay hybrid composite is given below(fig. 1.14)

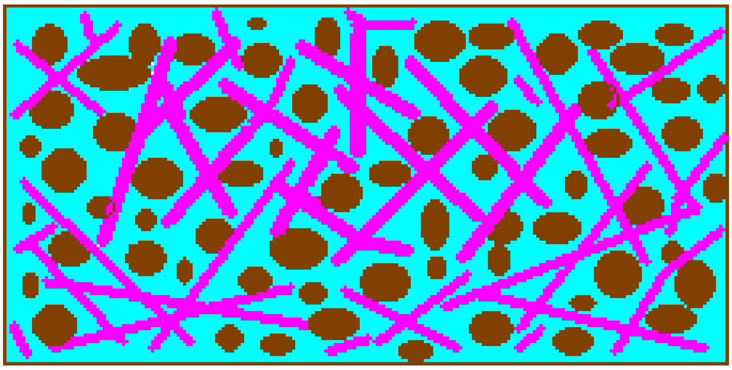


Figure 1.14 Structure of polymer/nanoclay/short glass fibre hybrid composites.

1.6.2 Synergistic effect of glass fibre and organomodified nanoclay in hybrid composites

Liu *et al.*[48] has shown that inclusion of nanoclay alters the crystallinity of the matrix and lead to a decrease in impact strength. But glass fibres on the other hand are excellent impact modifiers and simultaneous addition of modified nanoclay and glass fibre synergistically modifies all the other mechanical properties also. Hence the resultant hybrid composite can be considered as a superior product having strength, toughness and stiffness comparable to other materials used for sophisticated engineering applications

1.6.3 Advantages of hybrid composites

- Enhanced mechanical strength and toughness
- Can reduce micro filler loadings
- Easy mouldability
- Better surface characteristics and texture
- Reduced weight and increased stiffness
- High thermal stability and flame retardancy
- Better rheological properties

1.6.4 Applications of hybrid composites

- Automotive parts
- Gas barrier films,
- Scratch-resistant coating
- Flame-retardant cables
- Important role in longer-range missiles and a greater payload for aircraft
- Fire retardant coatings
- Rocket propulsion insulation, rocket nozzle ablative materials

1.7 Research in PP/clay and HDPE/clay nanocomposites

PP and HDPE are the most widely used polyolefin polymers. Since PP and HDPE have no polar groups in the chain, direct intercalation of PP/HDPE in the silicate galleries is impossible. Overcoming this difficulty, Usuki *et al.* [49] first reported a novel approach to prepare PP/clay nanocomposites using a functional oligomer (PP–OH) with polar telechelic OH groups as a compatibilizer. In this approach, PP–OH was intercalated between the layers of 2C18-MMT, and then the PP–OH/2C18- MMT was melt mixed with PP to obtain the nanocomposite with intercalated structure

In the later work by Toyota Central R & D laboratories, Hasegawa *et al.*[50] prepared PP-clay hybrids using a twin screw extrusion process at 200-230°C, compatibilised with a maleic anhydride-modified PP oligmer (MAPP). More uniform dispersion was achieved with the increase of weight ratio between MAPP and clay. It was found that tensile moduli of hybrids became higher with increasing the MAPP content but the tensile strengths were almost comparable to that of neat PP. Similar melt blending approach was undertaken by Kawasumi *et al.*[51] and Kato *et al.*[52] to successfully fabricate the intercalated PP-clay hybrids, resulting in the increase of interlayer spacing and drastic reinforcement effect due to the clay homogeneous dispersion.

Liu *et al.*[53] utilised a co-intercation organophilic clay with a much larger interlayer spacing than the ordinary clay, only modified by alkyl ammonium to prepare PP/clay nanocomposites via grafting-melt compounding. Good clay dispersion in a partially intercalated/exfoliated structure was achieved. Mechanical properties for 7 wt% filled nanocomposites were greatly improved with increases of tensile strength and modulus up to 27% and 42%, respectively, compared to those of neat PP. The addition of clay did not change the crystal structure of PP, but it accelerated the crystallisation considerably. Lertwimolnun and Vergnes[54] prepared PP/organoclay nanocomposites via direct melt intercalation by varying the MAPP content, mixing time, rotor speed, mixing temperature in an internal mixer and the feed rate in a co-rotating twin screw extruder. The dispersion improvement was found mainly at the MAPP content between 10 wt% and 25 wt%, and the level of intercalation represented by the interlayer spacing was unaffected by processing parameters. However, increasing the shear stress, mixing time and decreasing the mixing temperature showed better exfoliation. Furthermore, identical results were obtained by Modesti *et al.*[55] that the optimised processing condition might be achieved at a higher screw speed and lower barrier temperature profile, leading to a high degree of intercalation and exfoliation as long as the strong compatibility occurred between clay and the PP matrix. In such processing condition, the significant improvement of mechanical properties was demonstrated with the maximum increase of tensile modulus of about 130% and impact strength of about 50% for 5 wt% filled nanocomposites. More recently, Kim *et al.*[56] studied the structural-property relationship of PP nanocomposites by melt processing with the main emphasis on the ratio of MAPP and organoclay. Morphological studies have revealed that the aspect ratio of clay particles decreases as the amount of clay in the nanocomposites increases.

Manias *et al.*[57-58] reported the preparation by melt intercalation technique of PP/organically modified MMT with both intercalated and exfoliated structures. In order to prepare nanocomposites, they (a) introduced functional groups in PP, and (b) used common alkylammonium

MMT and neat/unmodified PP and a semi-fluorinated surfactant modification for the MMT. Kaempfer *et al.*[59] reported the preparation of new nanocomposites via melt compounding of syndiotactic polypropylene (sPP) containing organoclay.

Jeon *et al.* [60] reported that intercalated morphology of HDPE-MMT nanocomposite can be prepared by solution blending with dodecylamine**.** Heinemann *et al.*[61] produced HDPE-layered silicate composites by melt compounding and obtained enhancement in mechanical properties. Privalko and coworkers [62] studied the thermo elastic behaviour of blow moulded HDPE/nanokaolin composites and obtained good results. Wang KH and coworkers [63] studied the effect of MA in HDPE/clay nanocomposites and obtained intercalated morphology and enhanced mechanical and thermal properties. The extent of exfoliation and intercalation completely depends on the hydrophilicity of the polyethylene grafted with maleic anhydride and the chain length of the organic modifier in the clay. An exfoliated nanocomposite was obtained when the number of methylene groups in the alkylamine (organic modifier) was larger than 16.

Alexandre and Dubois[64] prepared Polyethylene-layered silicate nanocomposites by the polymerization-filling technique and reported that the presence of nanoclay improved mechanical properties. Jin *et al.* [65] developed an in situ exfoliation method during ethylene polymerization by fixing a Ti-based Ziegler–Natta catalyst at the inner surface of MMT. The wide angle X-ray diffraction (WAXD) analysis and transmission microscopy (TEM) observation clearly indicates the exfoliation of MMT layers in the HDPE matrix.

1.8 Research in polymer/nanoclay/glass fibre hybrid composites

Researchers at NASA Langley Center developed transparent nanocomposites with chemically modified clay, which is lightweight and durable and suitable for a variety of aerospace applications[66]. For space applications, some critical issues are important, such as temperature extremes of 196°C to 125°C, higher toughness, dimensional stability (i.e., resistance to micro cracking), etc. Timmerman *et al.* [67] used nanoclays in carbon fibre/epoxy reinforced composites for cryogenic storage systems with improved mechanical and thermal expansion characteristics thereby avoiding micro cracking and thermal cycling. The Air Force Office of Scientific Research used aerospace grade resins and organoclays to understand the mechanism of the toughening effects at ambient and sub-ambient temperatures

Liu *et al.* [48] has shown that inclusion of nanoclay alters the crystallinity of the matrix and lead to a decrease in impact strength. But glass fibres on the other hand are excellent impact modifiers and simultaneous addition of modified nanoclay and glass fibre synergistically modifies all the other mechanical properties also. Hence the resultant hybrid composite can be considered as a superior product having strength, toughness and stiffness comparable for other materials used for sophisticated engineering applications. Javad Moftakharian and co workers [68] studied the effect of nanoclay and glass fibre on polystyrene, and reported that although inclusion of nanoclay is detrimental to impact properties, melt addition of both nanoclay and glass fibre synergistically modifies both impact and flexural strength of polystyrene. Normasmira A. Rahman [69] and coworkers reported that Incorporation of glass fibre into PP lowers the tensile strength of the binary composite, indicating poor fibre-matrix interfacial adhesion. However, introducing nanoclay increased the strength of the ternary composites

Tensile modulus was enhanced with the incorporation of glass fibre, and further increased with an introduction of nanoclay. Flexural strength and flexural modulus, thermal and dynamic properties are all enhanced with an increase in glass fibre and nanoclay loading. Dorigato *et al.* [70] reported a lowering of the fibre-matrix contact angle values when organomodified clays and glass fibre were added to the epoxy resin**.** Kusmono and Zainal Arifin Mohd Ishak[71] prepared unsaturated polyester /glass fibre/clay composites by hand layup method. The effect of clay loading on the morphological and mechanical properties of unsaturated polyester /glass fibre composites was investigated in this study. X-ray diffraction (XRD) was used to characterize the structure of the composites. The mechanical properties of the composites were determined by tensile, flexural, un-notched charpy impact and fracture toughness tests. XRD results indicated that the exfoliated structure was found in the composite containing 2 wt% of clay while the intercalated structure was obtained in the composite with 6 wt% of clay. The tensile strength, flexural strength, and flexural modulus of the composites were increased in the presence of clay. The optimum loading of clay in the unsaturated polyester/glass fibre composites was attained at 2wt%, where the improvement in in tensile strength, flexural strength, and flexural modulus were approximately 13, 21, and 11%, respectively. On the other hand, the highest values in impact toughness and fracture toughness were observed in the composites with 4wt% of clay. The effect of addition of nanoclay in to polymer-glass fibre composites were also studied by Sharma *et al*., Kornmann *et al*., Behzad Kord and co-workers, A. Ramsaroop etc [72-75].

1.9 Processing techniques for polymer matrix composites

1.9.1 In-situ polymerization

In-situ polymerization was first systematically introduced by Toyota research group to develop nylon 6/clay nanocomposites in the early 1980's [76-77]. Monomer is first mixed with the layered silicates prior to the polymerisation. The monomer has lower viscosity than the polymer to facilitate breaking up silicate clusters using a high shear device and achieve more uniform particle mixing with the monomer. As a result, high monomer diffusion takes place in the interlayer area, and the morphology of nanocomposites is easily controlled by the reaction conditions and surface modification. In-situ polymerisation can be employed to prepare polymer/clay nanocomposites in both thermoset system like epoxy[78], polyurethane[79-80] and thermoplastic system such as polyethylene terephthalate (PET)[81], polyethylene (PE)[65,82] and poly methyl methacrylate [83]. Nevertheless, its drawback lies in the complex reaction conditions in the presence of additives and the inconvenience of capacity due to the great demand for large material supplies in industrial manufacturing.

Roy and Hussain[84-85] manufactured E-glass fibre/PP clay nanocomposites using prepreg tapes with extruder and pultrusion machine. They achieved improvements in compressive strength and modulus using this technique. Fielding *et al*.[86] achieved uniform dispersion of the nanoclay of carbon fibre reinforced epoxy nanocomposites using RFI in the autoclave.

1.9.2 Solution casting

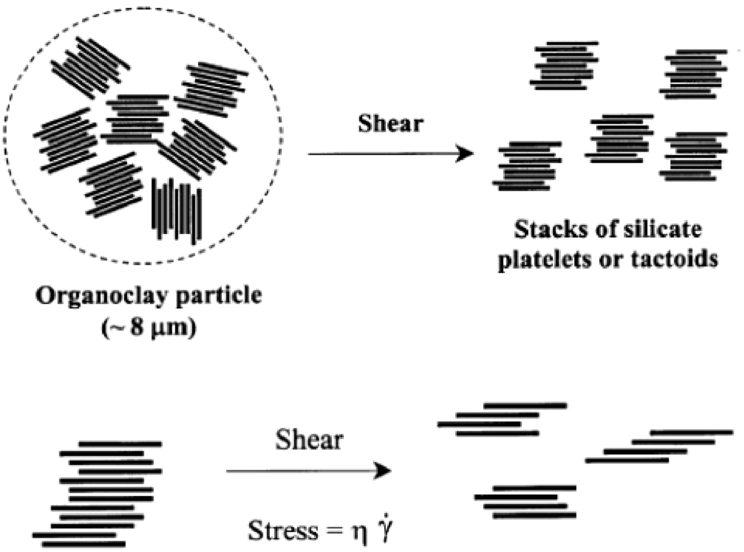
In the solution casting, solvents are used to disperse the layered clay silicates and dissolve the polymers. Adequate solvents help to delaminate the stack of layers caused by the weak van der Waal's forces. Polymer chains then can be absorbed onto the delaminated layers. Upon the removal of the solvents, the silicate layers are reassembled to form the well-ordered intercalated nanocomposites. The disadvantages of solution casting include the difficulty in preparation of exfoliated nanocomposites and the higher cost of the solvents that are limited in application and not environmentally friendly. Nevertheless, it is still a very effective chemical method to prepare soluble polymer/clay nanocomposites due to the polar and hydrophilic characteristics of such polymers to actively interact with clay silicate surfaces without any cation exchange reaction. For example, PEO[87-91]and PVA [88,92] /clay nanocomposites are normally fabricated using this method.

1.9.3 Melt compounding

Melt compounding directly uses organically modified silicates to be well mixed with the melted polymers under the high shearing mechanism by employing either a high shear mixer[54,93] or a twin screw extruder[50,53.54,94]. This process can eliminate the solvents as the medium and accommodate the conventional polymer blending methods such as extrusion and injection moulding processes at an effective cost. A very broad range of polymer based nanocomposites are successfully fabricated with clay silicates including nylon 6 [2,95-96], PP[50,53,54,93,94], PE[97-98] and PET[99].

There are many advantages to direct melt intercalation over solution intercalation. For example, direct melt intercalation is highly specific for the polymer, leading to new hybrids that were previously inaccessible. In addition, the absence of a solvent makes direct melt intercalation an environmentally sound and an economically favourable method for industries from a waste perspective.

This process involves annealing a mixture of the polymer and nanoclay above the softening point of the polymer, statically or under shear. While annealing, the polymer chains diffuse from the bulk polymer melt into the galleries between the silicate layers (fig.1.15). A range of nanocomposites with structures from intercalated to exfoliated can be obtained, depending on the degree of penetration of the polymer chains into the silicate galleries. So far, experimental results indicate that the outcome of polymer intercalation depends critically on silicate functionalization and constituent interactions. In melt compounding polymer intercalation depends on the existence of polar interactions between the organoclay and the polymer matrix. Although there is an entropy loss associated with the confinement of a polymer melts with nanocomposite formation, this process is allowed because there is an entropy gain associated with the layer separation, resulting in a net entropy change near zero. Thus, from the theoretical model, the outcome of nanocomposite formation via, polymer melt intercalation depends primarily on energetic factors, which may be determined from the surface energies of the polymer and organoclay.



Shearing of platelet stacks leads to smaller tactoids

Platelets peel apart by combined diffusion/shear process

Figure1.15 Dispersion mechanism for melt compounding of polymer/clay nanocomposites [50]

Polystyrene was the first polymer used for the preparation of nanocomposites using the melt intercalation technique with alkylammonium cation modified montmorillonite nanoclay(MMT)[24]. The resultant hybrid exhibits a WAXD pattern corresponding predominantly to that of the intercalated structure. Therefore, direct melt intercalation enhances the specificity for the intercalation of polymer by eliminating the competing host–solvent and polymer–solvent interactions. Vaia *et al.*[100] also applied same method to intercalate PEO in Na^+-MMT layers. Intercalation of PEO in layered silicate was accomplished by heating the PEO with the Na^+ -MMT at 80°C. Nanocomposites were prepared using a Haake, co-rotating, intermeshing twin-screw extruder, which was operated at 240°C with a screw speed of 280 rpm, and a feed rate of 980 g/h.

1.9.4 Effect of process parameters and filler content on the performance of composites

While many studies on nanocomposites focus on the importance of chemical surface modification of the clay or the effect of adding compatibilizers, in order to increase the compatibility between clay and host polymer, the role of processing conditions are not extensively studied. Composites with desired property enhancement and product quality will be obtained only when prepared with optimum processing conditions. Materials, design and process variables are the three main barriers for getting a suitable product and they are interlinked as shown in figure 1.16.

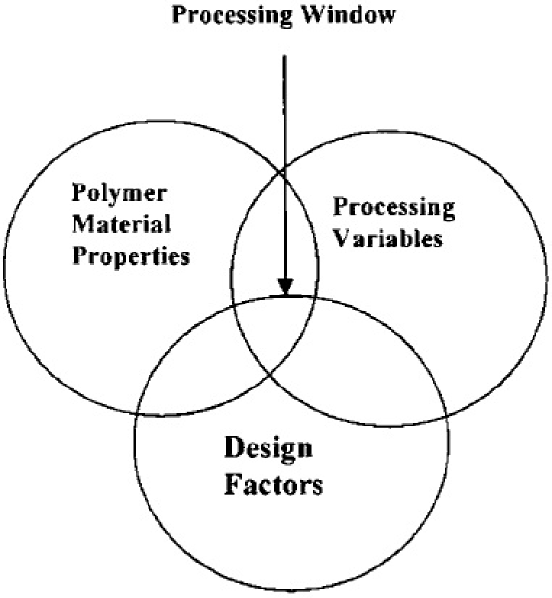


Figure 1.16 Factors that depend on the product quality of composites

The dependence on the mechanical, thermal and morphological properties of nano as well as hybrid composites on process variables and filler content can be summarized from literature as follows:

(a) **Temperature**: As the processing temperature increases, the mechanical properties in general increases for nano as well as hybrid composites. Then the properties reach an optimum value and then decreases as the temperature is further raised. Vaia and Giannelis [101] interpreted the intercalation process by thermodynamic approach. They believe that the intercalation process is influenced by enthalpy of the system which is affected by the rate of diffusion of polymer chain into the galley of nanoclay. If the diffusion process of chains obey the Arrhenius equation [$D=D_0\exp(-\Delta E/RT)$], the diffusivity of polymer into the nano layers will increase with temperature, where D is the diffusion coefficient, D_0 is the pre-exponential factor of the diffusion process independent from temperature, ΔE is the activation energy, T is the absolute temperature and R is the gas constant. In other words, with the increase of temperature the mobility of polymer chains and consequently the rate of diffusion increases and so facilitates the intercalation process. Further increase in temperature beyond optimum value will cause the decay of polymer matrix and clay layers (as shown in fig.1.17), and that may be the reason for decrease in mechanical properties after a certain value.

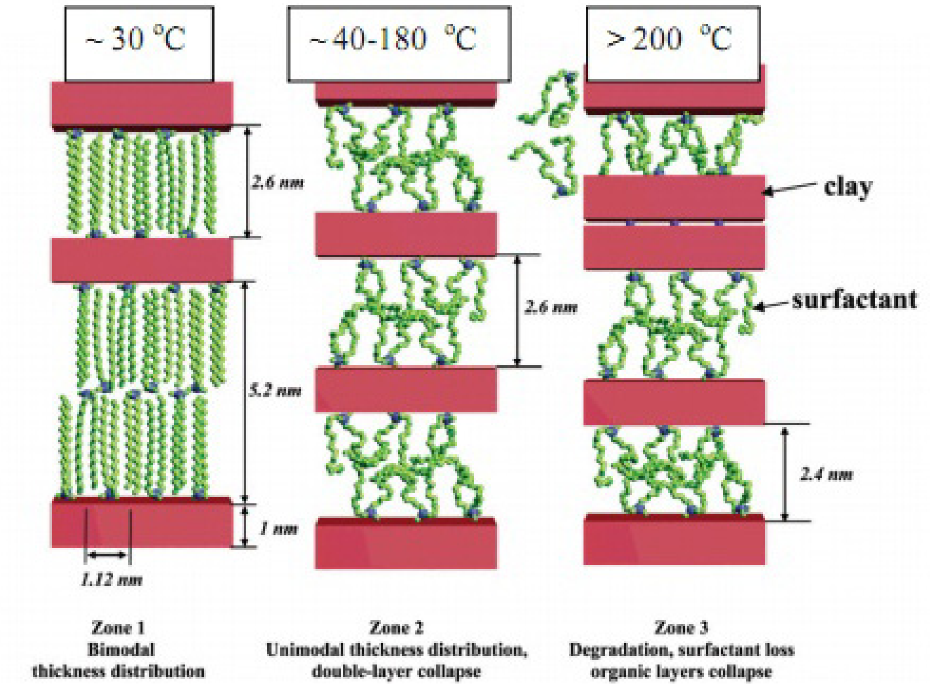


Figure 1.17 Degradation and changes in organoclay structure at elevated temperatures[73]

(b) **Processing time:** Time of melt compounding is an important factor which affects the mechanical properties of PP/HDPE hybrid composites. As the processing time sufficient for all the components to mix thoroughly, the mixing torque to become a steady value. This is the optimum processing time for producing intercalated or exfoliated composites. Ghasemi *et al*. studied the effect of processing time and temperature on the tensile strength polymer clay nanocomposites and reported that increasing the temperature and the mixing time contribute to a better organoclay dispersion which results in improved mechanical properties. They also reported that thermal degradation occurs on continuously shearing the material for longer processing time.

(c) **Nanoclay content:** Effect of nanoclay content on polymer matrix is studied by many researchers after the successful intervention of Toyota research group where they invented the first polymer clay nanocomposite- nylon6/clay hybrid [102]. Most of all the literatures report highly enhanced mechanical and thermal properties on the addition of nanoclay even at low loadings into the polymer matrix [4,27,49,60,103-110]. The enhancement of mechanical properties was more pronounced at 1-3 wt% nanoclay content. At this loading rate nanoclay remain well dispersed in the polymer matrix. Further addition may result in agglomeration leading to the formation of microcomposites. Surface modification of nanoclay increases the filler matrix adhesion and lead to improved mechanical properties.

(d) **Glass fibre content:** Effect of glass fibre content on mechanical properties of PP was studied by Lee and Jang [111] and reported that there is an enhancement in mechanical properties at about 50 wt% filler content. Norasmira *et al.* [112-113] reported that incorporation of glass fibre into PP lowers the tensile strength of the binary composite, indicating poor fibre-matrix interfacial adhesion. There was also not much increase as expected on thermal and dynamic mechanical properties on the addition of gf in to polymer matrix. Other researchers like Haque and Thomson [114-116] also reported similar effects.

1.10 Steps involved in engineering research

Steps involved in the engineering research are summarized in the figure 1.18. The primary step is to collect all data regarding the process including the factors affecting the performance of the product and the responses quantifying the performance. The second step is to choose an appropriate design that yield maximum required information from minimum set of experiments. In the consequent step, we plan the experimental design to set the factors affecting the responses, conduct experiments and measure each and every response in each run. This is followed by the fourth step to develop a mathematical model that best describe the process and best fit the experimental data with the process. The final step is to find the optimum operating conditions that make the composite with targeted product quality. The first to final step require the process knowledge and engineering judgement where the skill of the researcher and knowledge from literature review is employed. The second, third and fourth steps are mathematical which require a proper engineering design, computer based knowledge or the help of softwares to accomplish smoothly. The engineering design selected in the present study is Box-Behnken design of Response Surface methodology and the software tool used was Minitab –IV.

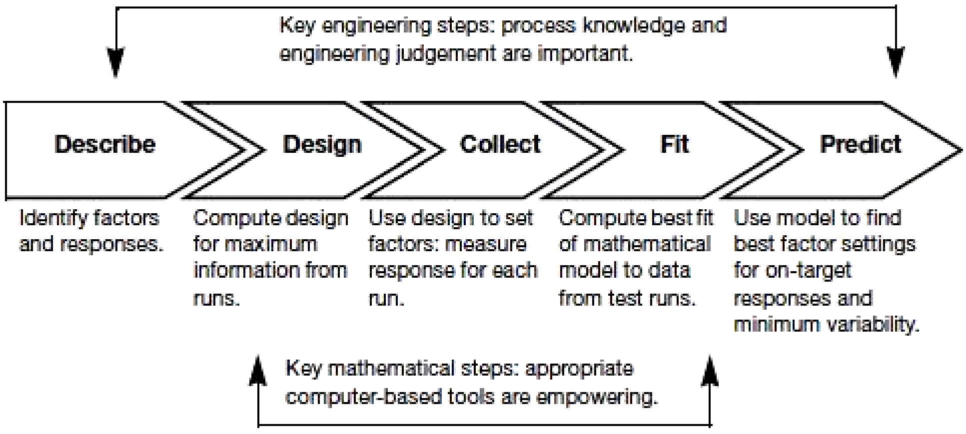


Figure 1.18 Steps in engineering research

1.11 Design of Experiments (DoE)- optimization technique for process variables

Polymer layered silicate nanocomposites have been studied for nearly 50 years[2,96], but few references deal with the importance of how the organoclay was processed into the plastic of choice. Many articles focus on the importance of the chemistry used to modify the surface of the clay, usually montmorillonite, without including the role of processing[2]. It is well known that mixing is a keystep in almost every polymer processing operation, affecting material properties, processability and cost[117]. Processing conditions are important variables that must be optimized to achieve a high degree of exfoliation and dispersion. The degree of exfoliation depends on the properties of the components, competitive interactions and preparation conditions[118]. For this purpose, statistical approach can be used to understand the impact of variables on the process.

The classical approach of changing one factor at a time (OFAT) to study the effect of a variable on the response is very widespread in experimental research. In a simple system with one variable, it is efficient and effective. However, Hockmain and Jenkins[119] (1994) reported that this approach depends upon guesswork, luck, experience and intuition for its success. This type of experimentation requires large resources to obtain a limited amount of information about the process. OFAT experiments often are unreliable, time consuming, inefficient and may yield false optimum conditions for the process[120].

Design of Experiments (DoE) are a set of statistical techniques which can be used for optimizing multivariable systems. Response surface methodology (RSM) under DoE is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. It usually contains three stages[121]: (1) design of experiments, (2) response surface modelling through regression, and (3) optimisation. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions[122-123]. The experimental data were utilized to build mathematical models using regression methods. Once an appropriate approximating model is obtained, this model can then be analyzed using various optimisation techniques to determine the optimum conditions for the process. The optimisation process involves measuring the response when statistically designed combinations are used. The coefficients for a mathematical model that best fits the experimental conditions are then estimated. This model can then be used to predict the optimum conditions to produce a maximum or minimum response (as desired). These conditions can then be run, to check the adequacy of the model.

The principal response surface methodologies are the Central Composite Design and Box-Behnken Design. These have been widely used[124-125]. Box-Behnken is a spherical and revolving design, which has been applied to optimisation of chemical and physical processes[126-129]. A comparison between the Box-Behnken design and other response surface designs has demonstrated that the Box-Behnken design is slightly more efficient than the Central Composite design and much more efficient than the three-level full factorial designs[128].

1.11.1 Benefits of DoE

DoE allows experimenters to identify the critical variables affecting a process, optimize the process variables (or parameters) and thereby substantially improve the product and process performance [130]. Experimental design methods have great potential for applications in engineering design and development including: [130-131]

- studying product or process behaviour over a wide range of operating conditions
- improving the yield, stability and reliability of an continuous manufacturing process
- determining the optimal parameter settings of a process
- reducing production time and process design and development time
- increasing process productivity by reducing scrap, rework etc.
- studying the relationship between a set of independent process variables (i.e., process parameters) and the output (i.e., response).
- understanding the process under study and thereby improving its performance

Experiments are often conducted to determine whether changing the values of certain variables leads to worthwhile improvements in the mean yield of a process or system. DoE assists experimenters to determine at what levels these variables should be set to optimise performance. The advantage of experimental design is that it allows interactions between the parameters to be evaluated with the minimum of time, material and labour effort. DoE are particularly good at identifying the interaction between several factors. Interactions cannot be determined by OFAT[132]. If interactions are important, factors and their interactions can be modelled, and the optimum operating condition can be predicted.

The objective of the use of DoE in this study is to determine the optimum settings of the processing conditions that would maximise the mechanical properties of the nanocomposites. This study uses a Box-Behnken Design. As Box-Behnken design does not contain combinations for which all factors are simultaneously at their highest or lowest levels. It is particularly suited in polymer processing when otherwise unsatisfactory results are likely to occur[128].

1.11.2 Box-Behnken design

Box–Behnken designs are experimental designs for response surface methodology, devised by George E. P. Box and Donald Behnken in 1960, to achieve the following goals:

- Each factor, or independent variable, is placed at one of three equally spaced values. (At least three levels are needed for the following goal.)
- The design should be sufficient to fit a quadratic model, that is, one containing squared terms and products of two factors.
- The ratio of the number of experimental points to the number of coefficients in the quadratic model should be reasonable (in fact, their designs kept it in the range of 1.5 to 2.6).
- The estimation variance should more or less depend only on the distance from the centre (this is achieved exactly for the designs with 4 and 7 factors), and should not vary too much inside the smallest (hyper) cube containing the experimental points.

The Box-Behnken design is an independent quadratic design in that it does not contain an embedded factorial or fractional factorial design. In this design, the treatment combinations are at the midpoints of edges of the process space and at the centres (fig 1.19). These designs are rotatable (or near rotatable) and require 3 levels of each factor. The designs have limited capability for orthogonal blocking compared to the central composite designs[133].

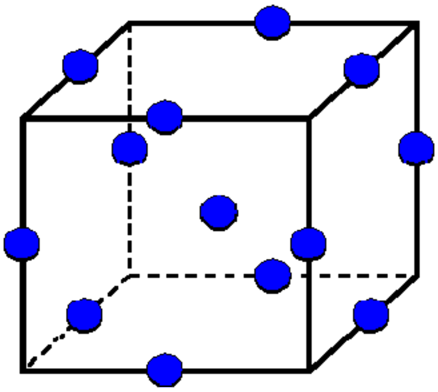


Figure 1.19 Box-Behnken design for three factors

The geometry of this design suggests a sphere within the process space such that the surface of the sphere protrudes through each face with the surface of the sphere tangential to the midpoint of each edge of the space.

Application of Box-Behnken design in the present study facilitates the following advantages

- Response equations can be developed for all the mechanical properties. Contour and surface plots illustrates the behaviour of the mechanical properties visually as the variables change from low to high level of experimental range.

- The main effects plots show the significance level of each factor. Interaction plots suggest that if there is any of extent of interaction between process parameters and filler content on the responses
- The fit of the developed model, the significance level of each factor, interaction effect of factors on the responses etc. can be clearly understood and quantified by the statistical tests like p test, ANOVA test and evaluation of statistical coefficients like correlation coefficient (R), average absolute relative error (AARE), average root-mean-square error (RMSE), normalized mean-biased error (NMBE) and scatter index (SI).

1.12. Characterization techniques for polymer matrix composites

1.12.1 Morphological properties

Two complementary techniques are generally used to characterise the state of dispersion and exfoliation of nanoparticles: X-ray diffraction (XRD) and transmission electron microscopy (TEM)[4,27,134-135]. Due to its ease of use and availability, wide-angle X-ray diffraction (WAXD) is the most commonly used technique to characterise the degree of nanodispersion of organoclay in a specific polymer. WAXD is non-destructive and does not require elaborate sample preparation, which partly explains the wide usage of this technique in material characterisation. Both techniques allow the determination of the spaces between structural layers of the silicate utilizing Bragg's law: $\sin \theta = n\lambda/2d$, where λ corresponds to the wave length of the x-ray radiation used in the diffraction experiment, d is the spacing between atomic planes in the crystalline phase and θ is the measured diffraction angle. By monitoring the position, shape, and intensity of the basal reflections from the distributed silicate layers, the nanocomposite structure (exfoliated or intercalated) may be identified. With XRD, *immiscible* materials have no change in *d*-spacing, meaning that no polymer has entered the gallery and that the spacing between clay layers is unchanged (basal reflections do not change). *Intercalated* nanocomposites have an increased *d*-spacing, indicating that polymer has entered the interlayer gallery, expanding the layers, leading to a shift of the diffraction peak towards lower angle, according to Bragg's law. On the other hand, *exfoliated* nanocomposite show no peak by XRD, suggesting that a great amount of polymer has entered the gallery space, expanding the clay layers so far apart that diffraction cannot be observed with wide-angle XRD techniques or because the nanocomposite does not present ordering[4,101]. WAXD is relatively a simple process but the analysis can be misleading and are not quantitative[135-136]. A few studies claim that a structure is exfoliated due to absence of a peak[137-138]. However the absence of a peak is not conclusive evidence of an exfoliated structure[135] Many factors must be considered to interpret WAXD scans. Intercalated structures may exhibit small or no peaks under a variety of circumstances which include if the sensitivity or counting time of the scan is low, when the tactoids are internally disordered or not well aligned to one another or when the peak falls outside the WAXD range[139]. This can lead the erroneous assumption that the clay layers are far apart when in reality they may be closely packed together. XRD is usually used in combination with a second technique (TEM) to overcome its limitation. The major drawbacks of XRD are that it may not be sensitive enough to be used with dilute clay loadings (<5 %), the results depend on order (such as orientation) and it cannot differentiate between types of dispersions[135,140]. TEM has the key advantage in that it can be used to analyse a system regardless of order or disorder in the clay and it can also determine the difference between a delaminated system and a disordered immiscible system[140]. Morgan and Gilman[135] revealed that the overall nanoscale dispersion of the clay in the polymer is best described by TEM, especially when mixed morphologies are present (regions of both exfoliated and intercalated nanostructures). TEM allows a qualitative understanding of the internal structure, spatial distribution and dispersion of the nanoparticles within the polymer matrix, and views of the defect structure through direct visualization[141]. However, special care must be exercised to guarantee a representative cross section of the sample.

Another technique used to assess micro, hybrid, agglomerate and the morphology of fracture surface of the specimen is scanning electron microscope (SEM). Because the electrons in a TEM pass through the sample, it is commonly used to look at the internal structure of the sample, while SEM looks at the surface (or the near-surface)[142]. Due to the relative narrower electron beam, SEM has a much greater depth of field (that is, the depth over which the object remains in focus) than TEM, thus yielding a characteristic three-dimensional appearance useful for investigating the surface of objects which have a complicated topography[143]. In conclusion, XRD results when properly interpreted and combined with TEM results give a clear picture of the nanoscale dispersion and overall bulk dispersion of the clay in nanocomposites polymer samples[135]. SEM is used to observe the microstructure of a conventional microcomposite. To provide the most accurate analysis of polymer clay nanocomposites of all types, it is sensible to utilize both XRD and TEM as complimentary tools in the characterisation of these materials. To provide the most accurate analysis of polymer clay microcomposites, it is sensible to use both XRD and SEM.

1.12.2 Rheological properties

The measurement of rheological properties of a polymeric material in the molten state is crucial to gain fundamental understanding of the processability of that material[144]. Polymeric materials, unlike other materials, exhibit liquid-solid (viscoelasticity) behaviour in the melt phase and this leads to added complications in processing. The rheology of polymeric materials often provides an additional insight into the molecular structure of the polymer under varied conditions and thus helps in controlling the desired properties of the final materials[145-147]. In the case of polymer/layered silicate nanocomposites, the measurement of rheological properties is not only important to understand the knowledge of the processability of these materials, but is also helpful to find out the strength of polymer-layered silicate interactions and the structure-property relationship in nanocomposites[144].

1.12.3 Thermal properties

Thermal analysis is an analytical experimental technique which is used to investigate the physical properties of a sample as a function of temperature or time under controlled condition[148]. Instruments used to measure these properties include the differential scanning calorimetry (DSC), thermogravimetry analysis (TGA), differential thermal analysis (DTA), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA).

Lee *et al*. found that the crystallisation temperature (Tc) decreased with the addition of clay when compared to neat polymer[149]. This was attributed to the large surface areas of nanoclay facilitate the polymer crystallisation process. The nanosized organo-montmorillonite (OMMT) plates provide large surface area due to their small size and thus it is reasonable to consider that the clay particles could act as effective nucleating sites of PLA crystallisation[149].

Several studies have shown that thermal stability increases with nanoclay loading[137]. This was attributed to an ablative reassembling of the silicate layers, which may occur on the surface of the nanocomposites, creating a protective physical barrier[137]. The increase in thermal stability was also attributed to the high thermal stability of clay and to the favourable interactions between the surface of nanoclay particles and the polymer matrix[150-151].

The studies conducted by Pluta *et al.* also showed an improvement in the nanocomposite thermal stability under oxidative conditions, reduced flammability, together with char formation, for polymer/MMT nanocomposites, compared to the microcomposites and pure polymer.[152-153]

1.12.4 Mechanical properties

Most studies of polymer/organoclay nanocomposites report dramatic improvements in mechanical and various materials properties compared with those of pure polymer. Many studies have shown increases in modulus and strength. Krishnamachari *et al.*[137] reported there was a 12 % increase in tensile strength and 16 % increase in Young's modulus with addition of just 1 % (w/w) of Cloisite® 30B. The addition of 4 phr of MMT to PLA increased the Young's modulus of the nanocomposites by 10 %[154]. Jiang *et al.*[155] also reported an increase in Young's modulus from 3500 to 5000 MPa in PP/MMT nanocomposites with 7.5 wt % concentration of MMT. The improvement in stiffness was attributed to the reinforcement effect of the rigid inorganic nanoclay, which constrains the molecular motion of polymer chains as well as, the existence of hydrogen–bonding interactions between polymer hydroxyl end groups and the nanoclay platelets surfaces and/or the hydroxyl groups of the ammonium surfactant in the organically modified clay. The polymer chain movement was also suppressed by organoclay tethering and gallery confinement[155].

The improvement in the modulus of polymer/nanoclay nanocomposites may also be caused by the intercalation and exfoliation of clay layers in polymer. When the clay particles are dispersed in intercalated and/or exfoliated form, it leads to a higher aspect ratio of the silicate layer, and a larger interfacial area. Both the higher aspect ratio and interfacial area will make stress transfer to the silicate layers more effective, and subsequently improve the mechanical properties of the formed nanocomposites. A dramatic improvement in modulus attributed to the exfoliated morphology has also been reported for polymer/nanoclay nanocomposites by other researchers[156,157].

1.13 Modelling of polymer matrix composites

The material properties of well aligned short-fibre composites have been successfully predicted by the conventional micromechanical models[158] in simple closed-form analytical solutions. These models can handle the factorial effects of filler geometry, content and orientation and the property ratio of filler and matrix on the reinforcement and mechanical properties of composites. Moreover, the simplified geometry for each constituent and the assumption of perfect bonding interfaces, though not accurate, have been widely admitted by the material manufacturers and engineers to predict the composite stiffness. Micromechanical models are extremely useful since they provide the ability to rapidly assess the aforementioned key factors for controlling the elastic behaviour and explore very large design spaces. Despite the successful fabrication and processing, mechanics of nanocomposites is not yet well understood due to the huge scale difference between nano fillers and the polymer matrix continuum. Attempts have been made with limited success to use some of the available micromechanical models such as Halpin-Tsai model and the rule of mixture to estimate the elastic modulus[158-161], thermo-mechanical properties[158] and the reinforcement efficiency of polymer/clay nanocomposites based on individual factors of fillers like aspect ratio, level of exfoliation and clustering[161].

Many composite analyses are performed using a macroscopic approach. In this approach, the properties of the composite are homogenized to produce an anisotropic, yet homogenized continuum before the analysis is conducted[162]. The true nature of the composite is generally one of a randomly spaced anisotropic reinforcement material in an isotropic medium. In contrast to the macroscopic approach, the micromechanical approach, to analysing composite instead considers the properties of the filler and matrix separately and applies the loading and boundary conditions at individual filler and matrix level. The overall properties of the composite are developed by relating the average stresses and strains. Hence the micromechanical approach may provide much more detail into true interactions between the filler and matrix, potentially leading to a more accurate model of the composite behaviour. The principle of micromechanical modelling is illustrated in figure 1.20.

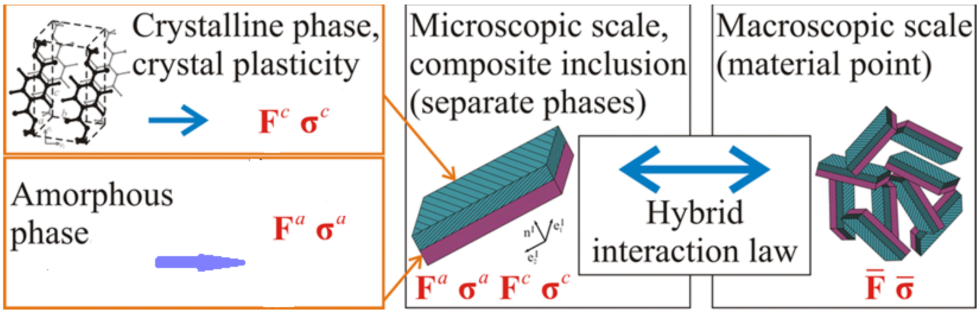


Figure 1.20 Principle of micromechanical analysis

The micromechanical modelling of polymer nanocomposites as well as hybrid composites are performed in this research using well known composites theories which are described in the following section.

1.13.1 Halpin-Tsai Model

Halpin-Tsai model[163] is a well-known composite theory in the fibre composites industry to predict the tensile modulus of unidirectional composites as the function of filler aspect ratio. It can deal with a variety of reinforcement geometries including discontinuous filler reinforcements such as fibre-like or flake-like fillers. The equations of Halpin-Tsai model are generally stated as

$$\frac{E_c}{E_m} = \frac{1+\zeta\eta\phi_f}{1-\eta\phi_f} \quad \ldots\ldots (1)$$

$$\eta = \frac{\frac{E_f}{E_m}-1}{\frac{E_f}{E_m}+\zeta} \quad \ldots\ldots (2)$$

where E_c, E_f, E_m are Young's moduli of composites, fillers and the polymer matrix, respectively(in MPa); ζ is a shape parameter dependent on the filler geometry and loading direction. $\zeta=2(L/d_0)$ for fibres or $2(L/t)$ for disk-like platelets when calculating the elastic modulus E, whereas, as an approximation, $\zeta=2$. L, d_0, t, are the length, diameter and thickness of dispersed fillers, respectively. The symbol ϕ_f denotes the volume fraction of the filler.

1.13.2 Modified Halpin-Tsai Model

It is worth noting that 2-D disk-like clay platelets can make less contribution to the unidirectional reinforcement compared to 1-D fibre-like fillers. Thus, a modulus reduction factor (MRF) for platelet fillers is introduced in the modified Halpin-Tsai model as follows,

$$\frac{E_c}{E_m}=\frac{1+\zeta(MRF)\eta\phi_f}{1-\eta\phi_f} \quad \text{..} (3)$$

where modified Halpin-Tsai model with MRF=0.66[164] has demonstrated very good prediction for the tensile modulus of rubber/clay nanocomposites over a wide range of clay volume fractions.

1.13.3 Voigt Upper Bound Model

When $\zeta \rightarrow \infty$, the Halpin-Tsai model equations reach the upper bound, which is normally called Voigt rule of mixtures (ROM)[165] where fibre and matrix have the same uniform strain (i.e. iso strain approach):

$$E_c=\phi_f E_f+(1-\phi_f)E_m \quad \text{..} (4)$$

1.13.4 Reuss Inverse Lower Bound Model

Conversely, when $\zeta \rightarrow 0$, the Halpin-Tsai model equations converge the lower bound under the equal stress (i.e. isostress approach), namely Reuss inverse rule of mixtures (IROM)[166]:

$$\frac{1}{E_c} = \frac{\phi_f}{E_f} + \frac{(1-\phi_f)}{E_m} \quad \text{...} (5)$$

Both Voigt and Reuss models provide initial estimates of the upper and lower bounds of the elasticity of multi-phase composites with the only consideration of filler volume fraction but irrespective of filler shape/geometry, orientation and spatial arrangement.

1.13.5 Takayanagi Model

Takayanagi model is initially used to describe the visco-elastic properties of a variety of heterogeneous materials with two visco-elastic constituent phases based on simple mechanical models including elements connected partly in series and partly in parallel[32]. The recent work[167] has concentrated on the interface effect for tensile modulus of polymer nanocomposites. The tensile modulus of polymer nanocomposites with random oriented plate-like dispersed phase can be then expressed as

$$E_c = \left[\left[\frac{1-\sqrt{[2(\tau/t)+1]\phi_f}}{E_m} \right] + \frac{\sqrt{[2(\tau/t)+1]\phi_f} - \sqrt{\phi_f}}{\{1-\sqrt{[2(\tau/t)+1]\phi_f}\}E_m + \sqrt{[2(\tau/t)+1]\phi_f}\,(k-1)E_m/\ln k} + \frac{\sqrt{\phi_f}}{\{1-\sqrt{[2(\tau/t)+1]\phi_f}\}E_m + \{\sqrt{[2(\tau/t)+1]\phi_f} - \sqrt{\phi_f}\}(k+1)E_m/2 + \sqrt{\phi_f}\,E_f} \right]^{-1} \qquad (6)$$

where τ is the thickness of interfacial region, *t* is the thickness of plate-like dispersed phase and *k* represents the modulus ratio of interface neighbouring on the surface of a particle. It is assumed that the modulus of the interfacial region tends to have a linear decreasing gradient along the normal direction to the surface of dispersed phase.

A simplified two phase version of Takayanagi model is obtained when the interphase effects are neglected which can be described as follows[169-170]. Here $\beta = \sqrt{\Phi_f}$

$$E_c = E_m \left[(1-\beta) + \frac{\beta}{(1-\beta) + \beta \frac{E_f}{E_m}} \right] \text{...} (7)$$

1.13.6 Ji Model

Ji *et al.* proposed a micromechanical model and it is already used by Ait Hocine *et al.*[171] for the case of a polyamide-12 reinforced by nano-platelets with a good agreement between experimental data and model predictions. This model is a three-phase model (matrix, inclusion and interphase) and links in parallel and in series the matrix, the reinforcement and the interphase (including its size). For platelet reinforcement having a thickness t and both length and width ξ (with ξ>>t), the effective Young's modulus E_c is expressed as

$$E_c = \left[(1-\alpha) + \frac{\alpha - \beta}{(1-\alpha) + \frac{\alpha(k-1)}{\ln(k)}} + \frac{\beta}{(1-\alpha) + \frac{\beta E_f}{E_m} + \frac{(\alpha-\beta)(k+1)}{2}} \right] E_m \text{.........} (8)$$

where $k = E_i/E_m$

$$\beta = \sqrt{\phi_f} \text{..} (9)$$

$$\alpha = \sqrt{[2(\tau/t)+1]\phi_f} \text{..} (10)$$

τ is the thickness of interphase which is taken as 2nm[169] and E_i is the modulus of surface of platelet which is taken as 25000MPa.Here Φ_f represents the volume fraction of the filler. When the effects of interphase are neglected the Ji's model reduces to two phase model of Takayanagi, which is described as equation (7) in the above section.

1.13.7 Three phase Halpin-Tsai Model

The Halpin-Tsai model is applied to predict the modulus of hybrid composites. Mike *et al.*[172] carried out the micromechanical modelling of PA/clay/gf composites using a three phase model developed from the well known Halpin-Tsai model. As the glass fibres may align in longitudinal and transverse directions of applied load in the case of hybrid composites prepared by melt compounding, two equations are developed to calculate the modulus in both longitudinal and transverse directions.

The equations may be stated as follows:

a) For fibres aligned in longitudinal direction

$$\frac{E_{IIhc}}{E_m} = \frac{(1 + V_{fgf}\xi_{gf}\eta_{gf})}{(1 - \eta_{gf}V_{fgf})} \times \frac{E_c}{E_m} \quad \text{...} \quad (11)$$

b) For fibres aligned in transverse direction

$$\frac{E_{\perp hc}}{E_m} = \frac{(1 + 2V_{fgf}\eta_{gf})}{(1 - \eta_{gf}V_{fgf})} \times \frac{E_c}{E_m} \quad \text{...} \quad (12)$$

where

$$\eta_{gf} = \frac{(E_{gf} / E_{clay}) - 1}{(E_{gf} / E_{clay}) - \xi_{gf}} \quad \text{...} (13)$$

The relative modulus of the hybrid composite is then carried out by Krenchel's approach using the following equation:

$$\frac{E_{hc}}{E_m} = \eta_0 \left(\frac{E_{IIhc}}{E_m} \right) + (1 - \eta_0) \left(\frac{E_{\perp hc}}{E_m} \right) \text{.......................................}(14)$$

where η_0 is the orientation efficiency which is taken as 0.25 [172].

ξ_{gf}, the shape factor of fibres is taken as 2(l/t), E_f is the modulus of glass fibres, MPa, E_c is the modulus of nanocomposite, MPa and E_{hc} is the modulus of hybrid composite, MPa.

1.14 Scope and objectives of present study

Obtaining the right material is a fundamental need for any technology. It is also important that such materials are cost effective. Polymer based composites constitute a good platform for developing such materials. Nanofillers have emerged as ultimate reinforcing agents for polymers because of their large specific surface area which results in strong interactions with the surrounding polymer matrix. Even though montmorillonite and smectite types of nanoclays are most preferred, kaolinite clays are less employed due to their low dispersion characteristics. To ensure proper dispersion, surface modified nanokaolinite clay can be used. Short glass fibres are one of the most important reinforcements used in plastics for engineering applications. The mechanical properties of composites improve with increase in the volume fraction of glass fibres. The large volume fraction of fibre can cause difficulties in the large scale production of polymer products by injection moulding and extrusion. Incorporation of nanofillers can upgrade commodity plastics –PP and HDPE into high performance materials. Modifying such plastics by hybrid fillers can significantly improve the performance. The effect of processing conditions on the properties of composites is also a less investigated area of research. DoE can be used for combined optimization of processing conditions and filler content. Thus an attempt is done to employ low cost and abundantly available nanokaolinte clay in surface modified form to produce high performance material along with PP, HDPE and E-glass fibre and optimizing the process variables using Box-Behnken method of Design of Experiments. Specific objectives of research work are

- To upgrade the commodity plastics - PP and HDPE by incorporating nanokaolinite clay and E glass fibre by melt compounding
- To improve the state of dispersion of nanokaolinite clay in the polymer matrix using surface modified nanoclays.
- To optimize the blend composition and to study the effect of compatibilizers in both nano and hybrid composites.
- To optimize the melt compounding parameters and filler content using Box-Behnken method of DoE and Minitab software
- To perform the statistical analysis of the developed composite for obtaining the significance level and interaction effects of process variable during melt compounding.
- To characterize both polymer nanocomposites and hybrid composites by mechanical, thermal, rheological, dynamic crystallization and morphological analysis.
- To perform micro mechanical modelling to analyse the behaviour of the composites under load bearing conditions.

The outline of current research approach is illustrated step by step in figure 1.21.

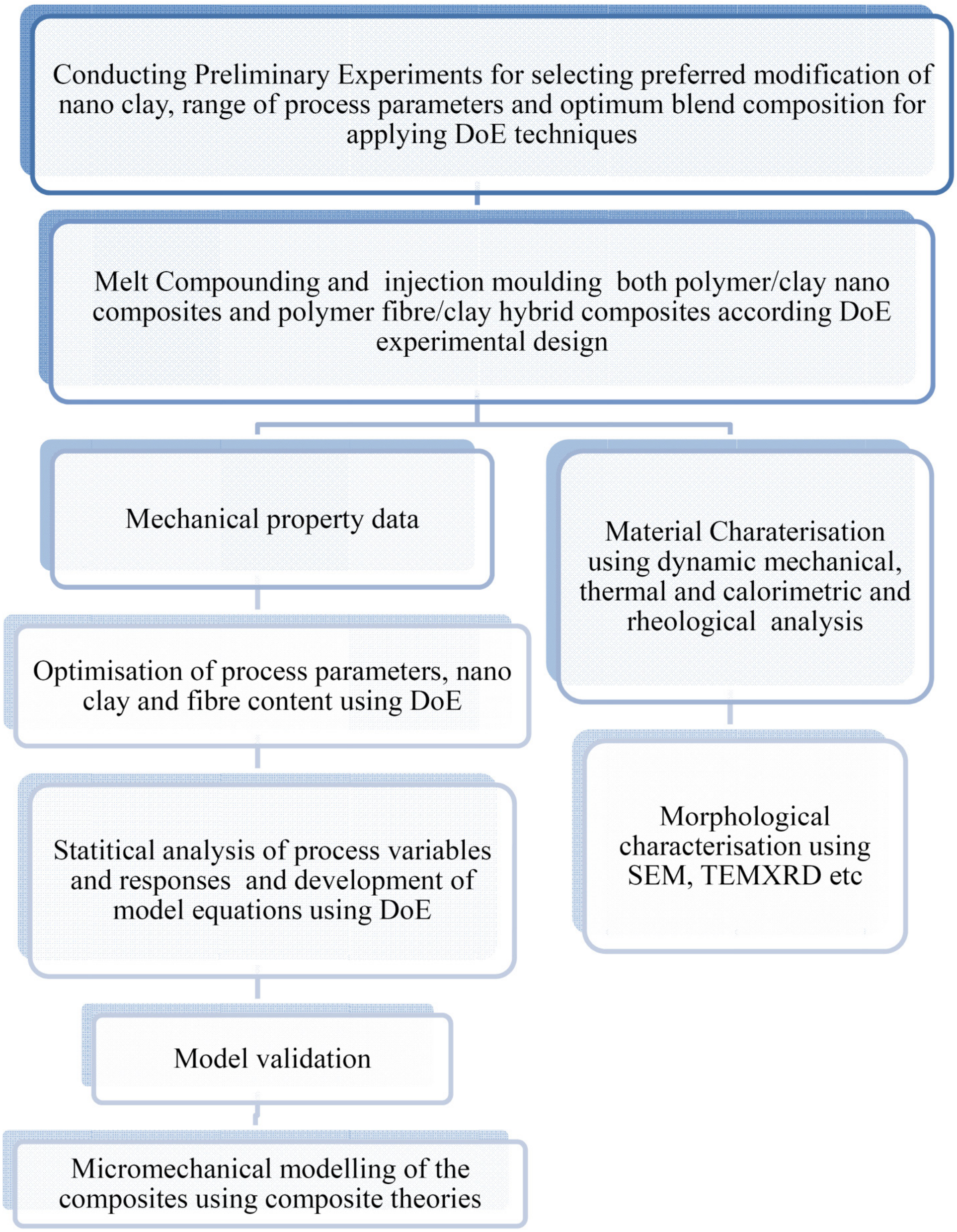


Figure 1.21 Outline of research approach in this study

References

[1]. Yano K, Usuki A, Okada A, Kurauchi T, Kamigato O (1991) "Synthesis and properties of polyamide clay hybrid". J Polym Prep, Japan 32:66-67.

[2]. Dennis H.R., Hunter D.L., Chang D, Kim S, White J.L., Cho J.W., Paul D.R. (2001) "Effect of melt processing condition on the extend of exfoliation in organo-clay based nanocomposites". Polymer 42:9513-9522.

[3]. Vaia R.A., Giannelis E.P. (1997) "Lattice of polymer melt intercalation in organically modified layered silicates". Macromolecules 30:7990-7999.

[4]. Alexandre M, Dubois P (2000) "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials". Mater Sci Engg 28:1-63.

[5]. Chirawithayaboon A, Kiatkamjornwong S (2004) "Compatabilisation of high-impact polystyrene/high density polyethylene blends by styrene/ethylene-butylene/styrene block copolymer". J Appl Polym Sci 91(2):742-755.

[6]. Jordan J, Jacob K.I, Tennenbaum R, Sharaf M.A., Jaisu I (2005) Mater Sci Eng A 393:1-11.

[7]. Masenelli Varlet K, Reynaudm E, Vigier G, Varlet J (2002) Polym Sci B Polym Phy 40:272-2835.

[8]. Hussain F, Hojjati M (2006) Review article: Polymer-matrix Nanocomposites, Processing,Manufacturing, and Application: An Overview. J Compos Mater 40(17):1511–65.

[9]. Rong M.Z., Zhang M.Q., Zeng Y.X., Zeng H.M., Friedrich K (2001) Polymer 42:3301-3304.

[10]. Yu V.T., Mark J.E., Pham L.H., Engelhardt M (2001) J Appl Polym Sci 82:1391.

[11]. Pinnavaia T.J., Beall G.W. (eds) (2001) "Polymer clay nanocomposites". Wiley, NewYork, Chapter 11 and chapter 13.

[12]. Mousa A, Karger Kocsis J (2001) J Macromol Matter Engg 286:260.

[13]. Ray S.S., Bousmina M (2006) "Biodegradable Polymers and their layered silicate nanocomposites: In greening the 21st century materials world". Progress in Material Science 50:962-1079.

[14]. Lagashetty A, Venkataraman A (2005) Polymer Nanocomposites: Resonance 10:49-57.

[15]. Chen J.S., Poliks M.D., Ober C.K., Zhang Y, Wiesner U, Giannelis E (2002) "Study of the interlayer expansion mechanism and thermal-mechanical properties of surface-initiated epoxy nanocomposites". Polymer 43:4895-4904.

[16]. Lan T, Kaviratna P.D., Pinnavaia T.J. (1995) "Mechanism of clay tactoid exfoliation in epoxy-clay nanocomposites". Chemistry of Materials 7:2144-2150.

[17]. Ogawa M, Kuroda K (1997) "Preparation of Inorganic-organic nanocomposites through intercalation of organo-ammonium ions into layered silicates". Bulletin of the Chemical Society of Japan 70:2593-2618.

[18]. Theng B.K.G. (1974) The chemistry of organoclay reactions/B.K.G. Theng, New York: Wiley.

[19]. Tseng C.R., Wu J.Y., Lee H.Y., Chang F.C. (2001) "Preparation and crystallization behavior of syndiotactic polystyrene-clay nanocomposites". Polymer 42:10063-10070.

[20]. Vaia R.A., Ishii H, Giannelis E.P. (1993) "Synthesis and properties of two-dimensional nanostructure by direct intercalation of polymer melts in layered silicates". Chemistry of Materials 8:2628-2635.

[21]. Okamoto M, Morita S, Kotaka T (2001-b) "Dispersed structure and ionic conductivity of smectic clay/polymer nanocompoites". Polymer 42:2685-2688.

[22]. Markarian J (2005) “Automotive and packaging offer growth opportunities for nanocomposites”. Plastics, Additives and Compounding 7:18-21.

[23]. Okada A, Kawasumi M, Usuki A, Kojima Y, Kurauchi T, Kamigaito O (1990) “Synthesis and properties of nylon-6/clay hybrids”. In: Schaefer DW, Mark JE, editors”. Polymer based molecular composites. Mrs Symposium Proceedings. Pittsburgh, vol 171:45-50.

[24]. Vaia RA, Ishii H, Giannelis EP (1993) “Synthesis and properties of two-dimensional nanostructure by direct intercalation of polymer melts in layered silicates”. Chem mater 5:1694-1696.

[25]. Grim (1968).Clay and Clay Mineralogy, McGrawHill Publications.

[26]. Marek Zbik, Roger St AC Smart.(1998).“Nanomorphology of Kaolinites: Comparitive SEM and AEM studies”. Clay and Clay Minerals, 46, 153-60.

[27]. Giannelis E.P. (1996) “Polymer layered silicate nanocomposites”. Adv Mater 8:29-35.

[28]. Giannelis E.P., Krishnamoorti R, Manias E (1999) “Polymer silicate nanocomposites; model systems for confined polymers and polymer brushes”. Adv Polym Sci 138:107-147.

[29]. Le-Baroon P.C., Wang Z, Pinnavaia T.J (1999) “Polymer layered silicate nanocomposites: an overview”. Appl Clay Sci 15:11-29.

[30]. Vaia R.A., Price G, Ruth P.N., Nguyen H.T., Lichtenhan J (1999) “Polymer/layered silicate nanocomposites as high performance ablative materials”. Appl Clay Sci 15:67-92.

[31]. Biswas M, Sinha Ray S (2001) “Recent progress in synthesis and evaluation of polymer-montmorillonite nanocomposites”. Adv Polym Sci 155:167-221.

[32]. Giannelis E.P. (1998) “Polymer/layered silicate nanocomposites: synthesis, properties and applications”. Appl Organomet Chem 12:675-680.

[33]. Xu R, Manias E, Synder A.J., Runt J (2001) "New biomedical poly (ureathane uera)-layered silicate nanocomposites". Macromolecules 34: 37-39.

[34]. Bharadwaj R.K. (2001) "Modeling the barrier properties of polymer layered silicate nanocomposites". Macromolecules 34:1989-1992.

[35]. Messersmith P.B., Giannelis E.P. (1999) "Synthesis and barrier properties of poly (ε-caprolactene)-layered silicate nanocomposites". J Polym Sci Part A: Polym Chem 53:1047-57.

[36]. Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O (1993) "Synthesis and properties of polyimide-clay hybrid". J Polym Sci Part A: Polym Chem 31:2493-2498.

[37]. Brindly S.W., Brown G, editors (1980) "Crystal structure of clay minerals and their X-ray diffraction". London: Mineralogical Society.

[38]. Aranda P, Ruiz-Hitzky E (1992) "Poly (ethylene oxide)-silicate intercalation materials". Chem Mater 4:1395-1403.

[39]. Greenland D.J. (1963) "Adsorption of poly (vinyl alcohols) by montmorillonite". J Colloid Sci 18:647-64.

[40]. Blumstein A (1965) "Polymerization of adsorbed monolayers: II. Thermal degradation of the inserted polymers'. J Polym Sci A 3:2665-2673.

[41]. Krishnamoorthi, Vaia R.A., Giannelis E.P. (1996) "Structure and dynamics of polymer-layered silicate nanocomposites". Chem Mater 8:1728-1734.

[42]. Grim R.E. (1953) Clay Mineralogy. McGraw-Hill, New York, N.Y.

[43]. Zeng Q.H., Yu A.B., Lu G.Q., Paul D.R. (2005) "Clay based polymer nanocomposites: research and commercial development:. J Nanosci. Nanotechno 5:1574-1592.

[44]. Garces J.M., Moll D.J., Bicerano R, Fibiger, Mcleod D.G. (2000) "Polymeric nanocomposites for automotive applications". Adv Mater 12:1835-1839.

[45]. Sherman L.M. (2004) “Chasing nanocomposites”. Plastics Technology, November. [http://www.ptonline.com/articles/200411fa2.html]

[46]. FORTE^{TM} nanocomposite website [http://www.noblepolymers.com/prod/forte.html]

[47]. Kasiwagi T, Harris R.H., Zhang X, Briber R.M., Cipriano B.H., Raghavan S.R., Awad W.H., Shields J.R. (2004) “Flame retardant mechanism of polyamide 6-clay nanocomposites”. Polymer 45:881-891.

[48]. Liu J, Boo W.J., Clearfield A, Sue H.J. (2006) “Intercalation and Exfoliation: A Review on morphology of olymer nanocomposites reinforced by inorganic layer structures”. Materials and Manufacturing Processes 21:143-151.

[49]. Usuki A, Kato M, Okada A, Kurauchi T (1997) “Synthesis of polypropylne-clay hybrid”. J Appl Polym Sci 63:137-138.

[50]. Hasegawa N, Kawasumi M, Kato M, Usuki A, Okada A (1998) “Preparation and mechanical properties of polypropylene clay hybrids using a maleic anhydride-modified polypropylene oligomer”. J Appl Polym Sci 67:87-92.

[51]. Kawasumi M, Naoki Hasegawa, Kato M, Usuki A, Okada A (1997) “Preparation and mechanical properties of polypropylene-clay hybrids”. Macromolecules 30:6333-6338.

[52]. Kato M, Usuki A, Okada A (1997) “Synthesis of polypropylene oligomer – clay intercalation compounds”. Appl Polym Sci 66:1781-1785.

[53]. Liu X.H., Wu Q.J. (2001) “PP/clay nanocomposites prepared by grafting-melt intercalation”. Polymer 42:10013-10019.

[54]. Lertwimolnum W, Vergnes B (2005) “Influence of compatibiliser and processing conditions on the dispersion of nanoclay in a polypropylene matrix”. Polymer 46:3462-3471.

[55]. Modesti M, Lorenzetti A, Bon D, Besco S (2005) “Effect of processing conditions on morphology and mechanical properties of compatibilized polypropylene nanocomposites”. Polymer 46:10237-10245.

[56]. Kim D.H., Fasulo P.D., Rodgers W.R., Paul D.R. (2007) “Structure and properties of polypropylene-based nanocomposite: Effect of PP-g-MA to organoclay ratio”. Polymer 48:5308-5323.

[57]. Nam P.H., Maiti P, Okamoto M, Kotaka T (2001) “Foam processing and cellular structure of polypropylene/clay nanocomposites”. Proceeding Nanocomposites, June 25-27, 2001, Chicago, Illnois, USA:ECM Publication.

[58]. Manias E, Touny A, Wu L, Lu B, Strawhecker K, Gilmam J.W., Chung T.C. (2000) “Polypropylene/silicate nanocomposites, synthetic routes and material properties:. Polym Mater Sci Engg 82:282-283.

[59]. Kaempfer D, Thomman R, Mulhaupt R (2002) “Melt compounding of syndiotactic polypropylene nanocomposites containing organophilic layered silicates and in situ formed core/shell nanoparticles”. Polymer 43:2909-2916.

[60]. Jeon H.G., Jung H.T., Lee S.W., Hudson S.D. (1998) “Morphology of polymer silicate nanocomposites: High density polyethylene and a nitrile”. Polym Bull 41:107-113.

[61]. Heinemann J, Reichert P, Thomson R, Mulhaupt R (1999) “Polyolefin nanocomposites formed by melt compounding and transition metal catalyzed ethane homo-and copolymerization in the presence of layered silicates”. Macromol Rapid Commun 20:423-430.

[62]. Privalko V.P., Calleja F.J.B., Sukhorukov D.I., Privalko E.G., Walter R, Friedrich K (1999) “Composition dependent properties of polyethylene/ kaolin composites Part II. Thermoelastic behavior of blow-molded samples”. J Mater Sci 34:497-508.

[63]. Wang K.H., Choi M.H., Koo C.M., Choi Y.S., Chung I.J. (2001) “Synthesis and characterization of maleated polyethylene/clay nanocomposites”. Polymer 42:9819-9826.

[64]. Alexandre M, Dubois P, Sun T, Graces J.M., Jerome R (2002) “Polyethylene layered silicate nanocomposites prepared by the polymerization fitting technique: synthesis and mechanical properties”. Polymer 43:2123-2132.

[65]. Jin Y.H., Park S.J., Im S.S., Kwak S.Y., Kwak S (2002) "Polyethylene/clay nanocomposite by in situ exfoliation of montmorillonite during Ziegler Nata polymerization of ethylene". Macromol Rapid Commun 23:135-140.

[66]. Transparent nanocomposites for Aeropace Applications, Advanced Composites Bulletin, Feb 2014.

[67]. Timmerman J, Hayes B, Seferis J (2002) "Nanoclay reinforcement effects on the cryogenic micro cracking of carbon fiber/epoxy composites". Composites Science and Technology 62:1249-1258.

[68]. Javad Moftakharian Esfahani, Masou Esfandeh, Ali Reza Sabet (2011) "High velocity impact behaviour of glass-fibre reinforced polyester filler with nanoclay". Journal of Applied Polymer Science, Vol. 125:583-591.

[69]. Hassan A, Normasmira A.R., Yahya R (2011) "Extrusion and injection-molding of glass fiber/MAPP/polypropylene: Effect of coupling agent on DSC, DMA and mechanical properties". J. Reinf. Plast. Compos. 30(14):1223-1232.

[70]. Andrea Dorigato, Stefano Morandi and Alessandro Pegoretti (2011) "Effect of nanoclay addition on the fibre/matrix adhesion in Epoxy/glass composites". Journal of Composite Materials 46(12):1439-1451.

[71]. Kusmono and Zainal ArifinMohd Ishak (2013). "Effect of Clay Addition on Mechanical Properties of Unsaturated Polyester/Glass Fiber Composites". International Journal of Polymer Science Volume 2013, Article ID 797109, 7 pages

[72]. Sharma B, Mahajan S, Chhibber R, Mehta R (2012) "Glass Fiber Reinforced Polymer-Clay Nanocomposites: Processing, Structure and Hydrothermal Effects on Mechanical Properties" Procedia Chemistry 4:39-46.

[73]. Kornmann X, Rees M, Thomann Y, Necola A, Barbezat M, Thomann R, (2005) "Epoxy-layered silicate nanocomposites as matrix in glass fibre-reinforced composites". Composites Science and Technology, Vol. 65, No. 14:2259-2268.

[74]. Behzad kord and Seyed Mohsen Hosseini Kiakojouri (2011) “Effect of nanoclay dispersion on physical and mechanical properties of wood flour/ polypropylene/ glass fiber hybrid composites”. Hybrid Nanocomposites, Bio resources 6(2):1741-1751.

[75]. Ramsaroop A, Kanny K, Mohan T.P (2010) “Fracture Toughness Studies of Polypropylene - Clay Nanocomposites and Glass Fibre Reinfoerced Polypropylene Composites”. Materials Sciences and Applications, 1:301-309.

[76]. Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima Y, Kurauchi T, Kamigaito O (1993) “Synthesis of nylon 6-clay hybrid”. J Mater Res 8:1179-1184.

[77]. Usuki A, Koiwai A, Kojima Y, Kawasumi M, Okada A, Kurauchi T, Kamigaito O (1995) “Interaction of nylon 6-clay surface and mechanical properties of nylon 6-clay hybrid”. J Appl Polym Sci 55:119-123.

[78]. Beker O, Varley L, Simon G (2002) “Morphology, thermal relaxations and mechanical properties of layered silicate nanocomposites based upon high functionality epoxy resins”. Polymer 43:4365-4373.

[79]. Wang Z, Pinnavaia T.J. (1998) “Nanolayer reinforcement of elastomeric polyurethane”. Chem Mater 10:3769-3771.

[80]. Zilg C, Thomman R, Mulhaupt R, Finter J (1999) “Polyurethane nanocomposites containing laminated anisotropic nanoparticles derived from organophilic layered silicates”. Adv Mater 11:49-52.

[81]. Sekelik D, Stepanov E, Schiraldi D, Hiltner A. Baer E (1999) “Oxygen barrier properties of crystallized and talc-filled poly(ethylene Terephthalate)”. J Polym Sci Part B 37:847-857.

[82]. Gopakumar T, Lee J, Kontopoulou M, Parent J (2002) “Influence of clay exfoliation on the physical properties of montmorillonite/polyethylene composites”. Polymer 43:5483-5491.

[83]. Okamoto M, Morita S, Taguchi H, Kim Y, Kataka T, Tateyama H (2000) "Synthesis and structure of smectic clay/poly(methyl methacrylate) and clay/polystyrene nanocomposites via in situ intercalative polymerization". Polymer 41:3887-3890.

[84]. Roy S, Hussain F, Lu H, Narasimhan K (2005) "Characterization and modelling of strength enhancement mechanism in polymer clay nanocomposites". In: AIAA Conference Proceedings, Texas.

[85]. Roy S, Hussain F, Vengadassalam K, Lu H (2006) "Manufacturing, mechanical characterization and modelling of a pultruded thermoplastic nanocomposite in nanoengineering of structural, functional and smart materials". Schulz MJ, Kelker AD, Sundarasen Mj (ed). 1st edn., CRC Taylor & Francis, USA, ISBN 0849316537; chapter 17.

[86]. Fielding J.C., Chen C, Borges J (2004) "Vacuum infusion process for nanomodified aerospace epoxy resins". In: SAMPE Symposium and Exhibition, Long Beach, CA.

[87]. Varia R.A., Sauer B.B., Tse O.K., Giannelis E.P. (1997) "Relaxations of confined chains in polymer nanocomposites: glass transition properties of poly (ethylene oxide) intercalated in montmorillonite". J Polym Sci Part B 35:59-67.

[88]. Ogata N, Kawakage S, Ogihara T (1997) "Poly (vinyl alcohol)- clay and poly (ethylene oxide)- clay blends prepared using water as a solvent". J Appli Polym Sci 66:573-581.

[89]. Ruiz-Hitzky E, Aranda P, Casal B, Galvan J.C. (1995) "Nanocomposite materials with controlled ion mobility". Adv Mater 7:180-184.

[90]. Bujdak J, Havkett E, Giannelis EP (2000) "Effect of layer change on the intercalation of poly (ethylene oxide) in layered silicates: implications on nanocomposite polymer electrolytes". Chem Mater 12:2168-2174.

[91]. Hyun Y.H., Lim S.T., Choi H.J., Jhon M.S. (2001) "Rheology of poly (ethylene oxide)/organoclay nanocomposites". Macromolecules 34:8084-8093.

[92]. Strawhecker K.E., Manias E (2000) “Structure and properties of poly (vinyl alcohol)/Na$^+$ montmorillonite nanocomposites”. Chem Mater 12:2943-2949.

[93]. Lei S.G. (2003) “Formulation and mechanical properties of polypropylene nanocomposites”. M.ASc thesis, Concordia University, Department of Mechanical and Industrial engineering.

[94]. Wang Y, Cheng F.B., Wu K.C. (2004) “Twin screw extrusion compounding of polypropylene/organoclay nanocomposite modified by maleated polypropylenes”. J Appl Polym Sci 93:100-112.

[95]. Fornes T.D., Yoon P.J., Keskkula H, Paul D.R. (2001) “Nylon 6 nanocomposites: the effect of matrix molecular weight”. Polymer 42:9929-9940.

[96]. Cho J.W., Paul D.R. (2001) “Nylon 6 nanocomposites by melt compounding”. Polymer 42:1083-1094.

[97]. Lee J.H., Jung D, Hong C.E., Rhee K.Y., Advani S.G. (2005) “Properties of polyethylene-layered silicate nanocomposite prepared by melt intercalation with a PP-g-MA compatibilizer”. Compos Sci. Technol 65:1996-2002.

[98]. Zhao C, Qin H, Gong F, Feng M, Zhang S, Yang M (2005) “Mechanical, thermal and flammability properties of polyethylene/clay nanocomposites”. Polym. Degrad. Stabil 87:183-189.

[99]. Calcagno C.I.W., Mariani C.M., Teixeira S.R., Mauler R.S. (2007) “The effect of organic modifier of the clay on morphology and crystallization properties of PET nanocomposites”. Polymer 48:966-974.

[100]. Vaia R.A., Vasudevan S, Krawiec W, Scanlon L.G., Giannelis E.P. (1995) “New polymer electrolyte nanocomposites: melt intercalation of poly(ethylene oxide) in mica type silicates”. Adv Mater 7:154-156

[101]. Vaia R.A, Giannelis E.P (1997) “Polymer melt intercalation in organically-modified layered silicates: Model predictions and experiment”. Macromolecules, 30:8000-8009.

[102]. Okada A, Usuki A (2007) "Twenty-Year Review of Polymer-Clay Nanocomposites at Toyota Central R&D Labs., Inc.," SAE Technical Paper 2007-01-1017, doi:10.4271/2007-01-1017.

[103]. Sinha Ray S, Yamada K, Okamoto M, Ueda K (2003-c) "New polylactide-layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology". Polymer 44**:**857-866.

[104]. Theng B.K.G (1979) "Formation and properties of clay-polymer complexes". Elsevier, Amsterdam.

[105]. Wolf D, Fuchs A, Wagenknecht U, kretzschmar B, Jehnichen D, Haussler L (1999) "Nanocomposites of polyolefin clay hybrids". In proceedings of the Eurofiller 99, Lyon-Villeur-Banne.

[106]. Mehrabzadeh M and Kamal M.R. (2004) "Melt processing PA-66/clay, HDPE/clay and HDPE/PA -66/clay nanocomposites". Polym Eng Sci 44(6):1152-1161.

[107]. Kawasumi M, Kohzaki M, Kojima Y, Okada A, Kamigaito O (1989) United States patent no. 4810734, assigned to Toyota Motor Co., Japan.

[108]. Jacquelot E, Espuche E, Gerard J.F., Mazabraud P (2006) "Morphology and gas barrier properties of polyethylene based nanocomposites". Journal of Polymer science: Part B: Polymer physics Vol 44:431-440.

[109]. Lee Y.H., Zhemg W.G., Park C.B., Kontopoulou M (2005) "Effect of clay dispersion on the mechanical properties and flammability of polyethylene/clay nanocomposites". Antec Vol 1:1428-1432.

[110]. Krishnamoorti R (2000) "Dynamics of nano and macro filled polymer systems". American physical society, annual march meeting, march 20-24, Minneapolis, abstract# A8. 002.

[111]. Lee N.J., Jang J (1999) "The effect of fibre content on the mechanical properties of glass fibre mat/polypropylene composites". Compos. Part A. 30(6): 815-822

[112]. Normasmira A. Rahman, Aziz Hassan, Yahya R, Lafia-Araga R.A. (2013) "Glass Fiber and Nanoclay einforced Polypropylene Composites: Morphological, Thermal and Mechanical Properties". Sains Malaysiana 42(4):537–546.

[113]. Hassan A, Normasmira A.R., Yahya R (2011) "Extrusion and injection-molding of glass fiber/MAPP/polypropylene: Effect of coupling agent on DSC, DMA and mechanical properties". J. Reinf. Plast. Compos. 30(14): 1223-1232.

[114]. Haque A, Shamsuzzoha M, Hussain F, Dean D (2003) "S2-glass/epoxy polymer nanocomposites: manufacturing, structures, thermal and mechanical properties". J. Compos. Mater. 37(20):1821-1837.

[115]. Thomason J.L. (2002) "The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene: 5. Injection moulded long and short fibre PP". Compos. Part A. 33(12):1641-1652.

[116]. Thomason J.L., Vlug M.A., Schipper G, Krikor H (1996) "Influence of fibre length and concentration on the properties of glass fibre-reinforced polypropylene: Part 3. Strength and strain at failure". Compos. Part A. 27(11):1075-1084.

[117]. Manas-Zloczower I, Cheng H (1996) "Analysis of mixing efficiency in polymer processing equipment ". Macromolecular symposia 112:77-84.

[118]. Kutz M (2011) "Applied Plastics Engineering Handbook: Pocessing and materials". Elsevier science.

[119]. Hockman K.K., Jenkins M.W. (1994) "Design of experiments: neglected key to competitive R&D –Design of experiment give researchers unparalleled understanding of and power over the experimental process". Industrial Engineering Norcross 26:50-51.

[120]. Logothetis N (1992) Managing for Total Quality, Englewood cliffs, NJ, Prentice-Hall.

[121]. Myers R.H., Montgomery D.C. (1995) "Response surface methodology: process and product optimization using designed experiments" Wiley.

[122]. Lee J, Ye L, Landen J.R., W.O, Eitenmiller R.R. (2000) "Optimization of an extraction procedure for the quantification of vitamin E in tomato and broccoli using response surface methodology". Journal of food composition and analysis 13:45-47.

[123]. Poretta S, Birzi A, Ghizzoni C, Vicini E (1995) "Effects of ultra-high hydrostatic pressure treatments on the quality of tomato juice". Food chemistry 52:35-41.

[124]. Box G.E.P, Hunter W.G., Hunter J.S. (1978) Statics for experiments, John Wiley and Sons, Inc.

[125]. Dean A.M., Voss D.T. (1999) "Design and analysis of experiments". New York, Springer-Verlag, Inc.

[126]. Bae S, Shoda M (2005) "Statistical optimization of culture conditions for bacterial cellulose production using Box-Behnken design". Biotechnology and Bioengineering 90:20-28.

[127]. Dong C.H., Xie X.Q., Wang X.L., Zhan Y, Yao Y.J. (2001) "Polyactides: properties and prospects of an environmentally benign plastic from renewable resources". Macromolecular Symposia 175:55-56.

[128]. Ferreira S.L.C, Bruns R.E., Ferreira H.S., Matos G.D., David J.M., Brandao G.C., Da Silva E.G.P., Portugal L.A., Dos Reis P.S., Souza A.S., Dos Santos W.N.L. (2007) "Box-Behnken design: an alternative for th eoptimization of analytical methods". Analytica chimica acta 597:179-186.

[129]. Muthukumar M, Mohan D, Rajendran M (2003) "Optimization of mix proportions of mineral aggregates using Box-behnken design of experiments". Cement and concrete composites 25:751-758.

[130]. Antony J, Antony F.J. (1998) "Teaching advanced statistical techniques to industrial engineers and business managers". Journal of Engineering Design 9:89-100.

[131]. Antony J, Capon N (1998) "Teaching experimental design techniques to industrial engineers". International Journal of Engineering Education 14:335-343.

[132]. Czitrom V (1999) "One factor at a time versus designed experiments". The American Statistician 53:126-131.

[133]. Box-Behnken Design, Retrieved from Wikipedia.

[134]. Ray S.S., Okamoto M (2003-b) "Polymer layered silicate nanocomposites: a review from preparation to processing". Progress in polymer science 28:1539-1641.

[135]. Morgan A.B., Gilman J.W. (2003) "Characterization of polymer layered silicate(clay) nanocomposites by transmission electron microscopy and X-ray diffraction: A comparative study". Journal of Applied Polymer Science 87:1329-1338.

[136]. Vaia R.A., Liu W (2002) "X-ray powder diffraction of polymer/ layered silicate nanocomposites: Model and practice". Journal of Polymer Science Part B: Polymer Physics 40:1590-1600.

[137]. Krishnamachari P, Zhang J, Lou J, Yan J, Uitenham L (2009-a) "Biodegradable poly(lactic acid)/clay nanocomposites by melt intercalation: A study of morphological, thermal and mechanical properties". International Journal of Polymer Analysis and Characterization 14:336-350.

[138]. Denault J, Ton-That M.T, Bloch J (2006) "Poly (lactic acid) nanocomposites: fabrication microstructure and performance". Design, applications of composites proceedings of the sixth joint Canada-Japan workshop on composites, 11-19.

[139]. Paul D.R., Robeson L.M. (2008) "Polymer nanotechnology: Nanocomposites". Polymer 49:3187-3204.

[140]. Morgan A.B.G., J W, Jackson C.L. (2000) "Characterization of polymer-clay nanocomposites:XRD vs TEM". Polymeric Material Science and Engineering 82:270-271.

[141]. Monticelli O, Musina Z, Russo S, Bals S (2007) "On the use of TEM in the characterization of nanocomposites". Materials Letters 61:3446-3450.

[142]. Zhou W, Wang Z.L. (2007) "Scanning microscopy for nanotechnology: Techniques and applications". Springer.

[143]. Liu F, Wu J, Chen K, Xue D (2010) "Morphology study by using scanning electron microscopy". Microscopy: Science, Technology, Applications and Education. 1781-1792.

[144]. Sinha Ray S, Okamoto M (2001) "New polylactide/layered silicate nanocomposites, 6". Macromolecular Materials and Engineering 288:936-944.

[145]. Doyle P.S., Shaqfeh E.S.G., Gast A.P. (1997) "Rheology of wet polymer brushes via Brownian dynamics simulation: Steady vs Oscillatory shear". Physical Review Letters 78:1182-1185.

[146]. Bar-Chaput S, Carrot C (2006) "Rheology as a tool for the analysis of the dispersion of carbon filler in polymers". Rheologica Acta 45:339-347.

[147]. Krishnamoorthi R, Yurekli K (2001) "Rheology of polymer layered-silicate nanocomposites". Current opinion in colloid and interface science 6:464-470.

[148]. Hatakeyama T, Hatakeyama H (2004) Thermal properties of green polymers and biocomposites, Springer science+ business media.Inc.

[149]. Lee J.H., Park T.G., Park H.S., Lee D.S., Lee Y.K., Yoon S.C., Nam J.D. (2003) "Thermal and mechanical characteristics of poly(lactic acid) nanocomposite scaffold". Biomaterials 24:2773-2778.

[150]. Fischer H.R., Gielgens L.H., Koster T.P.M. (1999) "Nanocomposites from polymers and layered minerals". Acta Polymerica 50:122-126.

[151]. Petrovic Z.S., Javni I, Waddon A, Banhegyi J (2005) "Micro and nano structure in polypropylene/clay nanocomposites". Polymer 46:11624-11634.

[152]. Pluta M, Galeski A, Alexandre M, Paul M.A., Dubois P (2002) "Polylactide/montmorillonite nanocomposite and microcomposites prepared by melt blending: structure and some physical properties". Journal of Applied Polymer Science 86:1497-1506.

[153]. Pluta M (2006) "Melt compounding of polylactide/organiclay: structure and properties of nanocomposites". Journal of Polymer Science Part B-Polymer Physics 44:3392-3405.

[154]. Balakrishnan H, Hassan A, Wahit M.U., Yussuf A.A., Razak S.B.A. (2010) "Novel toughened polylactic acid nanocomposite: Mechanical, thermal and morphological properties". Materials& Amp; Design 31:3289-3298.

[155]. Jiang L, Zhang J, Wolcott M.P. (2007) "Composition of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composite: reinforcing effects and toughening mechanisms". Polymer 48:7632-7644.

[156]. Chang J.H., An Yu, Cho D, Giannelis E.P. (2003-a) "Poly (lactic acid) nanocomposites: comparison of their properties with montmorillonite and synthetic mica (II)". Polymer 44:3715-3720.

[157]. Wu T.M.. Wu C.Y. (2006) "Biodegradable poly (lactic acid)/chitosan-modified monymorillonite nanocomposites: preparation and characterization". Polymer Degradation and Stability 91:2198-2204.

[158]. Tucker C.L. (III) and Liang E (1999) "Stiffness predictions for unidirectional shortfiber composites: review and evaluation". Compos. Sci. Technol. 59:655-671.

[159]. Brune D.A., Bicerano J (2002) "Micromechanics of nanocomposites: comparison of tensile and compressive elastic moduli, and prediction of effects of incomplete exfoliation and imperfect alignment on modulus". Polymer 43:369-387.

[160]. Sheng N, Boyce M.C., Parks D.M., Rutledge G.C., Abes J.I., Cohen R.E. (2004) "Multiscale micromechanical modeling of polymer/clay nanocomposites and the effective clay particle". Polymer 45:487-506.

[161]. Luo J.J., Daniel I.M. (2003) "Characterization and modeling of mechanical behaviour of polymer/clay nanocomposites". Compos. Sci. Technol. 63:1607-1616.

[162]. Aboudi J (1989) “Viscoelastic behaviour of thermo-rheologically complex resin matrix composites”. Composite Science and Technology 36:351-365.

[163]. Halpin J.C., Kardos J.L. (1976) “The Halpin-Tsai equations: A review”. Polym. Eng. Sci. 16:344-352.

[164]. Wu Y.P., Jia Q.X., Yu D.S., Zhang L.Q. (2004) “Modeling Young’s modulus of rubber–clay nanocomposites using composite theories”. Polym. Testing 23:903-909.

[165]. Voigt W (1889) “Über Die Beziehung Zwischen den Beiden Elasticitäts constantan Isotroper Körper”. Ann. Phys., 38:573-587.

[166]. Reuss A (1929) “Berechnung der fliebgrenze von Mischkristalen auf Grund der Plastizitätsbedingung für Einkristalle”. ZAMM 9:49-58.

[167]. Dickie R.A. (1973) “Heterogeneous polymer-polymer composites: I. theory of viscoelastic properties and equivalent mechanical models”. J. Appl. Polym. Sci. 17:45-63.

[168]. Ji X.L., Jing J.K., Jiang W, Jiang B.Z., (2002) “Tensile modulus of polymer nanocomposites”. Polym. Eng. Sci. 42 (5):983-993.

[169]. Cauvin L, Kondo D, Brieu M, Bhatnagar N (2010) “Mechanical properties of polypropylene layered silicate nanocomposites: Characterization and micro-macro modelling”. Polymer Testing 29:245–250.

[170]. Dayma N, Satapathy B.K. (2011) “Microstructural correlations to micromechanical properties of polyamide-6/low density polyethylene-grafted-maleic anhydride nanoclay ternary nanocomposites”. J Mater Design doi:10.1016/j.matdes.2011.04.057

[171]. U. J. Counto (1964). Effect of the elastic modulus, creep and creep recovery of concrete. Mag. Concr. Res, 16:129.

[172]. Mike J Clifford, Tong Wan (2009) “Fibre reinforced nanocomposites: Mechanical properties of PA6/clay and glass fibre/PA6/clay nanocomposites”. J Polymer doi:101016.

……

Chapter 2

EXPERIMENTAL

2.1 Introduction

The materials, equipment and the methodologies used in the preparation and characterization of PNC as well as hybrid composites are described in this chapter. The melt compounding in Thermo Haake Rheocord is used as the method of preparation of composites. The techniques for characterization include mechanical measurements by Universal Testing Machine, rheology measurement by Rheometer and Melt flow indexer, thermal measurement by Thermogravimetric Analysis (TGA) and Differential scanning calorimetry, and morphology measurements by Wide-angle X-ray diffractometer (WAXD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). In addition the Box-Behnken experimental design used for optimization is also depicted in this Chapter.

2.2 Materials

2.2.1 Polypropylene (PP)

Polypropylene homopolymer (REPOL H110MA) with a melt flow index of 16g per 10 min was supplied by Reliance Industries Limited, Mumbai.. Properties of PP of grade H110MA from the technical data sheet is summarized in table 2.1

Table 2.1 Properties of H110MA grade Polypropylene

Property	ASTM Test Method	Unit	Typical Value*
Melt flow index, (230°C / 2.16kg)	D 1238	g/10 min	11
Tensile strength at yield (50mm/min)	D 638	MPa	32
Elongation at yield (50mm/min)	D 638	%	10
Flexural modulus (1% secant)	D 790A	MPa	1650
Notched Izod Impact strength (23°C)	D 256	J/m	27
Heat deflection temp. (455 kPa)	D 648	°C	104

2.2.2 High Density Polyethylene (HDPE)

High density polyethylene (HD50MA 180) with a melt flow index of 20g/10 min was supplied by Reliance Industries Limited, Mumbai, the properties of which are summarized in Table 2.2

Table 2.2 Properties of HDPE from technical data sheet

Property	ASTM Test Method	Unit	Typical Value*
Melt flow index, (190°C / 2.16kg)	D 1238	g/10 min	20
Density (23°C)	D1505	g/cm^3	0.95
Tensile strength at yield (50mm/min)	D 638	MPa	22
Elongation at yield (50mm/min)	D 638	%	12
Flexural modulus	D 790A	MPa	900
Notched Izod Impact strength	D 256	J/m	30
Vicat Softening polint	D 1525	°C	123

2.2.3 Glass fibre

E-glass fibre (RP10 Grade) with a diameter of about 10-13µm was obtained from Sharon Industries Ltd, Kochi. The properties of the E-glass from technical data sheet are compared with that of S-glass in Table 2.3. SEM image as glass fibre is shown in figure 2.1

Table 2.3 Cost comparison and properties of E & S glass fibres

Fiber type	Tensile strength (MPa)	Compressive strength (MPa)	Density (g/cm^3)	Thermal expansion (µm/m·°C)	Softening T (°C)	Price ($/kg)
E-glass	3400	1080	2.58	5.4	846	~2
S-glass	4800	1600	2.46	2.9	1056	~20

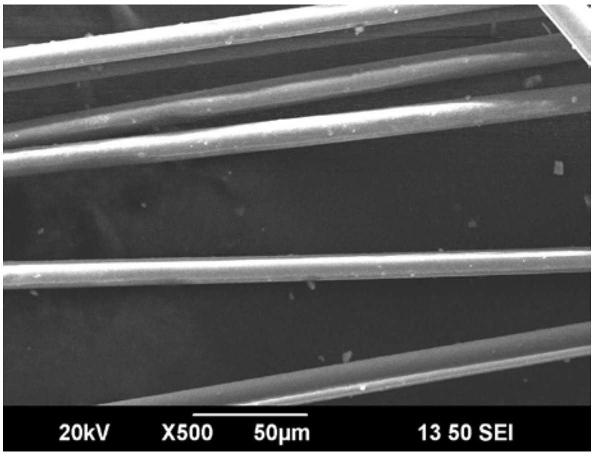


Figure 2.1 SEM image of glass E-glass fibre

2.2.4 Nanoclay

Nanoclay with the trade name-Nanocaliber was supplied by English Indian Clays Limited, Thiruvananthapuram, Kerala, India. The chemical structure of kaolinite clay is shown in figure 2.2, and the physical properties from the material data sheet are listed in table 2.4

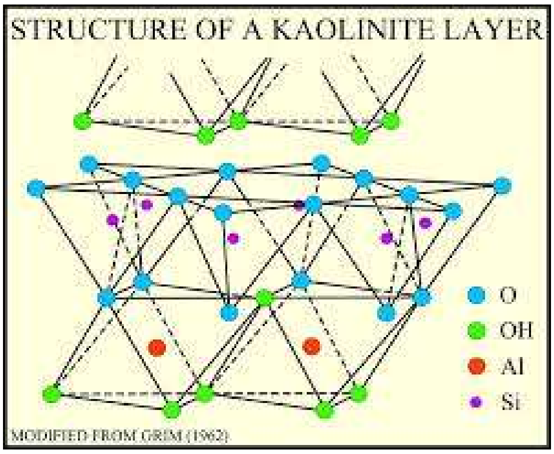


Figure 2.2 Structure of Kaolinite clay

Table 2.4 Physical properties of nanoclay (Nanocaliber)

Sl No.	Property	Approximate Value
1	Appearance	White/Off white powder
2	Average particle size	100.5nm
3	Plate thickness (SEM)	<80 nm
4	pH (10wt% suspension)	6.5-7.5
5	Bulk density	0.2-0.3 g/cc
6	Specific surface area (BET)	28-30 m^2/kg
7	Oil absorption (g/100gm)	48-50g/100g
8	Moisture	<1w/w%

Both unmodified nanoclay (NanocaliberN100) and four different types of surface modified nanoclays (Nanocaliber-N100A, Nanocaliber-N100V, Nanocaliber-N100Z, Nanocaliber-N100M) are used in this study. The organo clays differ only in the organic group used for surface modification. Surface modified clays shows better affinity and adhesion towards polymer matrix and is less agglomerated compared to unmodified nanoclay.

The SEM images of both modified nanoclay (N100A) and unmodified nanoclay (N100) are shown in figures 2.3 to 2.6

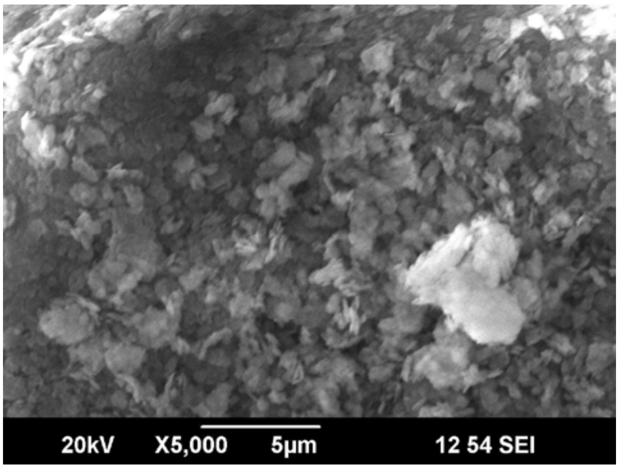


Figure 2.3 SEM image of unmodified nanoclay-N100

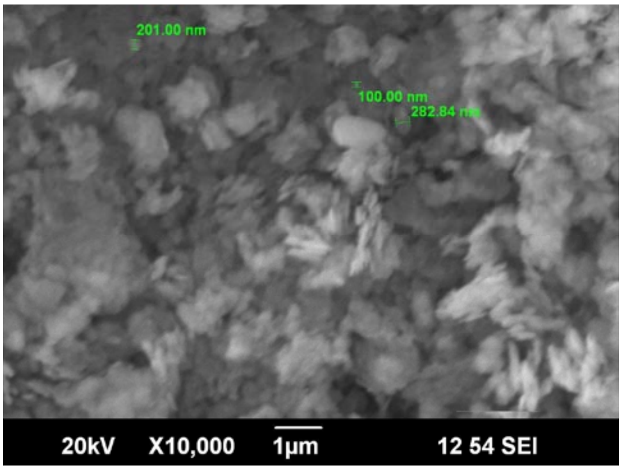


Figure 2.4 SEM image of unmodified nanoclay-N100 at higher magnification

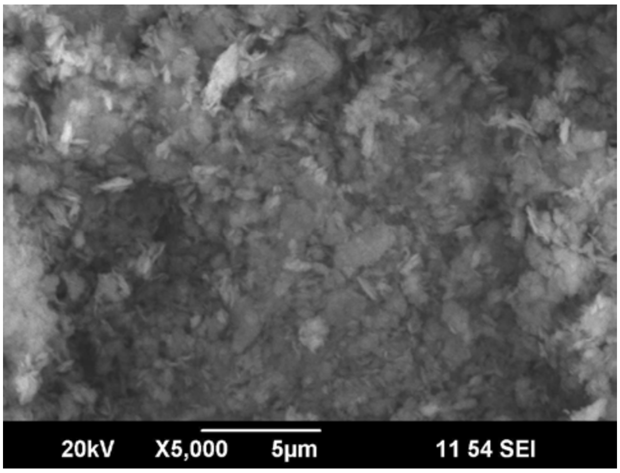


Figure 2.5 SEM image of modified nanoclay-N100A

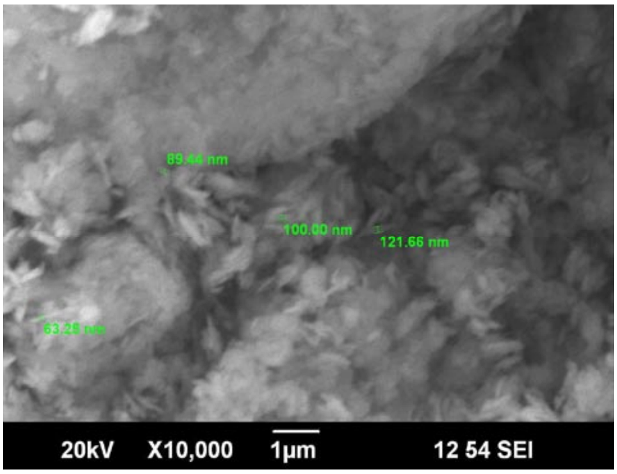


Figure 2.6 SEM image of modified nanoclay- N100A at higher magnification

2.3 Preparation of the composites

The melt mixing of polymers with particles or fillers is a simple and economically feasible method of producing new composite materials. This method was adopted for the preparation of all types of composites studied via, short glass fibre composites, nanoclay composites and short glass fibre/nanoclay hybrid composites of PP/HDPE blend.

The nanoclay is preheated at 100°C for 1 hour to get rid of the moisture content before melt compounding. The melt mixing was performed using a Thermo Haake Rheocord 600 (figure 2.7) mixing chamber with a volumetric capacity of 69cm^3 fitted with a roller type rotor (figure2.8). The rotors rotate in opposite direction in order to affect a shearing force on the material, mostly by shearing the material against the walls of the mixing chamber. The granules in the desired proportion are fed to the mixing chamber through a vertical chute with a ram. There is a small clearance between the heat con rotors which rotates at different speeds at the chamber wall. In these clearances dispersive mixing takes place. The shape and motion of rotors ensure that all particles undergo high intensive shearing flow in the clearances. The mixing consists of three sections and each section is heated and controlled by its own heater and temperature controller. Since mechanical dissipation heat is developed in the small gap between rotors and chamber, the heat conducts to the centre bowl and rises the set temperature. In this case, the connection between the heater and centre bowl is automatically cut off and circulation of cooling air is activated. For comparison, samples of unfilled polymer were also subjected to the same mixing procedure so as to have same similar processing histories for unfilled polymer and filler polymer composites. In all cases the torque is stabilized to a constant value within the specified time of mixing[1].

The melt compounding temperature, mixing shear and time of mixing are varied according to the combinations suggested by Box-Behnken experimental design table. The details of experimental design is described in Chapter 4 and in Chapter 6

Figure 2.7 Thermo Haake Rheocord 600

Figure 2.8 Roller type rotors for melt compounding

2.4 Preparation of test specimens

The hot mix from the mixing chamber was immediately pressed using a hydraulic press at a pressure of 100 kg/cm^2 and the resulting sheets were cut to small pieces. The test specimens were prepared using a plunger type semi automatic-Texstar Injection Moulding Machine (Model Jim 1H small series, 4508) with a barrel temperature suitable to each type of composites. The molten mix is injected in to the corresponding mould at a pressure of 1000Kg/cm^2 to get specimens of required shape.

2.5 Optimization techniques

In order to study the effect of process variables and filler loading on the mechanical properties of nano as well as hybrid composites and to get the optimized values, the Response surface methodology of Design of Experiments is used in this research. The principal response surface methodologies are the Central Composite Design (CCD) and Box-Behnken Design (BBD). These have been widely used[2-3]. Box-Behnken is a spherical and revolving design, which has been applied to optimisation of chemical and physical processes[4-7]. A comparison between the Box-Behnken Design and other response surface designs has demonstrated that the Box-Behnken Design is slightly more efficient than the Central Composite Design and much more efficient than the three-level full factorial designs[6].

Experiments are often conducted to determine whether changing the values of certain variables leads to worthwhile improvements in the mean yield of a process or system. DoE assists experimenters to determine at what levels these variables should be set to optimise performance. The advantage of experimental design is that it allows interactions between the parameters to be evaluated with the minimum of time, material and labour effort. DOE are particularly good at identifying the interaction between several factors. Interactions cannot be determined by changing one factor at a time[9]. If interactions are important, factors and their interactions can be modelled, and the optimum operating condition can be predicted.

Four factors are changed in three levels in Box-Behnken Design which provide an experimental design table of 27 set of experiments which is tabulated and explained in detail in Chapters 4 and 6. The composite is prepared with theses combination of variables and mechanical properties are evaluated. The variables that optimized in the preparation of nanocomposites are – melt compounding temperature, melt mixing time, mixing shear and nanoclay loading. The variables studied in optimizing the performance of hybrid composites are- melt compounding temperature, mixing time, nanoclay content and glass fibre content. Nano and hybrid composites were prepared with both surface modified clay (N100A) and unmodified nanoclay (N100).

2.6 Characterization techniques

2.6.1 Tensile properties

The tensile properties of the samples were determined according to ASTM D-638 using dumb shell shaped specimens on a 'Shimadzu Autograph AG-X series' Universal Testing Machine (UTM), at a cross head speed of 50mm/min (figure 2.9) . the length between the jaws at the start of each test was fixed to 40mm and at least 5-6 concordant measurement are taken to represent each data point. The thickness of the narrow portion was measured using a digital thickness gauge. The sample was held tight by

2 grips or jaws of UTM, the lower grip being fixed. The tensile strength, elongation at break and tensile modulus were determined.

Figure 2.9 Universal Testing Machine (Schimadzu AG-X series)

Tensile strength: It is the maximum tensile stress registered in tensile loading operation. It corresponds to yield strength if the breaking strength is less than the yield stress. It is measured as the force measured by the load cell at the time of break divided by the original cross sectional area of the sample at the point of minimum cross section.

In the SI system, the unit is the pascal (Pa), often megapascals (MPa), or equivalently to newtons per square metre (N/m²).

Tensile Stress, σ is defined as: $\sigma = \frac{\text{Force}}{\text{Area}}$

Tensile modulus: It is the slope of linear portion of stress-strain curve, $E = \frac{\sigma}{\varepsilon}$ where ε is the strain encountered by the sample.

Elongation at break (EB): It is the elongation of the specimen at the break or it is the maximum value of elongation expressed as a percentage of the original length. It is measured in terms of its original length (L_0) and final length (L_1) and is given as, $EB = \frac{(L_1 - L_0)100}{L_0}$

2.6.2 Flexural properties

Flexural properties of the samples were measured by three point loading system using Universal Testing Machine (UTM, Shimadzu AG-X) according to ASTM-D-790. The flexural properties were determined using rectangular shaped samples at a crosshead speed of 5mm/min. By the application of flexural force, the upper and lower surface of the specimen under three point bending load is subjected to compression and tension and the axi-symmetric plane is subjected to shear stress. This create two failure models in the materials, bending and shear failure. The specimen fails when bending or shear stress reaches the corresponding critical value.

Flexural strength: It is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced due to the flexural load are a combination of compressive and tensile stresses. It is equal to the maximum stress at the outer layer of specimen at the moment of break and is given by the formula

Flexural Strength, $S = 3PL/2bd^2$, Where S = Flexural Strength, P = maximum moment at the load of break, b = width of the specimen, L=length of the span, d = the thickness of the specimen

Flexural modulus: It is the ratio of stress to corresponding strain within the elastic limit. It is calculated from the slope of initial portion of the flexural stress-strain curve, by drawing a tangent to the steepest initial straight line portion of the load deflection curve and using the equation $E_B=L^3m/4db^3$, where E_B= modulus of elasticity in bending (MPa), L = support span (mm), b = width of specimen tested (mm), d = depth of specimen (mm), m= slope of the tangent to the initial straight line portion of the load deflection curve (N/mm of deflection).

2.6.3 Impact strength

The Izod impact strength (unnotched) of the rectangular samples were determined as per ASTM- D- 256 by using Resil Impactor Junior (CEAST), shown in figure 2.10.

Figure 2.10 Impact tester (RESIL)

Impact strength is the energy absorbed by the specimen during the impact process or it is the ability of the material to resist fracture under stress applied at high speed. It is given by the difference between the potential energy of the hammer or striker before and after the impact. The impact properties of the polymeric materials are directly related to the overall toughness of the material as the toughness is related to ability of the polymer to absorb applied energy.

The specimens were tested on the impact tester having 4J capacity hammer and striking velocity of 3.46m/s. A sample is clamped vertically in the base of the machine and the pendulum is released. The impact resistance of the strength is evaluated from the impact values directly read from the tester. Impact strength is expressed in unit KJ/m^2.

2.6.4 Melt flow index (MFI)

MFI is the mass flow rate, expressed in grams extruded isothermally in 10 min under constant load through a die of standard dimension. Melt flow index is measured using CEAST Modular Line Melt Flow Indexer (figure 2.11) as per ASTM D1238-90b. The melt index or melt flow rate (MFR) is a test which is applied to polyolefins to determine the rate of flow of the thermoplastic material through an orifice of specific length and diameter under specified temperature and load. The apparatus is reheated to a specified temperature and the material loaded into the cylinder from the top and a specified weight is applied on a piston. For example MFI is determined at a temperature of 230°C, 2.16 kg total load including piston and 298.22KPa pressure.

The melt mixed composite material is allowed to flow through the die, the appropriate cut of the extrudate is weighed and the melt index calculated in grams per 10 minutes. Melt index is an inverse measure of molecular weight and a low molecular weight polyolefin polymer will have a high melt index and vice versa[9]. MFI is also considered as an important parameter as it represents the flow properties of a polymer in the polymer processing industry.

Figure 2.11 Melt flow Indexer (CEAST)

2.6.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is used to investigate thermal degradation Thermogravimetric analysis (TGA) was carried out by using TGA Q 50 (TA Instruments) at a heating rate of 20°C/min from room temperature to 600°C with 5-6mg of the sample in the nitrogen environment (figure 2.12). Thermogravimetric analysis (TGA) is a technique by which the mass of the sample is monitored as a function of temperature or time, while the substance is subjected to a controlled temperature programme[10].

TGA Q 50 (TA Instruments) was used at a heating and cooling rate of 20°C/min from room temperature to 600°C. The chamber was continuously swept with nitrogen at a rate of 90ml/min. The corresponding weight changes were noted with the help of an ultrasensitive microbalance. The data of weight loss v/s temperature and time was recorded online in the TA Instruments Q series Explorer software. The analysis of thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were done using TA Instrument's Universal analysis 2000 software version 3.3BV.

Figure 2.12 Thermogravimetric Analyser (TA)

2.6.6 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis methods are useful in evaluating the effects of the fibre loading and fibre-matrix adhesion in the composites. For establishing such temperature dependent material data, the dynamic mechanical analysis is suitable[11]. The dynamic mechanical analysis of the samples was carried out using a dynamic mechanical analyzer (TA instrument Q 800) which is shown in figure 2.13.

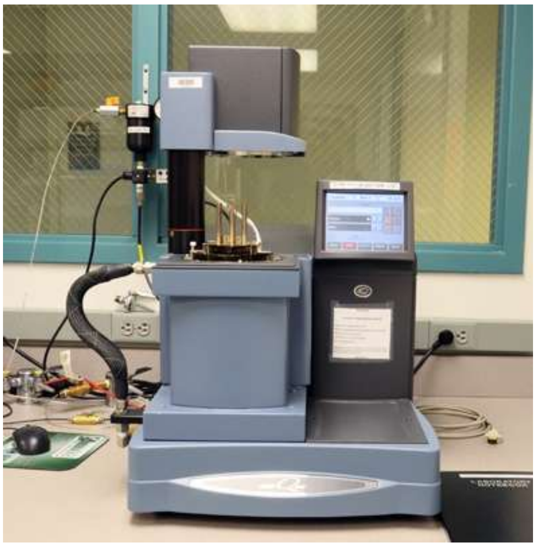


Figure 2.13. Dynamic Mechanical Analyser (TA)

Rectangular samples were subjected to temperature sweep at a frequency of 1 Hz over a temperature range of 35 to 120°C at a heating rate of 3°C/min to get the dynamic storage modulus (E') and loss modulus (E") of the samples. This analysis is used to determine the dynamic properties and the damping or internal friction tanδ (E"/E') by measuring the response of the material to periodic forces[12]. Generally the dynamic measurements are carried out over a frequency range at a constant temperature or over a temperature at a constant frequency. Storage modulus (E') corresponds to the elastic response to the deformation and it is a measure of stiffness. Loss modulus corresponds to the plastic response to the deformation and it is associated with the dissipation of energy as heat when material is deformed. Damping coefficient tan δ is useful for determining the occurrence of molecular transition such as glass transition temperature. This analysis is used to generate the information about crystalline as well as amorphous nature in polymers. The variation of these components as a function of temperature is used to study the molecular motion in the polymers.

2.6.7 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is used to investigate thermal transitions including phase changes, crystallization, melting, glass transition of a material as a function of temperature[13-14]. Incorporation of nanofillers in the polymer melt usually has varying effects on the crystallization[15]. The differential scanning calorimetry (DSC) studies were carried out on the neat polymer and its composites in order to determine any change in crystallinity, melt peak temperature and melt onset temperature on modification as compared to those of neat polymer. The DSC studies were carried out using DSC Q 100 model obtained from TA Instruments Inc (figure 2.13). Nitrogen gas is used to provide an inert atmosphere. Test specimens weighing 5-6 mg are placed in regular DSC crimped aluminium pans for testing. The sample pan and the empty reference pan made of the same material are then loaded into the test chamber. They are heated to at the rate of 10°C/min. The instrument measures the additional heat flow required to maintain the sample pan at the same temperature as the reference pan. This result is depicted as a plot of temperature v/s time. It consists of exothermic or endothermic peaks which are analysed by the Universal Analysis software provided by the TA Instruments.

Heat flow, ie, heat absorption (endothermic) or heat emission (exothermic) is measured, per unit time for the sample and the result is compared with that of thermally inert reference. The materials as they undergo changes in chemical and physical properties are detected by transducers, which changes into electrical signals that are collected and analysed to give thermograms. DSC directly gives a recording of heat of flow rate (Cp) against temperature. The kinetics of phase transformations can also be studied by DSC.

The melting and crystallization parameters, such as melting point (T_m), heat of fusion (ΔH_f), temperature of crystallization (T_c) and heat of crystallization were used for the comparison of composites.

Figure 2.14 Differential scanning calorimeter (TA)

Several researchers have reported the use of nanoparticles, such as organically modified nanoclays as crystallization promoters for a variety of polymers[16-17]. So to study the nucleating effect of modified nanoclay on polymer matrix, calorimetric measurements were done, using samples of 5-6mg. The samples were heated at a rate of 20°C /min from 35°C to 180°C, kept isothermally for 3 min to erase the thermal history and cooled from 180°C to 35°C at 20°C /min under nitrogen atmosphere (60ml/min flow) to get the nonisothermal crystallization characteristics of the samples.

2.6.8. Dynamic rheological analysis (DRA)

The rheological analysis is performed in Anton Paar Rheometer model MCR 102 (figure 2.15). A 25 mm diameter parallel plate measuring geometry, with a gap of about 1-2 mm was used for the measurements. Melt compounded composites is cut into small pieces and fed in the gap between the plates. The software used is Rheoplus version 32. The tests performed were amplitude sweep and frequency sweep tests. In the amplitude sweep angular frequency is kept at a constant value of 10 rad/s and amplitude is varied from 0.01 to 100% log values. In frequency sweep test the amplitude is kept at a constant value of 2.5% and frequency is varied from 100 to 0.1 rad/s in a log scale. The linear viscoelastic regions of the PP/HDPE blend and their nano and hybrid composites were initially determined by a dynamic oscillatory strain sweep followed by frequency sweep measurement. Rheological parameters (elastic modulus, E'; viscous modulus, E"; and complex viscosity, η*) were directly obtained using the manufacturer supplied computer software (Rheoplus software package) from the frequency sweep data. At least two trials were run for each experimental condition to check for reproducibility of the results.

Figure 2.15 Rheometer (MCR 102)

2.6.9 X-ray diffraction (XRD)

The XRD analysis was carried out with X-ray diffractometer, Bruker, D8 Advanced model (figure 2.16), employing Cu Kα radiation (λ=1.54A°) and Ni filter operating at 30kV and 20mA. The particle size was calculated using the Debye-Sherrer formula, [$Cs=0.9\lambda/\beta\cos\theta$] where Cs is the particle size, λ is the wavelength of the incident X-ray beam, β is the full width at half maximum (FWHM) of an X-ray diffraction peak at θ value where θ is half of the angle 2θ corresponding to the peak.

WAXD is the most useful and suitable technique for the measurement of the d-spacing of ordered immiscible and ordered intercalated polymer layered silicate nanocomposite, but it may be insufficient for distinguishing disordered and exfoliated materials that give no peak.

When d_{001} (d-spacing) of the clay in the composite is equal or lower than the one for the pure clay mineral, an ordinary composite was obtained which is not a nanocomposite. On the other hand, when d_{001} in the composite is higher than in pure clay, it means that polymer molecules were positioned between clay layers and hence an intercalated nanocomposite was produced. If the peak corresponding to d_{001} is not observed in a polymer/clay diffractograms, this implies that an exfoliated nanocomposite structure was obtained. The lack of peak may be misinterpreted in case where no peak is seen or the amount of clay was too low to be detected in WAXD analysis.

Figure 2.16.X-Ray Diffractometer

XRD is usually used in combination with a second technique (TEM) to overcome its limitation. The major drawbacks of XRD are that it may not be sensitive enough to be used with dilute clay loadings (<5 %), the results depend on order (such as orientation) and it cannot differentiate between types of dispersions[18-19]. TEM has the key advantage in that it can be used to analyse a system regardless of order or disorder in the clay and it can also determine the difference between a delaminated system and a disordered immiscible system[18]. Morgan and Gilman[18] revealed that the overall nanoscale dispersion of the clay in the polymer is best described by TEM, especially when mixed morphologies are present (regions of both exfoliated and intercalated nanostructures). TEM allows a qualitative understanding of the internal structure, spatial distribution and dispersion of the nanoparticles within the polymer matrix, and views of the defect structure through direct visualization[20].

2.6.10 Scanning electron microscopy (SEM)

Morphology of the fractured surfaces was investigated using SEM[21]. In this technique, the electron beam interacts with a thin film surface layer of the specimen resulting in back scattering of electrons of high energy, generation of secondary electrons of low energy and X-rays. In SEM, the emission of secondary electrons is used for the surface analysis. Emitted electron strikes the collector and the resulting current is amplified and used to modulate the brightness of the cathode ray tube. There is a one to one correspondence between the number of secondary electrons collected from any particular point on the specimen surface and the brightness of the analogous point on the screen and thus an image of surface is progressively built up on the screen. Thin specimens from the tensile fracture surfaces were prepared and mounted on a metallic stub with the help of a silver tape and conducting paint in the upright position. The stub with the sample was placed in an ion sputtering unit for gold coating of the sample to make it conducting and examined under Analytical Scanning Electron Microscope JEOL JSM-6390LA as shown in figure 2.17.

Figure2.17 Scanning Electron Microscope

2.6.11. Transmission electron microscopy (TEM)

TEM images were obtained using a JEOL 2100 electron microscope (Figure 2.18), with a Gatan ORIUS™ SC1000 digital camera. Most of the measurements were carried out using an accelerating voltage of 200 kV, while the exposure times were varied from 1 to 6 seconds. Samples were cut using a Diatome diamond knife on a Leica UC6 at room temperature to give sections with a nominal thickness of 75 nm. Sections were collected on to formvar and carbon coated copper grids. Due to some limitations, only a few samples were taken for measurements. The materials were sampled by taking several images of various magnifications to ensure that analysis was based on a representative region of the sample.

Figure 2.18 Transmission electron microscope

References

1] Thomas Abraham N, George K.E. (2005) Studies on recyclable composites: nylon fibre reinforced high density polyethylene composite. Plast. Rubber and Compos., 33(9):10

2] Box G.E.P, Hunter W.G., Hunter J.S. (1978) Statics for experiments, John Wiley and Sons, Inc.

3] Dean A.M., Voss D.T. (1999) "Design and analysis of experiments". New York, Springer-Verlag, Inc.

4] Bae S, Shoda M (2005) "Statistical optimization of culture conditions for bacterial cellulose production using Box-Behnken design". Biotechnology and Bioengineering 90:20-28.

5] Dong C.H., Xie X.Q., Wang X.L., Zhan Y, Yao Y.J. (2001) “Polyactides: properties and prospects of an environmentally benign plastic from renewable resources”. Macromolecular Symposia 175:55-56.

6] Ferreira S.L.C, Bruns R.E., Ferreira H.S., Matos G.D., David J.M., Brandao G.C., Da Silva E.G.P., Portugal L.A., Dos Reis P.S., Souza A.S., Dos Santos W.N.L. (2007) “Box-Behnken design: an alternative for theoptimization of analytical methods”. Analyticachimicaacta 597:179-186.

7] Muthukumar M, Mohan D, Rajendran M (2003) “Optimization of mix proportions of mineral aggregates using Box-behnken design of experiments”. Cement and concrete composites 25:751-758.

8] Czitrom V (1999) “One factor at a time versus designed experiments”. The American Statistician 53:126-131.

9] Shah V (2007) Handbook of Plastics Testing and Failure Analysis, 3rd edition, John Wiley and Sons, Hoboken, NJ.

10] Neil C.M (1989) editors Allen, Sir Geoffrey and Bevington J.C. Progress in Polymer Science. Comprehen polym Sci., Vol 5, Pergamon press, New York.

11] Wang H, Thompson D.G., Schoonover J.R., Steven R, Aubuchon S, Richard R.A.P. (2001) Macromol 34:7084.

12] Takayuki M (1978) Dynamic Mechanical Analysis of Polymeric Material, Elsevier, Amsterdam.

13] Zhu P.W., Zhang G.P., Yu J.Y., Dai G (2004) J Appl. Polym. Sci. 91:431.

14] Labour T, Vigier G, Segeula R, Gauthier C, Orange G, Bomal Y (2002) J PolymSciPartB: PolymPhys 40:31.

15] Rong M.Z., Zhang M.Q., Zhang Y.X., Zheng H.M., Friedrich K (2001). Improvement of tensile properties of nano-SiO2/PP composites in relation to percolation mechanism. Polym 42:3301-3304.

16] Ou C.F. (2003) Nanocomposites of poly(trimethylene terephthalate) with organoclay. J Appl Polym Sci 89:3315.

17] Ou C.F. (2003). Crystallization behavior and thermal stability of poly (trimethylene terephthalate)/clay nanocomposites" J PolymSciPartB: Polym Phys 41:2902.

18] Morgan A.B.G., J W, Jackson C.L. (2000) "Characterization of polymer-clay nanocomposites:XRDvs TEM". Polymeric Material Science and Engineering 82:270-271.

19] Morgan A.B., Gilman J.W. (2003) "Characterization of polymer layered silicate(clay) nanocomposites by transmission electron microscopy and X-ray diffraction: A comparative study". Journal of Applied Polymer Science 87:1329-1338.

20] Monticelli O, Musina Z, Russo S, Bals S (2007) "On the use of TEM in the characterization of nanocomposites". Materials Letters 61:3446-3450.

21] Arthur W.E. (1989) Atlas of Polymer Morphology, Hanser, New York.

…….

Chapter 3

PRELIMINARY EXPERIMENTS FOR SELECTION OF MATERIALS AND RANGE OF EXPERIMENTATION

Contents

3.1 Introduction

Composite materials are solid multiphase materials formed through the combination of materials with different structural, physical and chemical properties. This makes composites different from the other multi component systems such as blends and alloys. Composites are widely used in such diverse applications as transportation, construction and consumer products [1]. Composites offer unusual combinations of component materials properties, such as weight, strength, stiffness, permeability, electrical, biodegradability and optical properties that is difficult to attain separately by individual components. A composite material can be custom tailored to have specific properties that will meet special requirements. The optimum design of composite component materials and manufacturing process to meet the target properties for specific engineering application is very important. In a composite, one phase is continuous and is called matrix, while the other is filler material which make the dispersed phase. Composite materials based on the nature of matrix phase can be divided into polymeric, ceramic and metallic composites. Usually the filler phase is embedded to the host matrix phase to make a composite which has properties far from either phase alone. By the composite technology, polymer properties are improved while maintaining their light weight and ductile nature. [2]

A nanocomposite is defined as a composite material in which at least one dimension of at least one component is in the nanometer size scale (< 100 nm). Although the term nanocomposite represents a new and exciting field in material science and technology, the nanocomposites have actually been used by the nature. Using natural materials and polymers such as carbohydrates, lipids and proteins, nature makes strong nanocomposites such as bones, shells and wood [3]. However, in recent years the characterization and control of structures at the nanoscale have been studied, investigated and exploited by the learning from the natural surroundings. Consequently the nanocomposite technology has emerged as an efficient and powerful strategy to upgrade the structural and functional properties of synthetic polymers. This is the new nanocomposite science, so referred recently in nanotechnology, and was started by the Toyota report [4] on the superior improvement in the properties of nylon-6 by the preparation of exfoliated nylon-6/clay nanocomposites and has been continued by more recent studies with carbon nanotubes, carbon nanofillers, exfoliated graphite, nanocrystaline metals and fibres modified with inorganic fillers used in polymeric composites [5]. Toyota group started using nanocomposites in their bumpers making them 60% lighter and twice as resistant to denting and scratching. Likewise, the Chevrolet Impala makes use of polypropylene side body mouldings reinforced with montmorillonite. These novel nanomaterials save on weight but enhance the hardness.

Polymer nanocomposites have attracted great attention worldwide academically and industrially due to the exhibition of superior properties such as modulus, strength, toughness and barrier properties far from those of conventional micro composites and comparable with those of metals. However polymer nanocomposites have added advantage of lower density and ease of processability. In polymer nanocomposites, the filler has at least one dimension in the nanometer scale and its nanoscale dispersion within the polymer matrix leads to the tremendous interfacial contacts between the polymer and inorganic filler which imparts superior properties than those of bulk polymer phase. When the dimensions of filler particles are decreased to the nanoscale, their properties change significantly [6]. This is the well-known nano-effect. A broad spectrum of polymer properties can be improved by nanocomposite technology such as mechanical strength, thermal stability, barrier resistance, durability, chemical stability, flame retardancy, scratch/wear resistance, biodegradability as well as optical, magnetic and electrical properties [7-10]. The final properties of nanocomposites are determined by the component properties, composition, micro-structure and interfacial interactions. However it has been established that the properties of nanocomposites are strongly influenced by the dimensions and micro structure of filler phase [11]. In other words, the filler nature has a main effect on the final morphology and properties of the polymer nanocomposite.

Clays are one group of nano-fillers which have been widely used for the preparation of polymer nanocomposites. Recently there has been a growing interest for the development of polymer/clay nanocomposites due to their dramatic improved properties compared to the conventional filled polymers in a very low fraction of filler addition [12-13]. Polymer/clay nanocomposites have received intense attention and research interest driven by the unique properties which can never be obtained by micron size fillers or especially by other nanofillers. The value added properties enhanced without sacrificing pure polymer processability, mechanical properties and light weight, make the clays more important in modern polymer industry. Clay minerals belong to a main group of silicates with layered structure known as layered silicates. The layered silicates are natural or synthetic minerals consisted of the regular stacks of aluminosilicate layers with a high aspect ratio and high surface area. Layered silicates are easily available and have low cost. The current most popular layered silicates used in polymer nanocomposites preparation are clays. Clay is referred to a part of soil fraction with the particle size of less than 2 μm. The clay layers have a thickness of about 1 nm which is in the nanoscale.

Theoretical predictions have shown that the modulus for well aligned platelets can be three times that for well aligned fibres, especially as the aspect ratio of clay layers increases [14]. Other studies however, suggest that the modulus increase is not entirely due to the load-carrying ability of the platelets, but is caused by the volume of polymer constrained by the platelets [14]. This suggests that to optimise the increase in modulus, the degree of dispersion must be optimised do that the degree of matrix/filler interaction will be maximum. As the polymer intercalates and swells, the layers and the area of interaction between the polymer and the filler increases and the modulus increases significantly. The polymer/clay interaction plays a significant role in controlling mechanical behaviour is also evident from the fact that improvement in properties tends to be higher above the glass transition temperature than below it [15] . However, proper dispersion is critical for achieving this. Hasegawa [16], *et al.* studied the dispersion of clays in polypropylene. They found that the strain-to-failure ratio in nanocomposites remain high (>200%) even at reinforcement loadings of 3%. But even a small amount of aggregation decreased the strain-to-failure ratio to 5%-8%. A similar effect was also observed in polyimide matrices, in which the strain-to-failure ratio decreases by 72% due to aggregation. A significant improvement in flexural modulus (1.5 GPa to 2.1 GPa), tensile strength (29 MPa to 40 MPa) and impact strength (18 J/m to 24 J/m) of PP/clay nanocomposites is reported on addition of about 15% PP-g-MAH to PP-organoclay system [17]. Xu [18], *et al.* have reported similar improvements in tensile strength and impact strength of the composites with a nanoclay addition of 10 per cent to 15 per cent. Unprecedented combinations of properties have been observed in some thermoplastics too. The inclusion of equi-axed nanoparticles in semicrystalline thermoplastics has resulted in increase in yield stress, the tensile strength, and Young's modulus of the polymers.

The preparation of polymer/clay nanocomposites with good dispersion of clay layers within the polymer matrix is not possible by physical mixing of polymer and clay particles. It is not easy to disperse nanolayers in most polymers due to the high face to face stacking of layers in agglomerated tactoids and their intrinsic hydrophilicity which make them incompatible with hydrophobic polymers. Only a few hydrophilic polymers such as PEO and PVA can be miscible with clay nanolayers [19].

The intrinsic incompatibility of hydrophilic clay layers with hydrophobic polymer chains prevents the dispersion of clay nanolayers within polymer matrix and causes weak interfacial interactions. Incompatibility and weak interfacial interactions hinders the exfoliation and preparation of dispersed stable nanocomposite with improved properties. Modification of clay layers with hydrophobic agents is necessary in order to render the clay layers more compatible with polymer chains. Surface modification causes the reduction of surface energy of clay layers and match their surface polarity with polymer polarity. The organoclays with lowered surface energy are more compatible with polymers and polymer molecules are able to intercalate within their interlayer space or galleries under well defined experimental conditions. The surface modification of clay layers can be achieved through a cation exchange process by the replacement of sodium and calcium cations present in the interlayer space or clay galleries by alkylammonium or alkylphosphonium (onium) cations [20]. Another method of surface modification employed especially to kaolinite group of clay is to treat them with basal expanders like urea or DMSO, and then to incorporate organic intercalants like amono silane followed by hydrolysis of basal expander by guest displacement method. In addition to the surface modification and increasing the hydrophobicity of clay layers, the insertion of organic intercalants into the galleries causes some degree of increase in the interlayer spacing which promotes the following intrusion of polymer chains into the galleries during nanocomposite preparation [21]. Also the intercalants can provide functional groups which interact with polymer chains or initiate the polymerization and therefore increase the interfacial interactions. Figure 3.1 schematically shows the scheme of organic modification of kaoliniteclay using DMSO intercalation by guest displacement method.

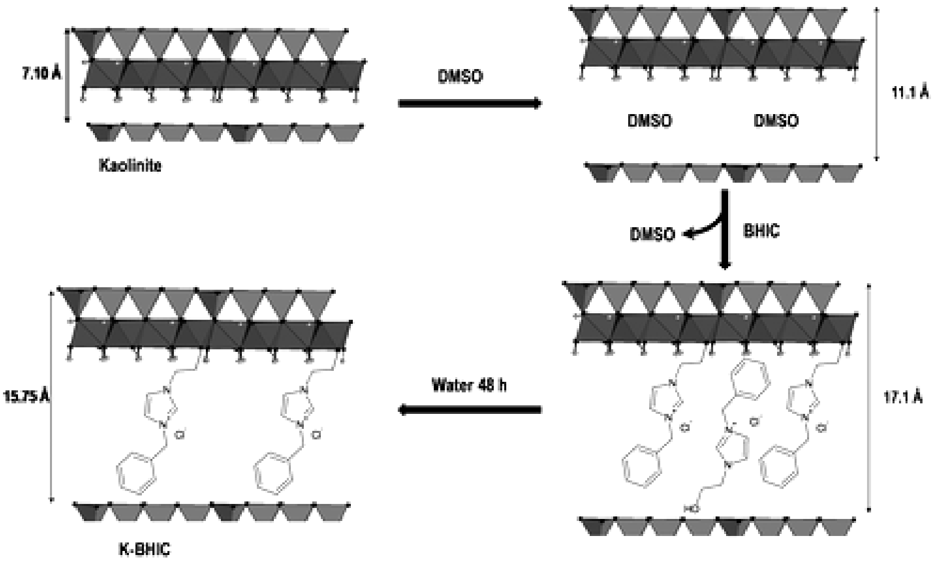


Figure 3.1 Organic modification of kaolinite clay using DMSO intercalation by guest displacement method

3.2. Methodology

The nanocomposites were prepared by melt compounding PP/HDPE and nanokaolinite clay in a Thermo Haake Rheocord fitted with roller type rotors operating at 50 rpm shear rate for 8 minutes. Five different types of commercially available nanokaolinite clays with different surface modifiers were used to upgrade PP/HDPE blend of 80/20 % by weight. In this section the effect of blend composition, melt compounding temperature, glass fibre length (in the case of hybrid composites) and effect of compatibilizers were also studied. The PP component was varied from 0% to 100% by weight at an increment of 20 wt% to study the effect of blend composition on mechanical properties in the presence of nanoclay. The melt compounding temperature was varied from 140°C to 180°C to study its effect on the mechanical properties of nanocomposite. The hybrid composites containing 2 wt% nanoclay with 10wt%, 20 wt% or 30 wt% glass fibre were prepared.

Glass fibres were added only after the mixture containing blend and nanoclay had melted and homogenized. In all cases the torque was stabilized to a constant value within 8 minutes ensuring proper mixing. Three types of compatibilizers MA/DCP, EPDM and SEBS were used and the mechanical properties investigated were tensile strength, flexural strength and impact strength. PP and HDPE were taken in the weight ratio 80/20 and nanoclay content were varied from 1 to 3 wt%. The compatibilisers were taken in the following proportions- 1 wt% EPDM and 1 wt% SEBS. For compatibilising with MA/DCP, pure PP is grafted with 2wt% MA and 0.2 wt% DCP and 5 wt% graft is mixed to prepare the nanocomposites. The mechanical properties of the resulting composites are compared with the composites without compatibilizers

After mixing, the melt is then hot pressed in a hydraulic press, cut into pieces and injection moulded in a plunger type semi automatic Texstar injection moulding machine (Model JIM 1H series, 4508) at 170°C. The breakage of short fibres is considered to be less in plunger type injection moulding machine than in screw type. The clays were pre dried before mixing by keeping in a vacuum oven at 70°C for 1 hour.

Tensile properties of the samples were determined using a Universal Testing Machine (Schimadzu AGX-I) at a cross head speed of 50mm/min as per ASTM-D-638[22]. The samples used for testing were dumb bell shaped specimens with an overall length of 115mm, a width in the gauge section of 8mm and thickness of 3.2±0.4mm. Flexural properties were measured by three point loading system on the same UTM, as per ASTM-D-790[23] at a cross head speed of 5 mm/min. Izod impact test on un-notched rectangular bar samples were carried out following ASTM D 256 [24] test method on a pendulum type RESIL IMPACT JUNIOR (CEAST). Flexural and impact specimens are rectangular bars of dimensions 40×12×3.2 mm^3 (width × length × thickness). A minimum of five samples were tested in each nano composites and the average results were recorded.

Melt flow index (MFI) was determined using CEAST Modular Line Melt Flow Indexer according to ASTM D 1238 [25]. Thermal stability of PP/HDPE (80/20) blend, and that of unmodified and modified clay nanocomposites were analyzed. Thermal analysis was done in a TA-Q 600 series instrument in nitrogen atmosphere for samples of 5–7 mg size and temperature range of 400–1,020 $^{\circ}$C at 20°C/min. The dynamic mechanical properties were determined using dynamic mechanical thermal analyzer [DMTA; Model 2980 supplied by TA Instrument (USA)]. The test sample is a rectangular strip of dimension 40 x 12 x 3.2 mm^3. The dual-cantilever mode of deformation was used under the test temperature range from 40 to 110°C with a heating rate of 30°C/min at a constant frequency of 10 Hz. The crystallization behaviour was analysed using DSCQ100 (TA Instruments). The morphology of the tensile fractured cross section was examined using a scanning electron microscope JEOL-JSM-6390 with an accelerator voltage of 20 kV in a vacuum atmosphere. The samples were subjected to gold sputtering prior to electron microscopy to give necessary conductivity. The samples were also analyzed in a Bruker AXS D8 Advance X-Ray Powder Diffractometer (Cu Ka radiation) to find the basal spacing of nanocomposites. The samples were scanned in the range of 3° –80° at incremental step of scanning 0.02° at a wavelength of 1.5406 A$^{\circ}$.

TEM images were obtained using a JEOL 2100 electron microscope, with a Gatan ORIUS™ SC1000 digital camera. Most of the measurements were carried out using an accelerating voltage of 200 kV, while the exposure times were varied from 1 to 6 seconds. Samples were cut using a Diatome diamond knife on a Leica UC6 at room temperature to give sections with a nominal thickness of 75 nm. Sections were collected onto formvar and carbon coated copper grids. Due to some limitations, only a few samples were taken for measurements. The materials were sampled by taking several images of various magnifications to ensure that analysis was based on a representative region of the sample.

3.3 Results and discussion

The mechanical properties and strength of polymer nanocomposites depend on the filler-matrix adhesion and compatibilization. As the nanoclay is intrinsically hydrophilic and polymer blend is hydrophobic, the compatibilization and proper dispersion of nanoclay in the matrix is difficult to achieve. To ensure proper dispersion of nanoclay and filler matrix adhesion, surface modification of nanoclay is carried out using different organic molecules. As kaolinite is having low cation exchange capacity, DMSO intercalation method is used to interchange the inorganic cation with organic molecule. In this section PP/HDPE blend is upgraded with five different types of surface modified commercially available nanoclay and the properties of the resultant nanocomposite are analysed.

3.3.1 Effect of surface modification of nanokaolinite clay on PP/HDPE blend

PP and HDPE are mixed in 80:20 weight ratio and modified with nano kaolinte clay. It is then melt compounded in Thermo Haake rheocord. The reinforcing effect of five types of nanoclay were studied in weight ratios 1, 2 and 3 and mixing is carried at 160°C and 50 rpm shear force for 8 minutes.

Mechanical properties

The first and important goal in the application of fillers to the polymer is improvement in the mechanical properties and therefore fillers are commonly called as reinforcement agents[26]. The mechanism of the reinforcement is based on the higher resistance of rigid filler materials against straining due to their higher modulus. When rigid filler is added to the soft polymer matrix, it will carry the major portion of applied load to the polymer matrix under stress conditions, if the interfacial interaction between filler and matrix is adequate [27-28]. Therefore the larger the interface between filler and matrix, and also more strong interfacial interactions, the great the reinforcement effect will be.

The tensile and flexural strength of the nanocomposite are plotted against nanoclay content for the five types of organoclays in figures 3.2 and 3.3. The nanocomposite containing aminosilane modified nanoclay shows maximum increase in tensile strength followed by that containing unmodified nanoclay. The modification by aminosilane group may increase filler matrix adhesion and particle dispersion. This may be the reason for the increase in tensile strength. The same trend as that of tensile strength is shown by flexural strength also. There is 22.5% increase in tensile strength and 19% increase in flexural strength than pure blend for nanocomposite containing amino clay.

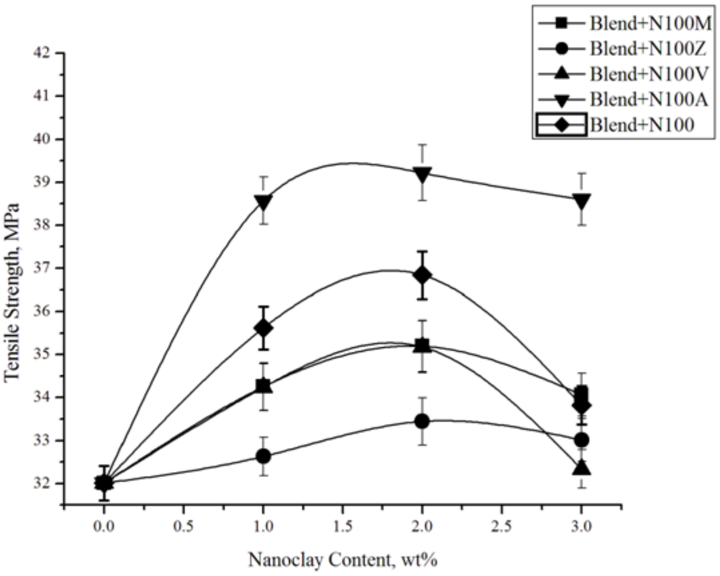


Figure 3.2 Effect of surface modification of nanoclay on tensile strength of PP/HDPE nanocomposites

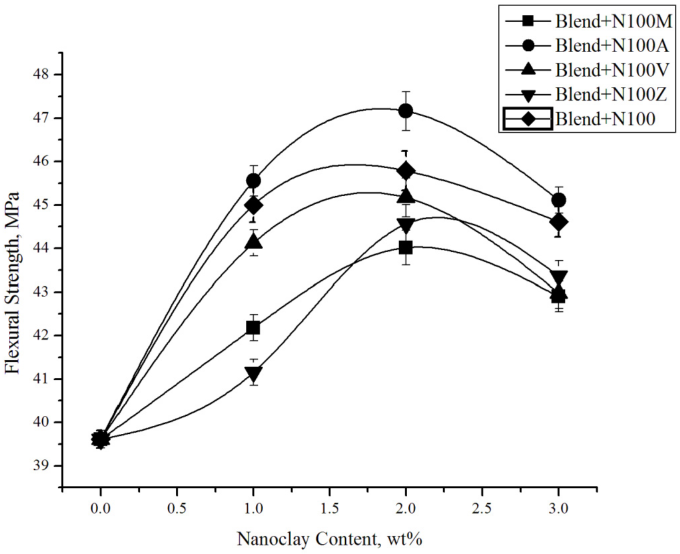


Figure 3.3 Effect of surface modification of nanoclay on flexural strength of PP/HDPE nanocomposites

The incorporation of clay minerals usually improves the tensile and flexural strength of polymers [29-31]. However the tensile and flexural strengths are influenced by the final morphology of nanocomposite. There are also a number of reports on the reduction of tensile strength by the addition of clay minerals [32-33]. Similar to modulus, any factor affecting on the degree of intercalation/exfoliation has an impact on the tensile strength of nanocomposite. The effect of clay fillers on the stress at break values for polymer nanocomposites depends on the interfacial interactions between polymer and clay layers. The stronger interfacial interaction causes increase of stress at break and the weak interfacial forces may lead to decrease of stress at break for nanocomposite. The polymers with more polarity such as nylon and rubber based polymers have more strong interfacial interactions with polar clay layers and their nanocomposites represent improved stress at break values compared to that of pure polymer [34]. Polyamide/clay nanocomposites have shown highly improved stress at break values, because of their higher degree of exfoliated structures based on the presence of strong ionic bonds between polymer chains and clay layers [32]. The nanocomposites of non-polar polymers such as polyolefines with clays exhibit weak interfacial interactions and low degree of exfoliation and consequently show decreased or slightly improved stress at break values. However, the modification of polymer chains or clay layers may be causes to improved stress at break characteristics for non-polar polymers.

The tensile modulus and flexural modulus of nanocomposite containing different types of kaolinte clay are illustrated in figures 3.4 and 3.5. There is an increase in tensile and flexural moduli for all nanocomposites containing different modified clay when compared to pure blend, but the enhancement is more pronounced in the case of nanocomposites containing amino and unmodified nanoclay.

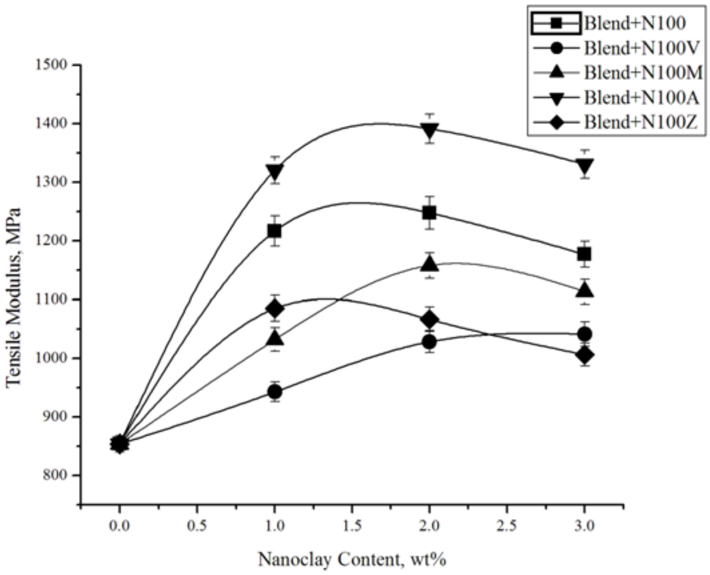


Figure 3.4 Effect of surface modification on tensile modulus of PP/HDPE nanocomposites

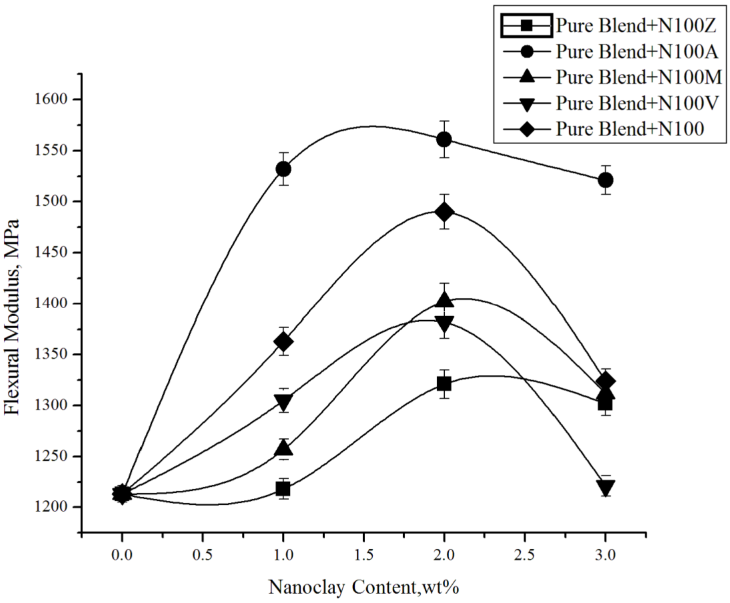


Figure 3.5 Effect of surface modifications on flexural modulus of PP/HDPE nanocomposites

The modulus increases by increasing the filler ratio in the composite or nanocomposite composition. Because of the rigid structure of clay layers and their high aspect ratio, they have proven to be very effective in increasing the modulus and stiffness of the polymer matrix in well-dispersed condition. In fact, due to the very higher aspect ratio of nano-clay fillers compared to that of regular fillers such as glass fibres, dramatic improvements in the mechanical properties of nanocomposites are achieved even at very low nanoclay additions [12]. In another approach, polymer chains, adhesive by strong physisorption forces onto the rigid clay monolayers, become equally a portion of rigid material and dramatically exhibit high modulus. Considering the large interfacial area in well dispersed nanocomposite structures, significant improvement in the modulus can be expected. However, any enhancement in the polymer-clay interfacial contact leads to the better stress transfer in the nanocomposite. It has been well demonstrated that the enhancement in the interfacial adhesion properties between clay and polymer by surface modification of polymer chains using a suitable polar compatibilizer causes increase in the mechanical properties of nanocomposite [35-36]. It should be noticed that in higher loadings of modified nanoclay and with some types of surface modifiers, they may cause some degree of plasticization due to their lower molecular weight, which negatively affect the modulus of nanocomposite [36]. This may be the reason for decrease of modulus after a certain degree of nanoclay content, and with some types of surface modifiers. Also, the use of organically modified clay filler increases both the modulus and stiffness of nanocomposite because of the greater intercalation/exfoliation achieved. Any parameter which helps the intercalation of polymer molecules within the clay galleries and consequently causes more exfoliation and interfacial interactions, will result in the greater improvement in the modulus. However it is difficult to achieve the complete exfoliation of clay layers and there are a great variety of platelet structures with different thicknesses (depending on the number of layers stacked together) in polymer matrix. Fornes and Paul [37] have analytically formulated the effect of incomplete exfoliation on the nanocomposite properties. Also it has been reported that the tensile modulus increases by increasing the filler volume fraction in the nanocomposite [38]. However, clay loading more than threshold limit value, causes the levelling-off in the increasing period of Young's modulus, which is due to the formation of partially exfoliated/ intercalated structure after that fully exfoliated structure formation [32,39]. Here the enhancement of mechanical properties is a maximum at 2 wt% nanokaolinite clay.

Elongation at the break for polymer/clay nanocomposites is similarly dependent to the interfacial interactions of polymer/clay system. There are both increasing and decreasing reports of elongation at the break for polymer/clay nanocomposites in literature [33,40]. Here in the present study, the elongation at break decreases as the reinforcement effect increases (figure 3.6.). Nanocomposites containing different types of nanoclay have less elongation at break than the pure blend. The aminosilane modified and unmodified clays containing nanocomposites have the least values of elongation at break. Usually break strain shows a reverse trend as that of tensile strength. As stiffness increases, break strain decreases and vice versa[32].

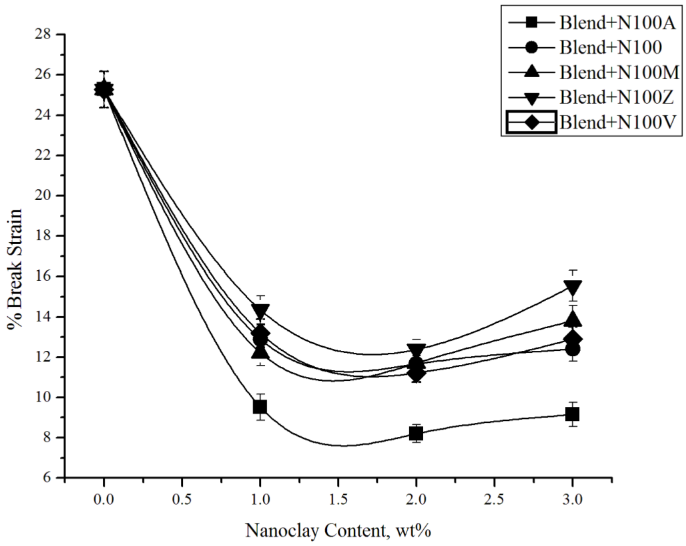


Figure 3.6 Effect of surface modification of nanoclay on break strain of PP/HDPE nanocomposites

The impact strength of polymer/clay nano composites was also studied and compared with that of pure polymer systems. The reports are usually emphasising on the increase of impact strength by the addition of a very low fraction of clay loadings such as 0.1 wt% [41-42]. In these studies organically modified clay fillers were added to the compatibilized polyolefines. There are also reports on the decreasing of impact resistance by the addition of clay materials [43]. The effect of adding different types of nanoclay are illustrated in figure 3.7. There is a decrease in value of impact strength as other properties are increased. This may be due to the alteration of crystallinity of the resultant nanocomposite.

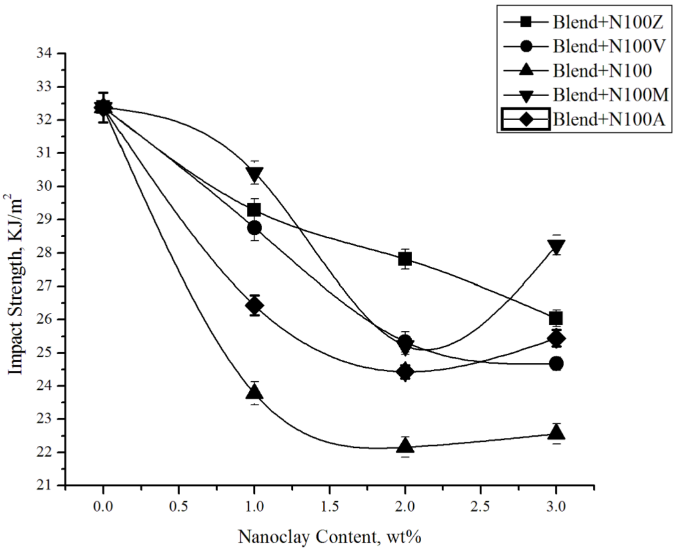


Figure 3.7 Effect of surface modification of nanoclay on impact strength of PP/HDPE nanocomposites

Thermal stability

One of the most accepted methods for studying the thermal properties of polymeric materials is the thermogravimetric analysis (TGA). Thermogravimetric curve represents the variation in the weight of the sample with temperature. They provide information about the nature, number of stages of thermal break down, weight loss of the material in each stage, threshold temperature, stability and extent of degradation of polymeric materials. Blumstein [44] first reported the improved thermal stability of PMMA/MMT nanocomposite. TGA showed that PMMA intercalated into the Na-MMT has 40-50°C higher decomposition temperature. Vyazovkin *et al.*[45] reported the thermal stability of polystyrene/clay nano-composite compared to pure PS. They have showed that PS/clay nanocomposites have 30-40°C higher degradation temperature compared to pure PS under nitrogen and air heating degradation conditions. Other studies have been showed that the nature of the clay modifier can affect on the thermal stability of modified clay and related nanocomposites[38]. Here comparisons of nanocomposites prepared with various type of modified clay with pure blend are shown in figure 3.8. All the nanocomposites except those prepared with dialkyl modified clay shows an increase in thermal stability. This may be due to the formation of highly carbonaceous ash cumulating on the nanocomposite surface. The degradation statistics of nanocomposites along with pure blend is tabulated in Table 3.2. There is an increase of 85°C in onset of thermal degradation for the nanocomposite containing N100A than the pure PP/HDPE blend.

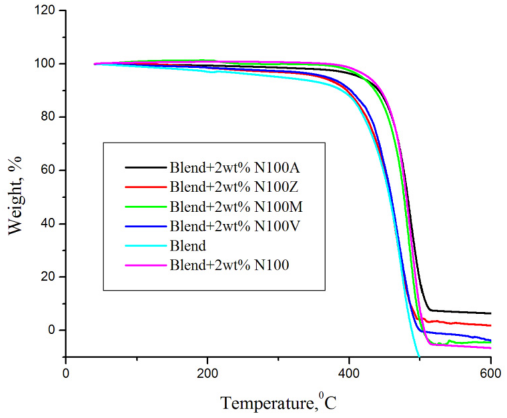


Figure 3.8 Effect of surface modification of nanoclay on thermal stability of PP/HDPE nanocomposites

Table 3.1 Thermal degradation characteristics of PP/HDPE blend and its nanocomposites

Samples	T_{onset}(°C)	10% Weight loss(°C)	50% Weight loss (°C)	80% Weight loss (°C)
Pure Blend	353	400	459	482
Blend+2wt% N100	433	444.85	482	654
Blend+2wt% N100 A	440	446.61	486.66	780
Blend+2wt% N100 M	382	442	478	522
Blend+2wt% N100 V	375	439.66	481	486
Blend+2wt% N100 Z	355	403	464	483.4

Dynamic mechanical analysis (DMA)

Polymers are useful in certain range of temperature-a low temperature limit below which they are brittle and a high temperature limit above which they soften, melt, degrade and ultimately decompose. Storage modulus is an important viscoelastic property which determines the behaviour of the material under varying conditions of applied load and temperature. Storage modulus of PP/HDPE blend as well as its nanocomposites, decreases with increase in temperature. It is observed that storage modulus of blend decreases with the increase in temperature, which is mainly attributed to the insufficient thermal energy to overcome the potential barrier for rotational and translational motion of segments of the polymer molecules in the glassy region which is above the glass transition temperature. However, incorporation of nanoclays results in an increase in the storage modulus of the PP/HDPE matrix over the entire range of temperature. The storage modulus curves display a rubbery plateau, indicating that addition of clay induces a reinforcing effect. The improvement in storage modulus of the nanocomposites over their pristine counterpart is more prominent in the rubbery region because in this region the material is soft and flexible. The enhancement of storage modulus strongly depends on the aspect ratio of the dispersed clay particles. When polymer matrix is reinforced with nanoclay, the polymer interface adjacent to the clay particle is highly restrained mechanically. Platelet edges of the clay particle act as a weak point and are sites of high stress concentration for the matrix. As aspect ratio of the filler increases, weak point decreases which results in the higher amount of stress transfer between the matrix and filler particles [46]. Dynamic mechanical analysis studies on polymer/clay nanocomposites have shown that usually storage modulus and glass transition temperature (Tg) are improved by the addition of clay nanofillers [47-50]. Here in this study all the nanocomposites (figure 3.9. and figure 3.10.) have larger storage modulus values and smaller tanδ values than PP/HDPE blend which indicates better reinforcement.

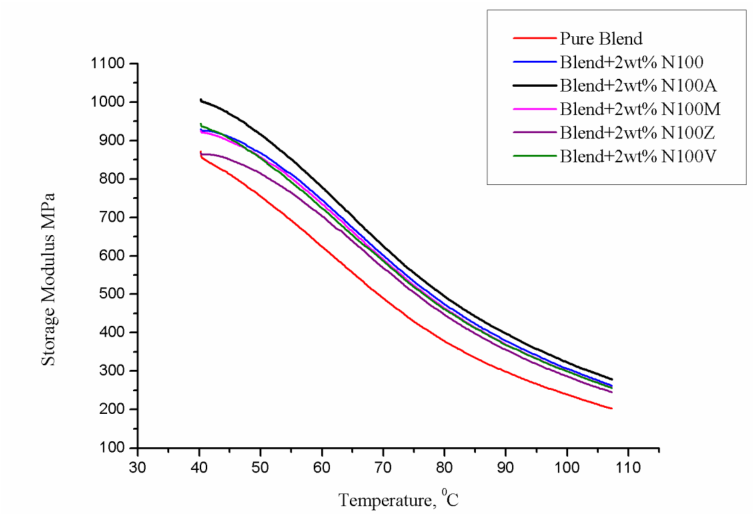


Figure 3.9 Effect of surface modification of nanoclay on storage modulus of PP/HDPE nanocomposites

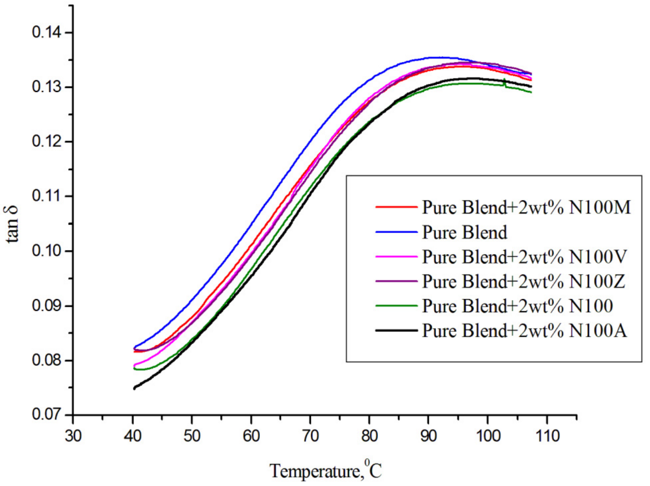


Figure 3.10 Effect of surface modification of nanoclay on damping coefficient of PP/HDPE nanocomposites

Differential scanning calorimetry (DSC)

The degree of crystallinity is one of the most important parameters for characterising crystalline and semicrystalline polymers. The miscibility, melting and crystallization behaviour of polymer blends can be analysed by differential scanning calorimetry. Differential scanning calorimetry (DSC) has been employed to study the melting and crystallization behaviour of PP/HDPE blend and their nanocomposites. The crystallization behaviour of a blend is more complex than that of a neat polymer due to the existence of a second crystallizing or non-crystallizing component. In a DSC study of PP and HDPE blend, Martuscelli *et al.*[51] revealed three different types of crystallization behaviour at three ranges of crystallization temperatures. Below 125°C, simultaneous crystallization of PP and HDPE was observed, from 125°C to 127°C, two crystallization peaks were observed with PP crystallizing first. Above 127°C, HDPE could not crystallize and the crystallization of PP was from a melt mixture of PP and HDPE. The addition of nanofiller may increase the melting and crystallization behaviour of the polymer according to the literature. The DSC heating and cooling scans of the PP/HDPE blend and their nanocomposites are illustrated in figures 3.11. and 3.12. The crystallization temperatures of the blend were altered by the addition of nanokaolinite clay.

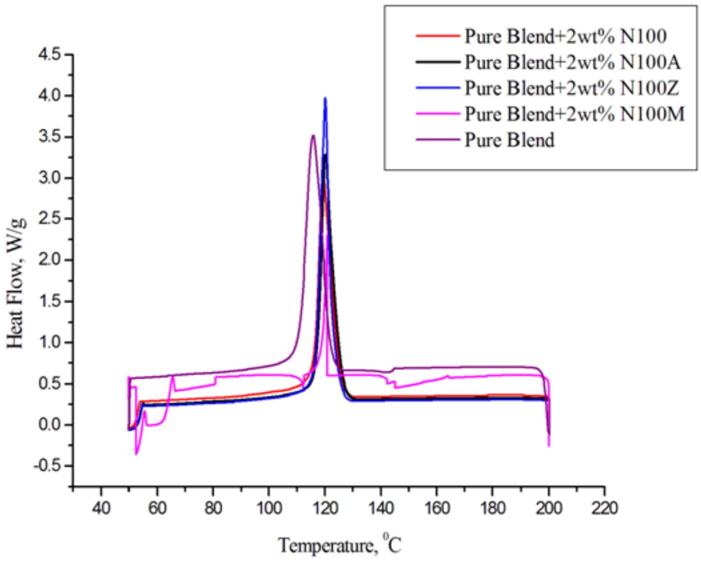


Figure 3.11 Effect of surface modification of nanoclay on crystallisation behaviour of PP/HDPE nanocomposites

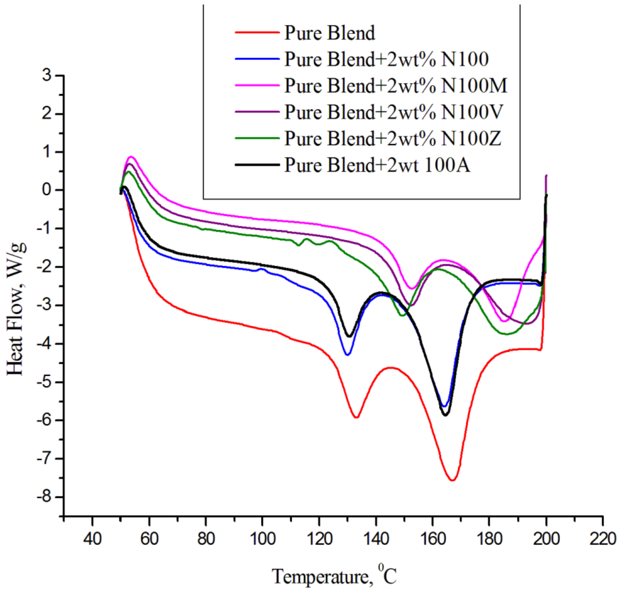


Figure 3.12. Effect of surface modification of nanoclay on melting behaviour of PP/HDPE nanocomposites

Table 3.2 Effect of surface modification of nanoclay on crystallization and melting characteristics of PP/HDPE nanocomposites

Sample	Tc, °C	Tm1, °C	Tm2, °C	ΔHc (J/g)	ΔHm1 (J/g)	ΔHm2 (J/g)
Pure blend	117.5	131.2	163.5	81.69	17.84	32.56
PP/HDPE/2wt% N100A	122.61	131.5	162	100.1	21.42	38.24
PP/HDPE/2 wt% N100	120.22	129.2	160.2	97.61	18.12	30.35

Melt flow index

Melt flow index is an easily determinable property which tells about the behaviour of the composite during processing stages such as moulding, extrusion etc. The melt flow index is determined by allowing the material to flow through a capillary under constant weight at an elevated temperature. The presence of interactions between the polymer chains and silicate surface may affect the mobility and rheological properties of the polymer chains. Therefore, nanoclay addition should decrease the polymer MFI in polar polymers. The MFI values of all the nanocomposites except that with dialkyl modified clay (due to plasticizing effect of surface modifier)shows a reduction in MFI values exhibiting more reinforcement. (Figure 3.13.)

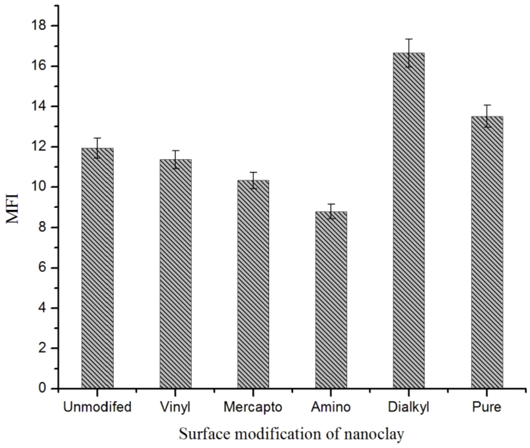


Figure 3.13 Effect of surface modification of nanoclay on MFI of PP/HDPE nanocomposites

X-ray diffraction (XRD)

The polymer/clay nanocomposite can be divided into three types – immiscible composites, intercalated composites and exfoliated composites. For the case called ‘‘immiscible composite” , the organoclay platelets exist in particles comprised of tactoids or aggregates of tactoids more or less as they were in the organoclay powder, i.e., no separation of platelets. Thus, the wide angle X-ray scan of the polymer composite is expected to look essentially the same as that obtained for the organoclay powder; there is no shifting of the X-ray d-spacing. Generally, such scans are made over a low range of angles, 2θ, such that any peaks from a crystalline polymer matrix are not seen since they occur at higher angles. For completely exfoliated organoclay, no wide angle X-ray peak is expected for the nanocomposite since there is no regular spacing of the platelets and the distances between platelets would, in any case, be larger than what wide angle X-ray scattering can detect. Often X-ray scans of polymer nanocomposites show a peak reminiscent of the organoclay peak but shifted to lower 2θ or larger d-spacing condition. The fact that there is a peak indicates that the platelets are not exfoliated. The peak shift indicates that the gallery has expanded, and it is usually assumed that polymer chains have entered or have been intercalated in the gallery. Placing polymer chains in such a confined space would involve a significant entropy penalty that presumably must be driven by an energetic attraction between the polymer and the organoclay [52-55]. It is possible that the gallery expansion may in some cases be caused by intercalation of oligomers or low molecular weight polymer chains. The early literature seemed to suggest that ‘‘intercalation’’ would be useful and perhaps a precursor to exfoliation. Subsequent research has suggested alternative ideas about how the exfoliation process may occur in melt processing and how the details of the mixing equipment and conditions alter the state of dispersion achieved [56-59]. The three types of nanocomposites along with the respective TEM and XRD images are illustrated in figure 3.14

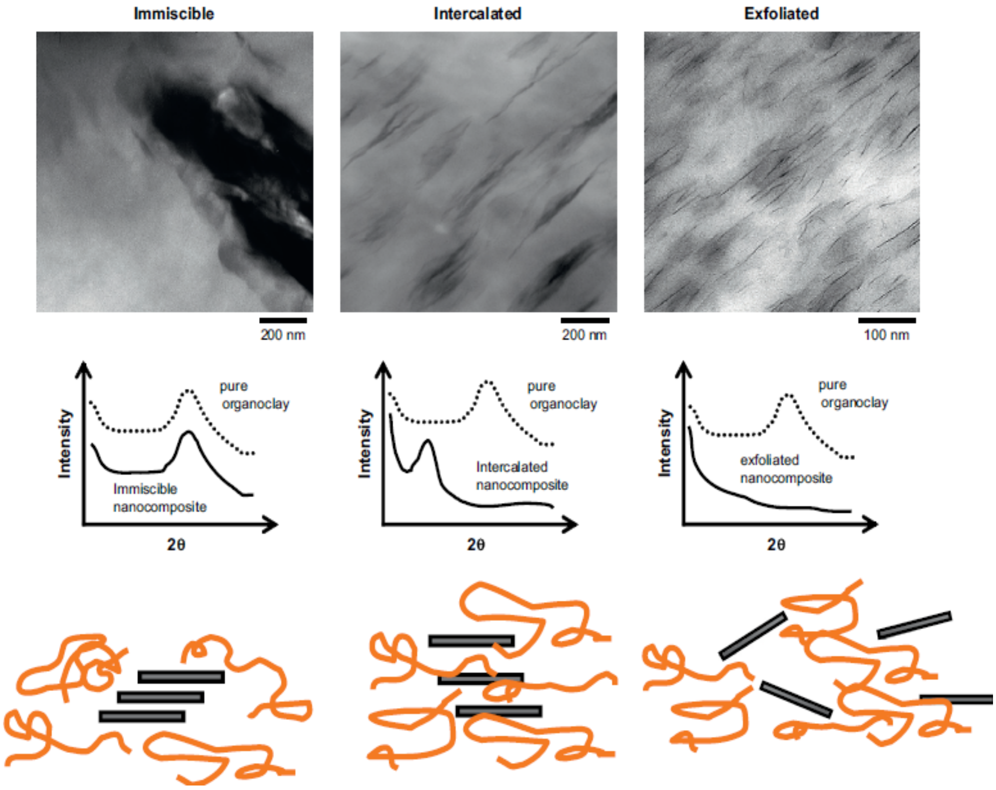


Figure 3.14 TEM images, XRD patterns and structure of three types of nanocomposites

The XRD patterns of the unmodified and amino modified nanoclay along with the nanocomposites are illustrated in figure 3.15. The peaks shift to the left side towards lower 2θ values/ increased d-spacing indicating the presence of intercalated composites. According to Zhu and Wilkie[60], both the position at which peak is found and its width are important. If the position is at a lower value of 2θ, this indicates that the d-spacing has increased and is indicative of nanocomposite formation. If the peak is broad, this may be interpreted as indicating disorder. If the peak is sharp, intercalation is likely. On the other hand, the absence of a peak could mean either that a delaminated structure has been produced, which has lost registry and thus shows no peak, or the tactoids are internally disordered (disordered immiscible or intercalated) or not well aligned to one another [60, 61]. From the XRD pattern it is interpreted that maximum shift in 2θ occurs for the composite containing N100A.

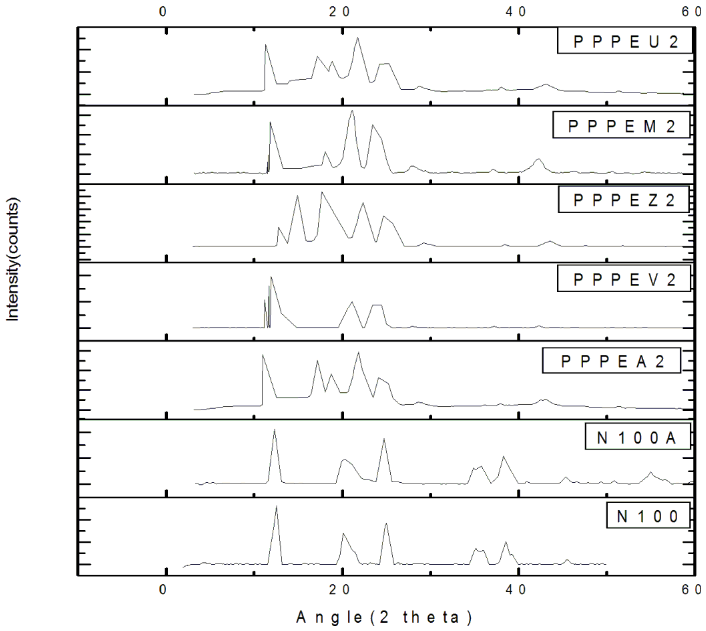


Figure 3.15 Effect of surface modification of nanoclay on X-ray diffraction pattern of PP/HDPE nanocomposites

Scanning electron microscopy (SEM)

SEM observations showed that the clays are distributed into PP/HDPE matrix in the form of large and small aggregates. It is very difficult to estimate the size of the aggregates because they are non- isometric and randomly dispersed in the matrix. The size of observed aggregates is, therefore strongly dependent on the orientation of the particles. However, the fracture mode of samples and dispersion quality of clays such as aggregate concentrations can be observed. Fig 3.16 is the SEM micrograph of pure blend (80PP/20HDPE). The observed morphology shows a good extent of compatibility between two phases at the present composition. Figures 3.17 to 3.23 are the SEM micrographs of the composites containing different surface modified nanoclays. However in fig. 3.18 the size of the nanoclay aggregates is reduced significantly compared to the morphology of other nanocomposites. This means that dispersion of nanoclay is improved significantly by intercalant-aminosilane. Therefore surface treatment of nanoclay is very important to improve the affinity between the nanoclay and the matrix and to break down the large aggregates. This can be attributed to the ability of surface treatment in reducing particle-particle attraction and promoting the expansion of gallery distance between clay sheets [62, 63]. For nanocomposites containing unmodified nanoclay the clay aggregate sizes obtained are in the range of 400-700nm whereas in the case of amino modified nanoclay it is of the range of 80-120nm.

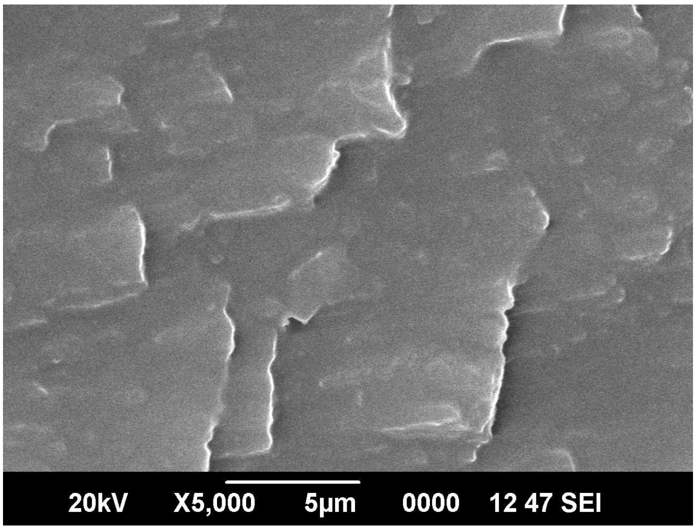


Figure 3.16 SEM micrograph of pure blend (80PP/20HDPE).

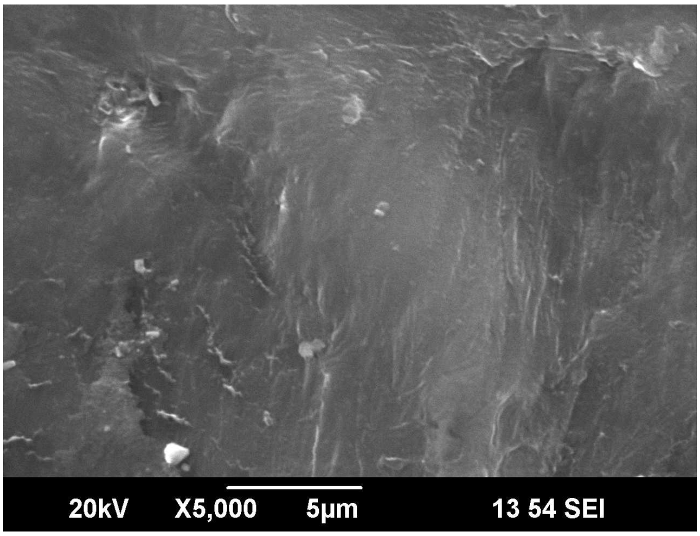


Figure 3.17 SEM micrograph of nanocomposite (80PP/20HDPE/N100A).

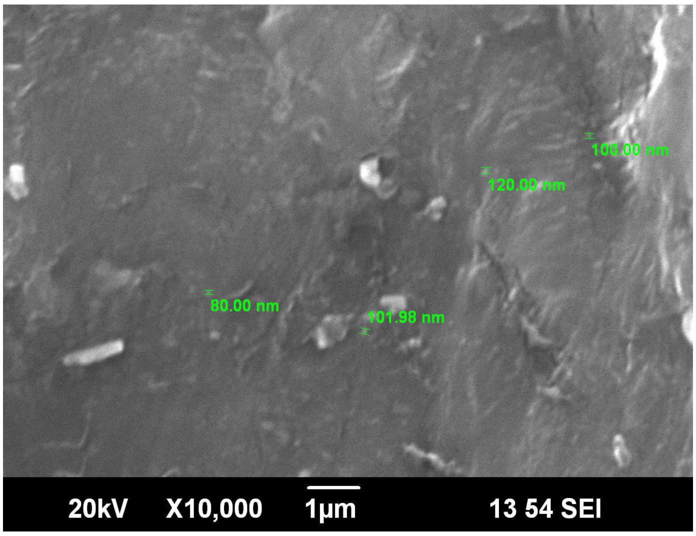


Figure 3.18 SEM micrograph of nanocomposite (80PP/20HDPE/N100A) at higher magnification.

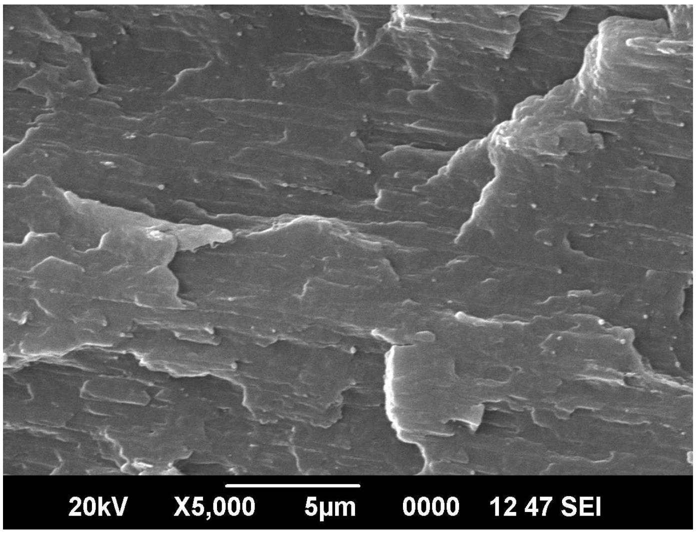


Figure 3.19 SEM micrograph of nanocomposite (80PP/20HDPE/N100Z).

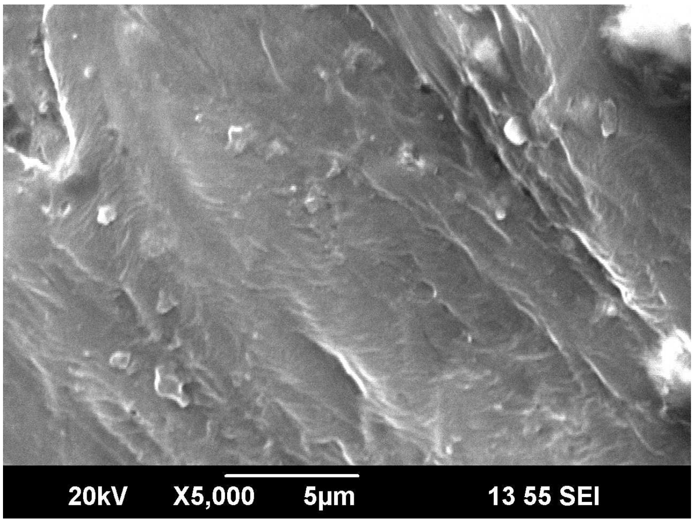


Figure 3.20 SEM micrograph of nanocomposite (80PP/20HDPE/N100M).

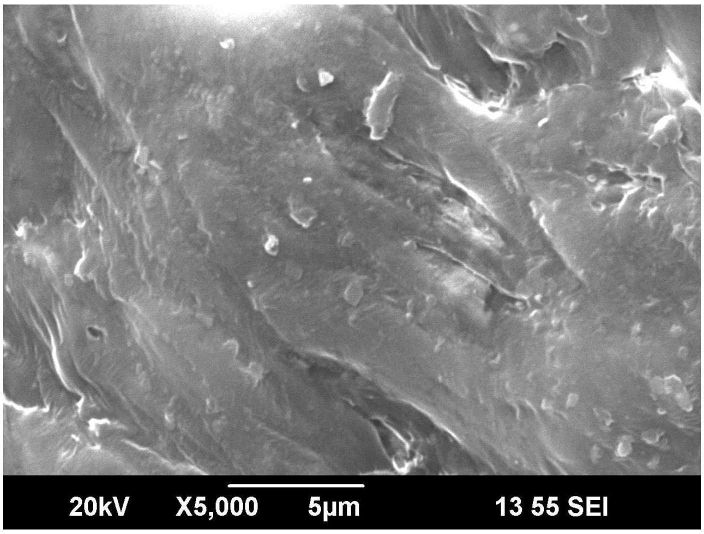


Figure 3.21 SEM micrograph of nanocomposite (80PP/20HDPE/N100V).

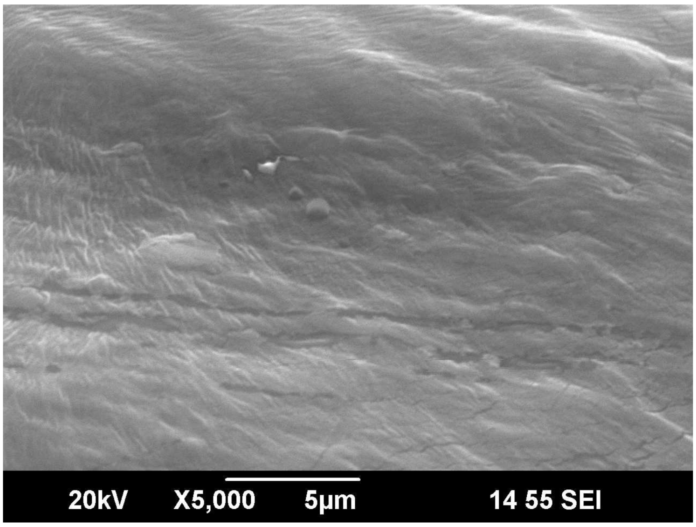


Figure 3.22 SEM micrograph of nanocomposite (80PP/20HDPE/N100)

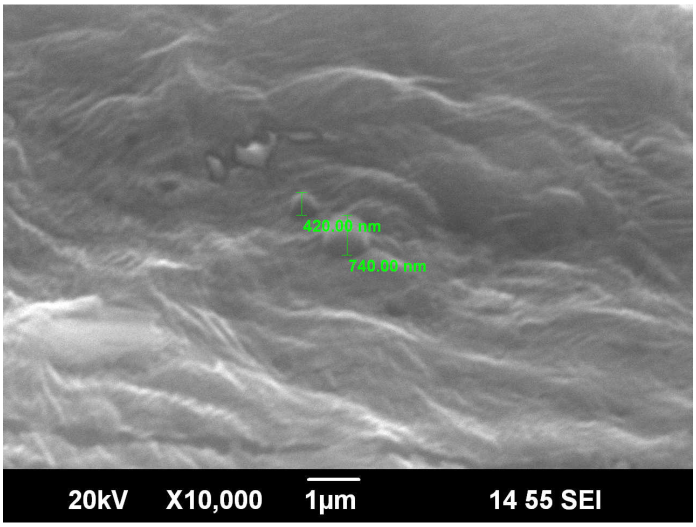


Figure 3.23 SEM micrograph of nanocomposite (80PP/20HDPE/N100) at higher magnification.

Transmission electron microscopy (TEM)

TEM is known as a complimentary technique which is used simultaneously together with XRD. TEM provides direct visual information of the morphology, atom arrangement, spatial distribution of the phases and structural defects of a selected area of the sample. Its only limitations are operational, since great care is needed in preparation of the sample in such a way as to enable a representative section to be examined[64]. XRD studies provide a quantitative understanding of the global morphology in reciprocal space, whereas TEM quantitatively visualizes the complimentary local structure in real space[65]. In XRD equipment, there is an angle below which results are not recorded, which defines the lower limit. To overcome the limitations of XRD and further differentiate between the intercalated and exfoliated morphologies, TEM is used to give a clear picture of the nanoscale dispersion and overall bulk dispersion of the clay in the polymer. Generally, it is hard to achieve complete exfoliation of clays directly by melt mixing due to the physical and chemical environment between the organic and inorganic component. Moreover, some of the silicate layers flocculate easily owing to hydroxylated edge–edge interaction among themselves[66]. The majority of the polymer nanocomposites reported in the literature is found to have intercalated or mixed intercalated-exfoliated nanostructures [67]. This is because the silicate layers are highly anisotropic, with lateral dimensions ranging from 100 to 1000 nm, and even when separated by large distances (i.e. when delaminated) cannot be placed completely randomly in the polymer matrix[19]. Hence an intercalated structure or mixed intercalated-exfoliated structure is expected for this type of melt-mixed nanocomposite.

Dispersion of nanoclay within the polymer matrix was further corroborated (in the case of unmodified and amino silane modified nanocomposites) with the TEM images depicted in figures 3.24 and 3.25. The dark lines represent the intersection of clay sheets while the white background corresponds to polymer matrix. In fig 3.25, the unmodified nanoclay show a poor amount of intercalation leading to aggregates of size more than 200nm which confirms the observations of SEM study. In the case of nanocomposites containing N100A (fig 3.24), clay sheets are properly intercalated or partially exfoliated leading to more improved nanocomposite. This results corresponds to the SEM image obtained for modified nanoclay composites (PP/HDPE/N100A) having the size of the clay aggregates in the range of 80-120 nm.

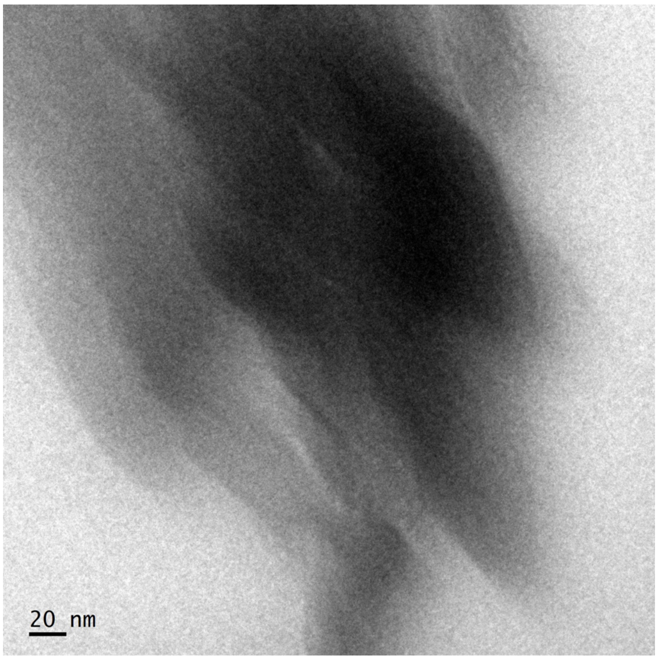


Figure 3.24 TEM micrograph of nanocomposite (80PP/20HDPE/N100A) at higher magnification

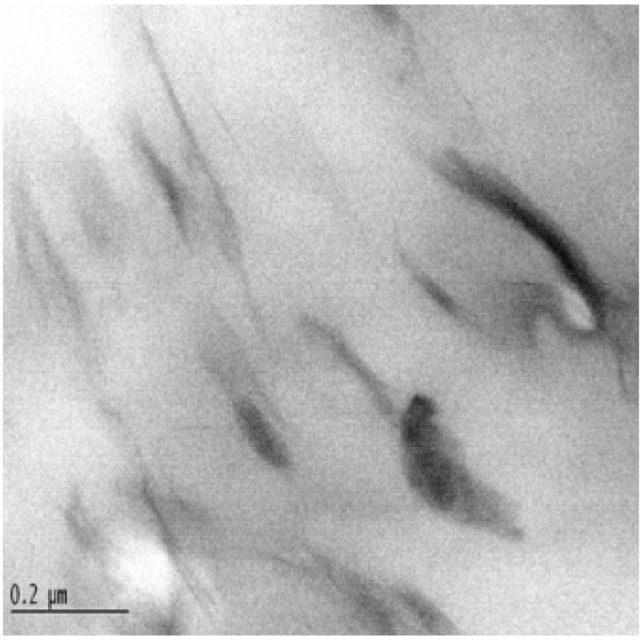


Figure.3.24A TEM micrograph of nanocomposite (80PP/20HDPE/N100A)

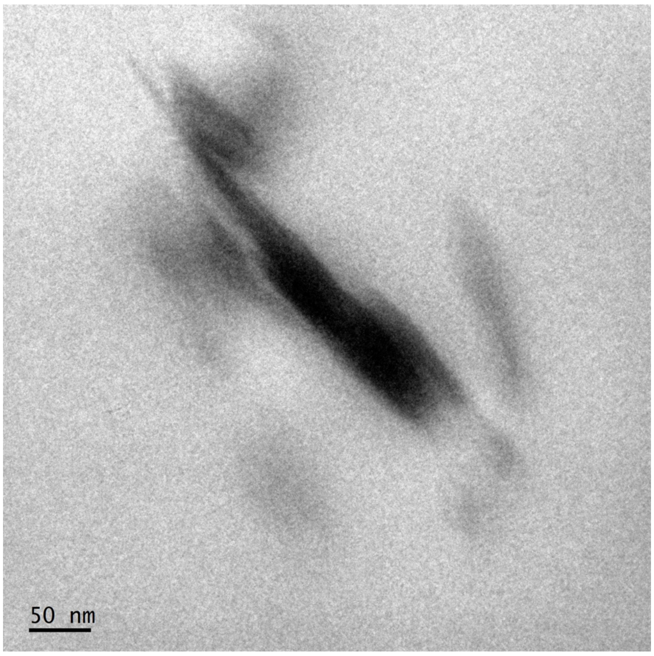


Figure 3.25 TEM micrograph of nanocomposite (80PP/20HDPE/N100) at higher magnification

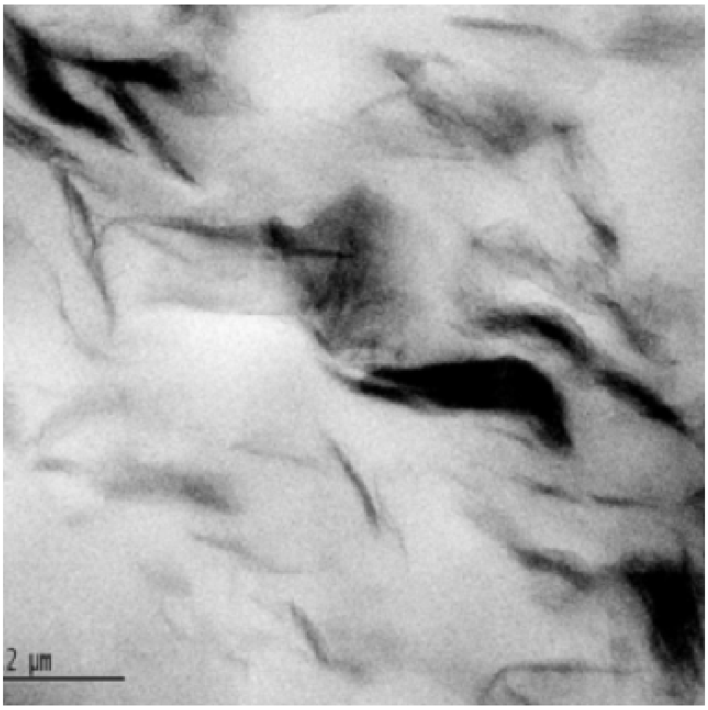


Figure 3.25A TEM micrograph of nanocomposite (80PP/20HDPE/N100)

3.3.2 Effect of blend composition on mechanical properties of both modified and unmodified nanocomposites.

Mechanical properties

Blending is an art of mixing two or more polymers for getting unique properties. Polymer blends have played a significant role in the last few decades in revolutionizing polymer technology, leading to important and useful applications. The term polymer blend may be defined as a combination of two or more structurally different polymers or copolymers giving rise to materials with a range of properties, not delivered by any of the constituents. Thus the reason for using blends includes the attainment of specific article performance, by improving the technical properties of the original polymers, or by adjusting the processing characteristics and reducing cost. The possibilities of blending of the major polymer are infinite, and the market place will dictate the tailoring of the blends. Most pairs of polymers are thermodynamically immiscible, but some polymer blends are compatible and exhibit excellent physical properties. In the presence of a third component such as a nanoparticle, the behaviour of the blend may be altered further. PP and HDPE are fairly compatible blends and in this section, the effect blending on the mechanical properties of PP/HDPE/nanokaolinite clay composites are studied. PP/HDPE was melt blended in different weight ratios from 100% PP to 100% HDPE with an increment of 20 wt%. Composites were prepared at each blend composition with both unmodified and surface modified nanoclay and the mechanical properties are studied.

The tensile strength of PP/HDPE blend with both modified and unmodified clay are plotted against weight% of PP in figures 3.26 and 3.27. The strength increases as PP content increases initially, reaches a maximum and then decreases. The maximum enhancement of tensile strength occurs at 80/20 weight ratio of PP/HDPE blend. The PP/HDPE/2 wt% clay nanocomposite shows the highest value of tensile strength. Although the same trend is exhibited by the composite containing unmodified clay, the improvement of properties is more for composites containing modified kaolinite clay.

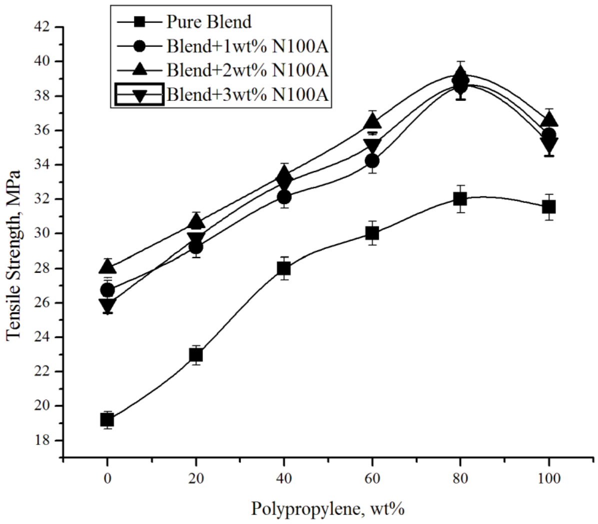


Figure 3.26 Effect of blend composition on tensile strength of PP/HDPE/N100A nanocomposites

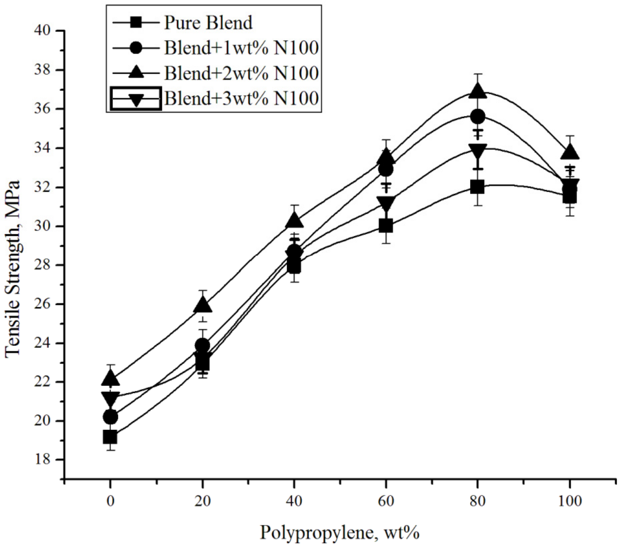


Figure 3.27 Effect of blend composition on tensile strength of PP/HDPE/N100 nanocomposites

The flexural strength of PP/HDPE blend with both modified and unmodified clay is plotted against weight% of PP in figures 3.28 and 3.29.

The strength increases as PP content increases initially, reaches a maximum and then decreases after 80PP/20 HDPE by weight.

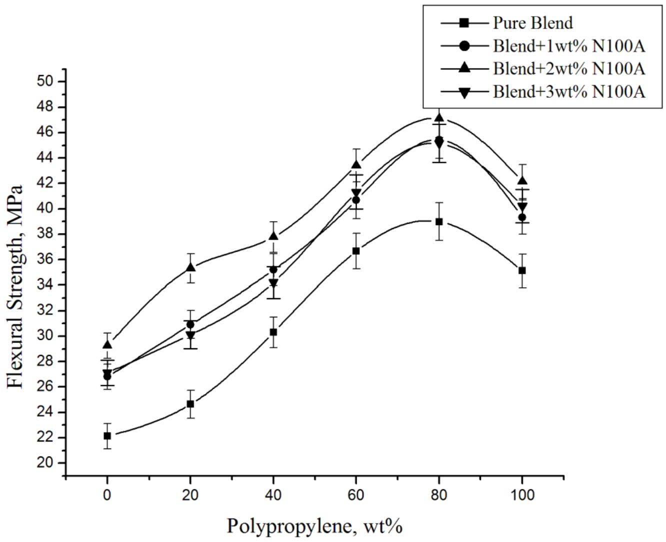


Figure 3.28 Effect of blend composition on flexural strength of PP/HDPE/N100A nanocomposites

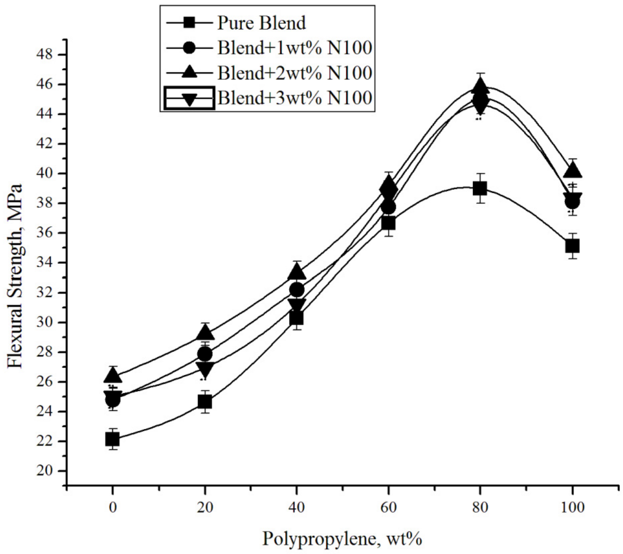


Figure 3.29 Effect of blend composition on flexural strength of PP/HDPE/N100 nanocomposites

The trend followed is similar for both modified and unmodified clay, but the flexural strength is more for composite containing modified nanoclay. Poon *et al.* [68] studied the adhesion and compatibility of PP/HDPE blends and reported that the adhesion and compatibility increases in the presence of an organic molecule. This may be the reason for increase of mechanical properties in the presence of modified nanokaolinite clay

The tensile modulus of PP/HDPE blend, with both modified and unmodified clay is plotted against weight% of PP in figures 3.30 and 3.31. The strength increases as PP content increases initially, reaches a maximum and then decreases after 80/20 weight ratio of PP and HDPE. The 80/20 weight% PP/HDPE blend shows more improvement in mechanical properties than with that of pure PP and HDPE, and hence it can be concluded that blending imparts a synergistic effect in the presence of nanoclay.

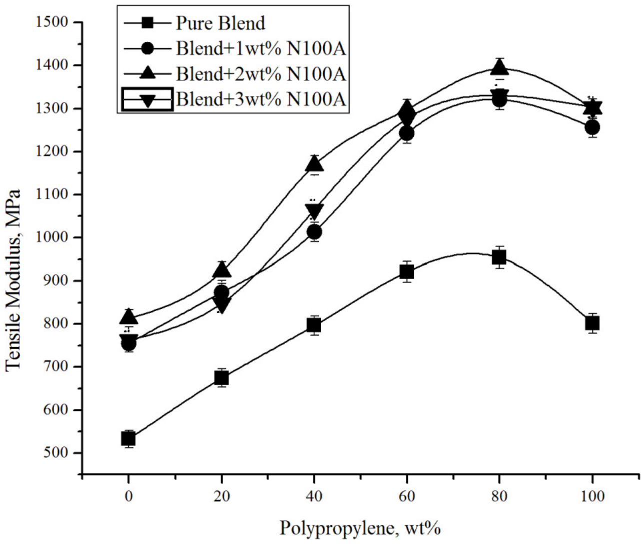


Figure 3.30 Effect of blend composition on tensile modulus of PP/HDPE/N100A nanocomposites

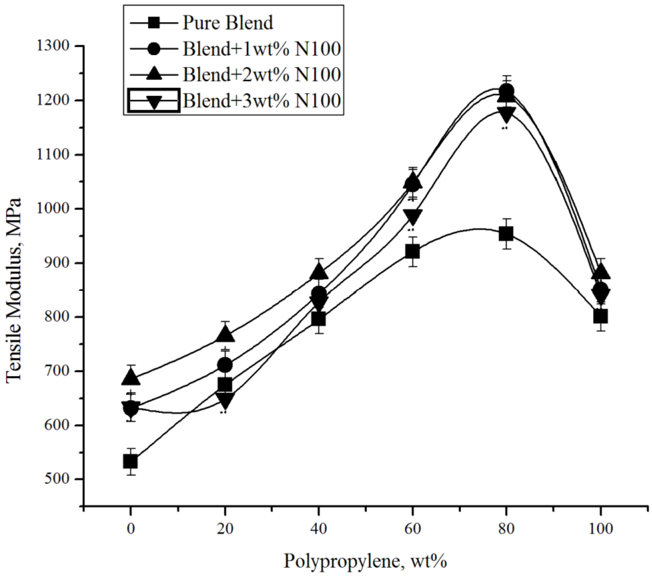


Figure 3.31 Effect of blend composition on tensile modulus of PP/HDPE/N100 nanocomposites

The flexural modulus of PP/HDPE blend with both modified and unmodified clay is plotted against weight% of PP in figures 3.32 and 3.33. The strength increases as PP content increases initially, reaches a maximum at 80/20 weight ratio of PP/HDPE and then decreases. High temperature thermoset polyimide is mixed with unmodified and modified montmorillonite (layered silicate) clay[69]. Dynamic mechanical analysis results showed a significant increase in the thermo-mechanical properties of clay loaded nanocomposites in comparison with the neat polyimide. Also higher glass transition temperature was observed and flexural properties measurements showed a significant improvement in the modulus and strength, with no loss in elongation. Doubling the clay loading percentage resulted in degradation of nanocomposite flexural properties.[69]

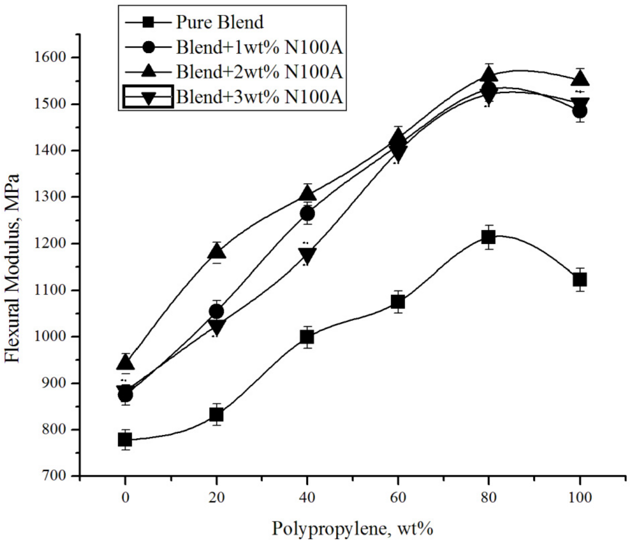


Figure 3.32 Effect of blend composition on flexural modulus of PP/HDPE/N100A nanocomposites

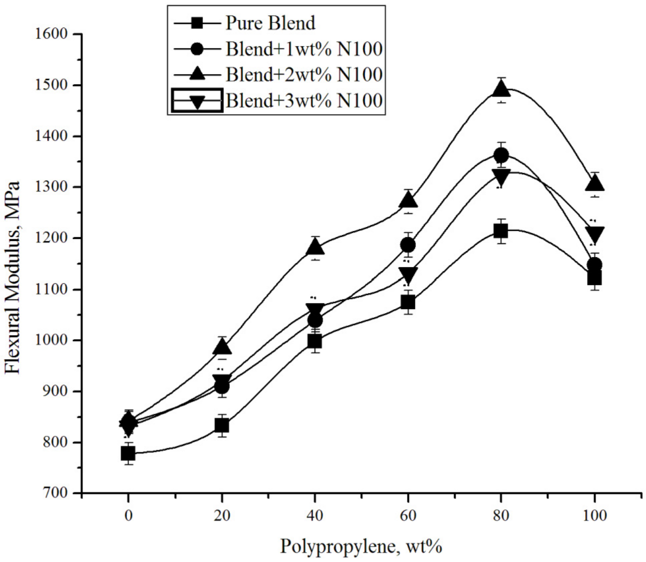


Figure 3.33 Effect of blend composition on flexural modulus of PP/HDPE/N100 nanocomposites

The impact strength of PP/HDPE blend with both modified and unmodified clay is plotted against weight% of PP in figures 3.34 and 3.35. The strength decreases as PP content increases and this may be due to the fact that PP is more crystalline than HDPE. The impact behaviours and properties are mainly improved by small particles with low aspect ratio, since large particles can be crack initiation sites. The particles that possess high aspect ratio induce large stress concentrations near their edges. It also should be pointed out that the interfacial interaction between fillers and polymer matrix significantly influence the mechanical properties of particulate filled polymers. Furthermore, since the nature of the particle–matrix interface influences the toughness of filled polymer, the amorphous nature of the interface is more effective in enhancing the toughness of the filled polymer than the crystalline interface.

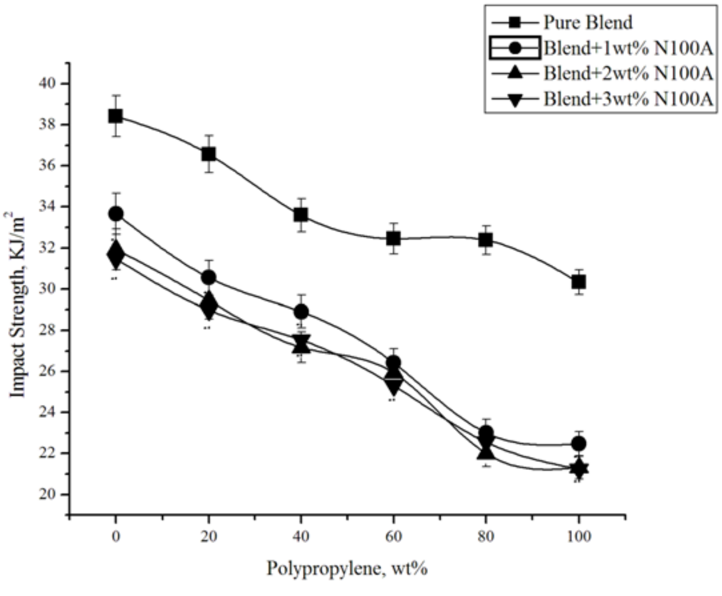


Figure 3.34 Effect of blend composition on impact strength of PP/HDPE/N100A nanocomposites

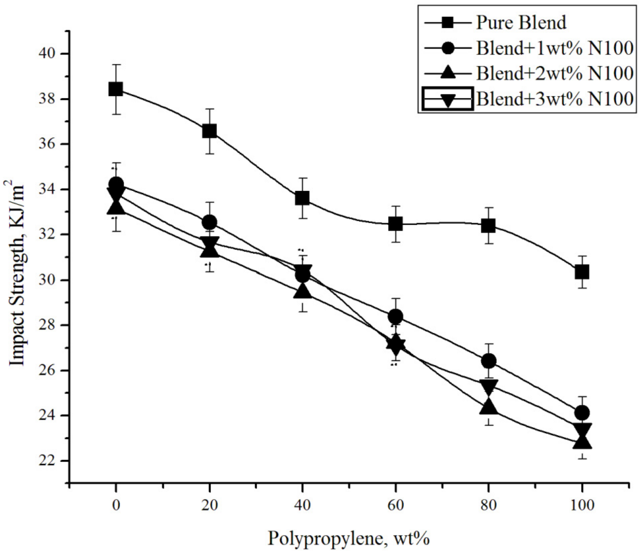


Figure 3.35 Effect of blend composition on impact strength of PP/HDPE/N100 nanocomposites

The observation of higher crystallinity in the nanocomposite is expected to have a negative effect on toughness. The study of impact toughness at high strain rates is of particular interest and relevance because yield stress increases with strain rate, promoting brittle mode of fracture. High tensile toughness may not necessarily mean high impact toughness. Experimental results for the response of nanocomposites impacted at low velocities by a rigid semi-sphere impact tester have been presented by Lin at al. [70]

The elongation at break of PP/HDPE blend with both modified and unmodified clay is plotted against weight% of PP in figures 3.36 and 3.37. The elongation at break decreases as PP content increases and this indicates that the interfacial adhesion increases and this lead to more reinforcement. The effect of nanoclay modified with polyol and mixed into an epoxy matrix system was studied by Isik *et al.*[71] The materials used are diglycidyl ether of bisphenol A as matrix system and montmorillonite Cloisite 30B modified with polyether polyol, which bonds well with epoxy. The tensile strength decreased with increasing amount of clay and constant content of polyol. The polyol appear to have a beneficial effect on tensile strength when its content is increased. This is due to the higher level of crosslinking induced by the polyol. The Young's modulus increased with increasing amount of nanoclay and constant amount of polyol. The extension at break was smaller for the clay nanocomposite than for the virgin polymer.

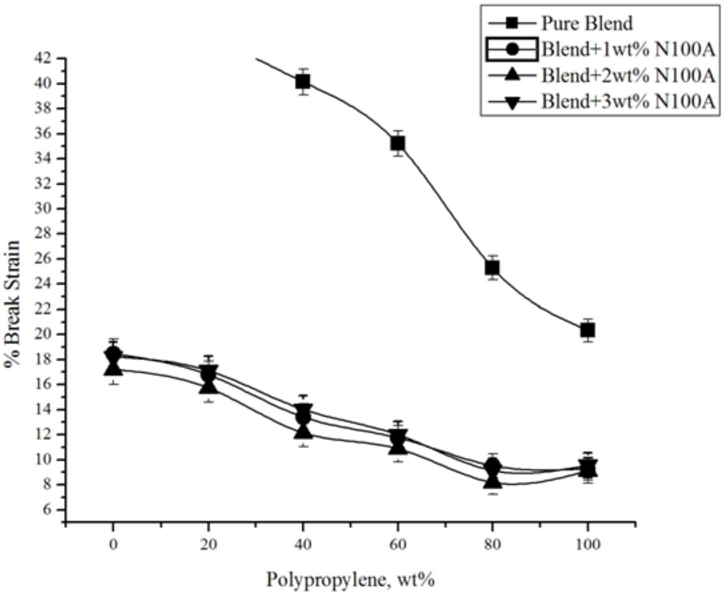


Figure 3.36 Effect of blend composition on break strain of PP/HDPE/N100A nanocomposites

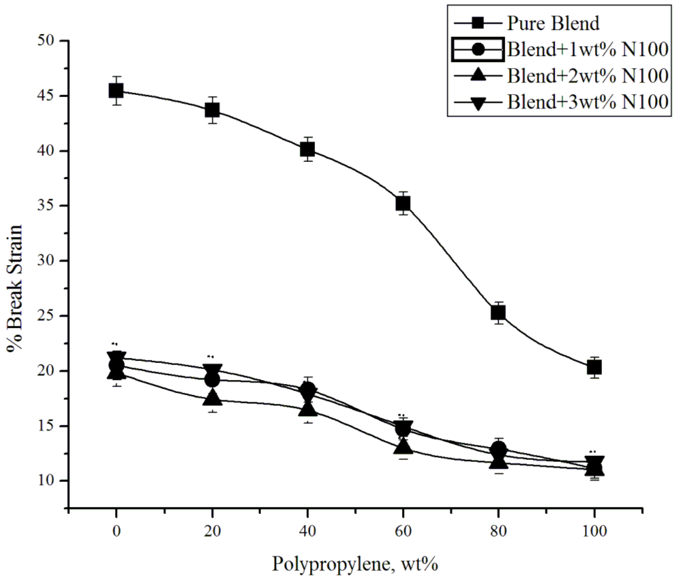


Figure 3.37 Effect of blend composition on break strain of PP/HDPE/N100 nanocomposites

The above results indicate that blending of PP and HDPE upgrades both the polymers and a new material is formed with superior properties. The tensile and flexural strength and moduli increase by blending and maximum enhancement is obtained at a wt % of 80PP/20HDPE. The blending imparts slight detrimental effect on impact strength and more research is to be done on this topic. The presence of modified nano kaolinite clay synergistically modifies the properties of the PP/HDPE blend. Based on the above study PP/HDPE blend of 80/20 wt % is chosen as the polymer matrix material for further research.

3.3.3 Effect of melt compounding temperature on mechanical properties of PP/HDPE/nanoclay composites

Nanocomposites can, in principle, be formed from clays and organoclays in a number of ways including various in situ polymerization.[72-80], solution polymerization [81-82], and latex polymerization [83-84] methods. However, the greatest interest has involved melt processing [52-55, 57-58, 85-147] because this is generally considered more economical, more flexible for formulation, and involves compounding and fabrication facilities commonly used in commercial practice. For most purposes, complete exfoliation of the clay platelets, i.e., separation of platelets from one another and dispersing them individually in the polymer matrix, is the desired goal of the formation process. But processing conditions especially melt compounding temperature is the most determining factor for the proper dispersion of nanoclay in the polymer matrix. Lower operating temperature lead to improper mixing and agglomeration of clay in the polymer matrix, and higher operating conditions lead to degradation of polymer matrix. Both conditions lead to reduced strength and toughness. So, selection of an experimental range of operating temperature is carried out in this study based on the mechanical properties of PP/HDPE/nanoclay composites with different types of kaolinite nanoclay prepared at various processing temperatures. The effect of temperature on mechanical properties of different nanocomposites processed at various melt compounding temperatures are shown here (figures 3.38 to 3.43).

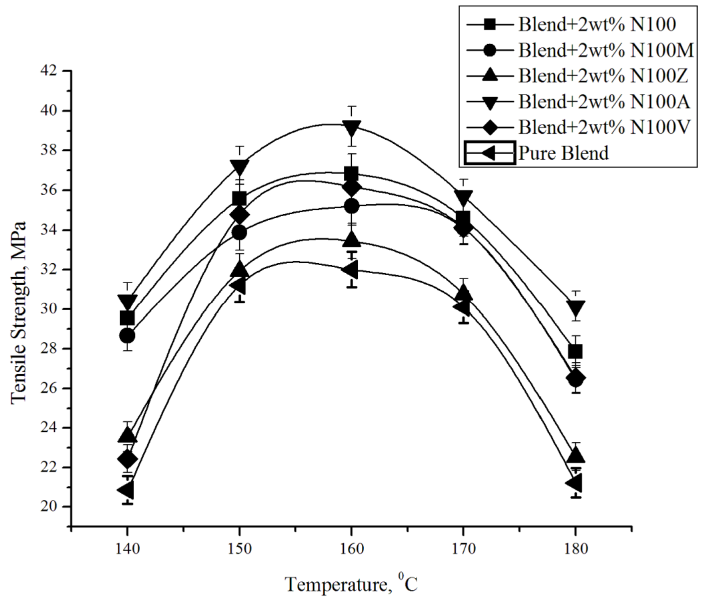


Figure 3.38 Effect of melt compounding temperature on tensile strength of PP/HDPE nanocomposites

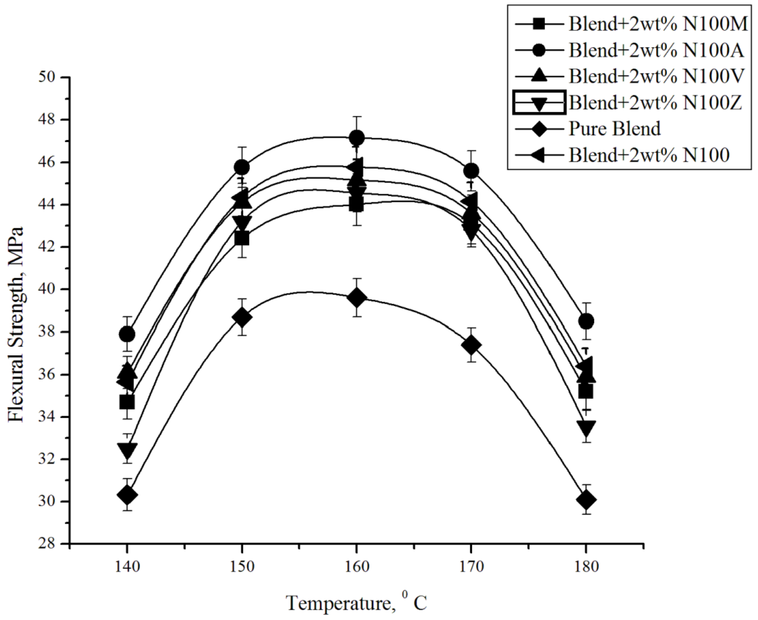


Figure 3.39 Effect of melt compounding temperature on flexural strength of PP/HDPE nanocomposites

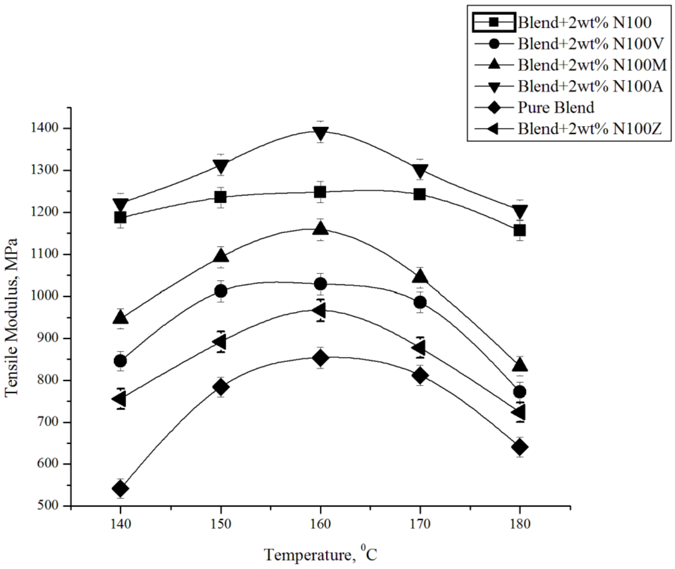


Figure 3.40 Effect of melt compounding temperature on tensile modulus of PP/HDPE nanocomposites

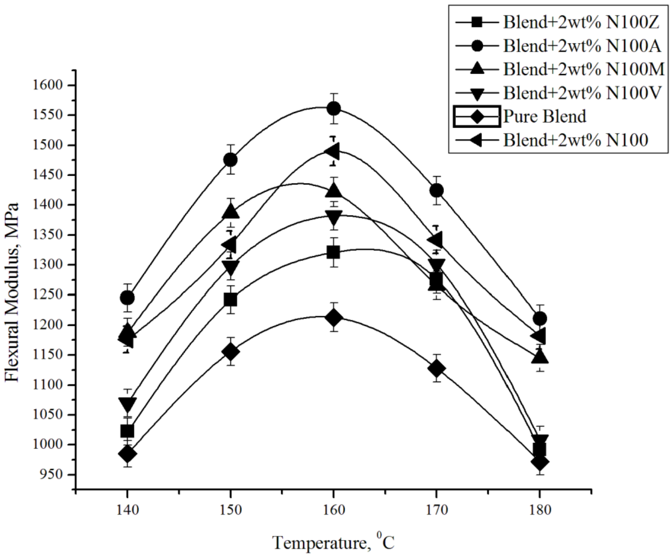


Figure 3.41 Effect of melt compounding temperature on flexural modulus of PP/HDPE nanocomposites

The relationship between morphology and the mechanical properties of thermoplastic olefin materials that are reinforced with organoclay fillers and prepared by melt processing was reported by Lee *et al.*[148]. The nanocomposites are prepared by melt compounding and mixing of PP, an ethylene–octene based elastomer, with a master batch material containing equal parts of maleated PP and an organically modified montmorillonite. The Young's modulus increases with increasing clay content, up to 60% for 7 wt% clay. The Yield strength increases initially with clay content up to 6% (increase of 7%) and then it is dropped to below the value of virgin polymer. However, the changes are very contained. The elongation at break gradually diminishes with presence of nanoclay, reaching about 66% decrease for 7% of clay content. The relative content of elastomer produces a decrease in Young's modulus and yield strength. The elongation at yield and the elongation at break increases instead. In this extend, the clay content do not have a comparable effect on Young's modulus and yield stress, but it lowered sensibly the value of elongation at break and at yield.

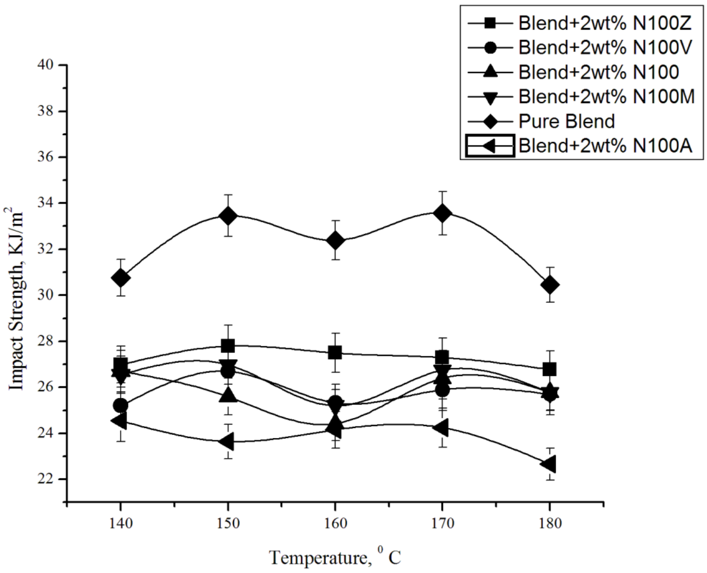


Figure 3.42 Effect of melt compounding temperature on impact strength of PP/HDPE nanocomposites

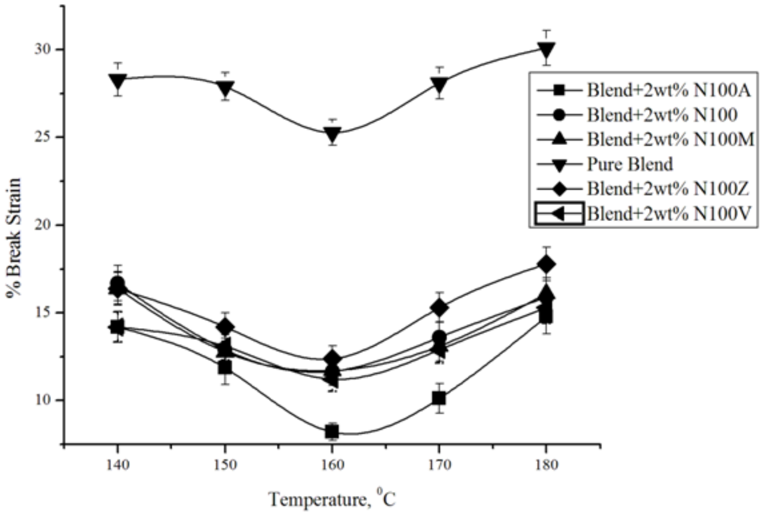


Figure 3.43 Effect of melt compounding temperature on break strain of PP/HDPE nanocomposites

The tensile and flexural strength and modulii first increases, reaches a maximum and then decreases after 160°C, and the properties are maxima for composites containing amino modified nanoclay. The processing temperature is not having much effect on impact strength when compared with type of clay modification. The elongation at break on the other hand decreases with increasing temperature, reaches a maximum and the decreases. The reduction of elongation at break indirectly suggests reduced mobility of polymer chains and clay platelets which is a sign of better reinforcement.[149-151]. Park *et al.* [152] tested a nanocomposite made of a mixture of epoxy, polymethyl-methacrylate (PMMA), and nanoclay as reinforcement. The manufacturing procedure uses melt blending technique where two epoxies (one aromatic and one aliphatic) were mixed with nanoclay (Cloisite 30B). Izod impact tests were performed on notched samples at room temperature. For PMMA-nanoclay composites the impact toughness was reduced as a result of the presence of clay, with values dropping up to 20% for clay content of 6wt%.

3.3.4 Effect of glass fibre composition on the mechanical properties of hybrid composites

Usually, clays are added to thermoplastic polymer matrices to reduce cost but currently modified clays have been used as reinforcing agent to improve the properties of the material. Nanoclays are known to increase the modulus, heat distortion temperature, flame retardancy and dyeability of thermoplastic materials with a reduction in other properties like strength. This can be rectified by adding short fibres into the same matrix which improve stiffness and strength. The simultaneous use of both clay and fibre fillers, so called hybridization leads in many cases to synergistic effects, improving properties such as wear resistance, stiffness, fracture toughness, dynamic response etc.[153-155]

The micro/nanoclay hybrids can exhibit superior properties when the nanoclay is in highly intercalated or exfoliated form. Molecular characteristics of the organo-modifier attached to the clay, and so polarity of the polymer, have been reported to influence the desired nanoclay exfoliated condition. Intercalation process is also influenced by polarity of the organic molecule. The non polar nature of PP and HDPE in contrast to the polar characteristics of nanoclay makes the nanoclay intrinsically incompatible with the polymer matrix. Surface modification of nanoclay changes the scenario. The modified organic molecule can act as a bridge between the non polar polymer and polar nanoclay surface. The improved adhesion obtained with surface modifiers results in enhanced mechanical properties, such as tensile strength, flexural modulus, impact strength and heat deflection temperature than pure blend.

The mechanical properties of hybrid composites with and without different surface modified nanoclay were plotted against glass fibre content in figures 3.44 to 3.49. The properties show an increase in value as glass fibre content increases, reaches a maximum and then decreases. The effect of glass fibre content on tensile and flexural strength is compared for PP/HDPE blend with and without nanoclay. The presence of nanoclay induces synergistic effect on strength and all the hybrid composites show increased tensile and flexural strength than pure short glass fibre micro composites. The strength increases initially as the fibre content increases and this may be due to the better interfacial adhesion between fibre and matrix in the presence of nanoclay. As the fibre content is increased further, there is a reduction in strength and this may be because the polymer matrix has reduced adhesion with fibres, after the critical fibre content.

The tensile and flexural moduli shows similar trend as the strength. As the clay is organo-modified, its surface is organophilic and its surface energy is low. It is found to be more compatible with polymer matrix. The higher level of interaction between the modified nanoclay-fibre and polymer matrix is responsible for increase in modulus of hybrid composite with aminosilane modified nanoclay.

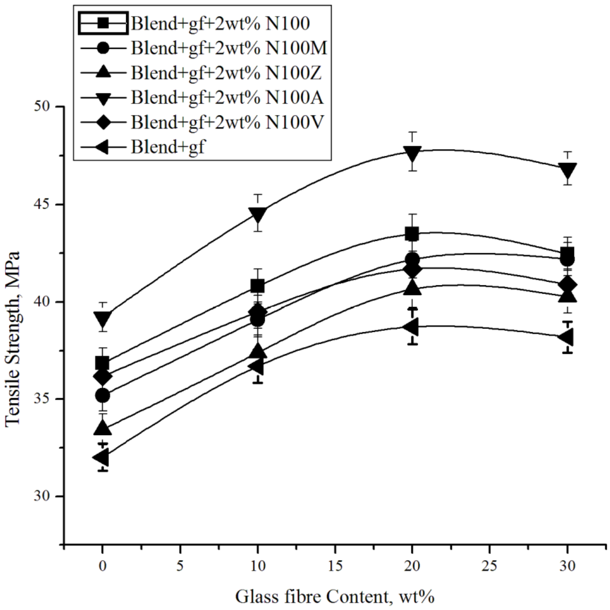


Figure 3.44 **Effect of glass fibre composition on tensile strength of PP/HDPE nanocomposites**

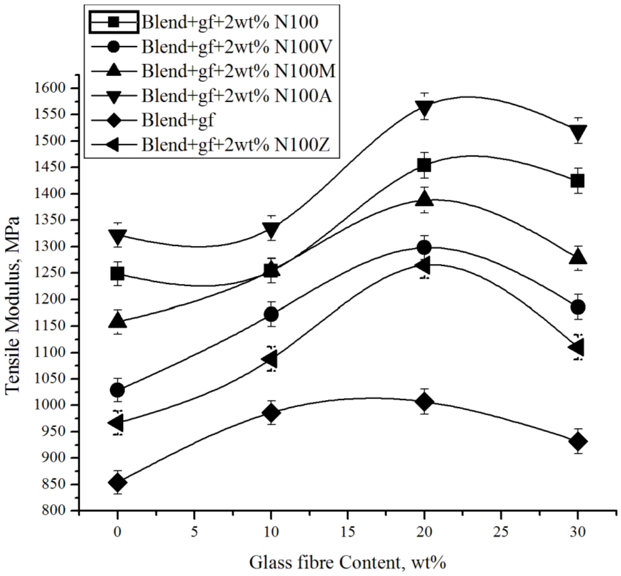


Figure 3.45 **Effect of glass fibre composition on flexural strength of PP/HDPE nanocomposites**

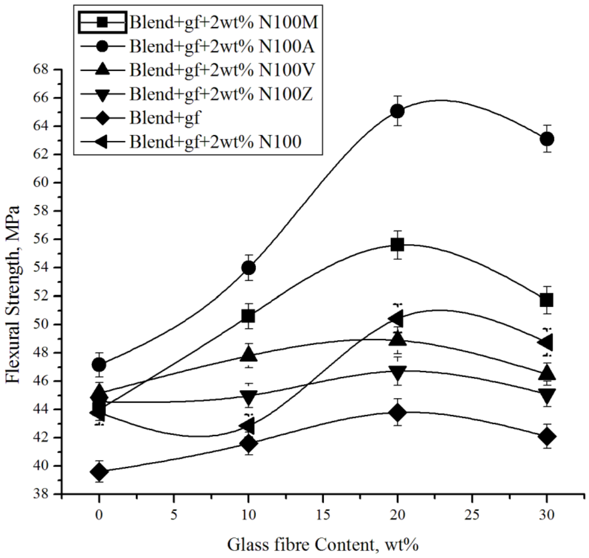


Figure 3.46 Effect of glass fibre composition on tensile modulus of PP/HDPE nanocomposites

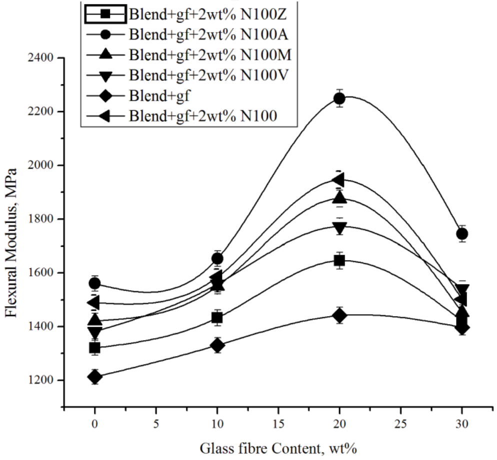


Figure 3.47 Effect of glass fibre composition on flexural modulus of PP/HDPE nanocomposites

The increase in impact strength can be attributed to the increase in toughness of the composite with increase in glass fibre content in the range of 10wt%-20wt%, but when the fibre content is higher than 20wt%, there exists a levelling off/decrease in the properties of the hybrid composites. This indicates that 20wt% glass fibre is the optimum fibre composition for upgrading PP/HDPE blend.

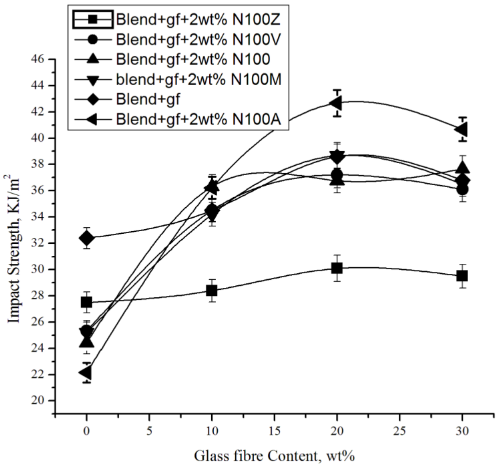


Figure 3.48 Effect of glass fibre composition on impact strength of PP/HDPE nanocomposites

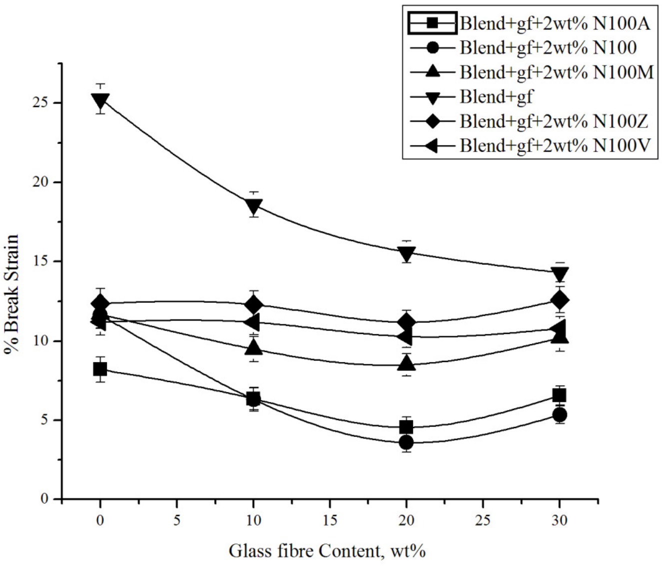


Figure 3.49 Effect of glass fibre composition on break strain of PP/HDPE nanocomposites

3.3.5 Effect of compatibilizers on PP/HDPE/unmodified nanokaolinite clay composites.

Polymer nanocomposites are one of the most widely studied engineering materials today. The main challenge facing the preparation of PNCs using nanoclay is that clay is naturally hydrophilic whereas PP and PE have no polar groups in their backbone and are two of the most hydrophobic polymers. In order to overcome this difficulty and to ensure proper dispersion either compatibilisers are added or organic modifiers are used to replace the inorganic cations (Na^+) with organic cations like dialkyl ammonium, alkyl amine, etc. The compatibilisers act as a bridge between the polymer chains and clay layer and ensure proper dispersion of clay sheets in the polymer matrix. The property of polymer nanocomposites differs widely in the presence of the additives which help to disperse the nanofillers on the polymer matrix. The effect of three different compatibilisers- Maleic Anhydride (MA)/Dicumyl Peroxide (DCP), styrene-ethylene-block polymer (SEBS) and ethylene-propylene-diene-copolymer (EPDM) on mechanical properties of Polypropylene (PP) /High Density Polyethylene (HDPE)/ nanokaolinite clay composites are investigated in this part of research work. The study shows that compatibilisers can improve the mechanical properties of such nanocomposites significantly. PP and HDPE are taken in the weight ratio 80/20 and nanoclay content is varied from 1 to 3 wt%. The compatibilisers are taken in the following proportions- 1 wt% EPDM and 1 wt% SEBS. For compatibilising with MA/DCP, pure PP is grafted with 2 wt% MA and 0.2 wt% DCP. The 5 wt% graft is mixed to prepare the nanocomposites. The mechanical properties of the resulting composites are compared with the composites without compatibilisers.

The tensile properties of the nanocomposites are shown in figure 3.50. The tensile strength of the composites increases on adding compatibilisers and maximum tensile strength is obtained for the composites containing 1% EPDM as compatibiliser. Also, on increasing nanoclay content the tensile properties increases and reaches a maximum on 2wt% nanoclay. The tensile strength of the PP/HDPE blend is 32.08 MPa.

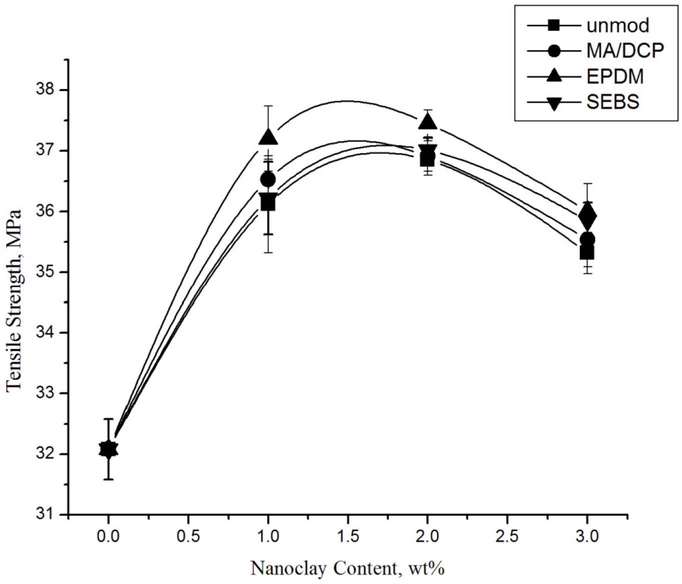


Figure 3.50 Effect of compatibilizers on the tensile strength of PP/HDPE/N100 composites

The flexural properties also show the trend as tensile properties. There is an increase for the composite containing 2wt% nanoclay and 1wt% EPDM compared to pure blend. The flexural properties of the nanocomposites are shown in figure 3.51.

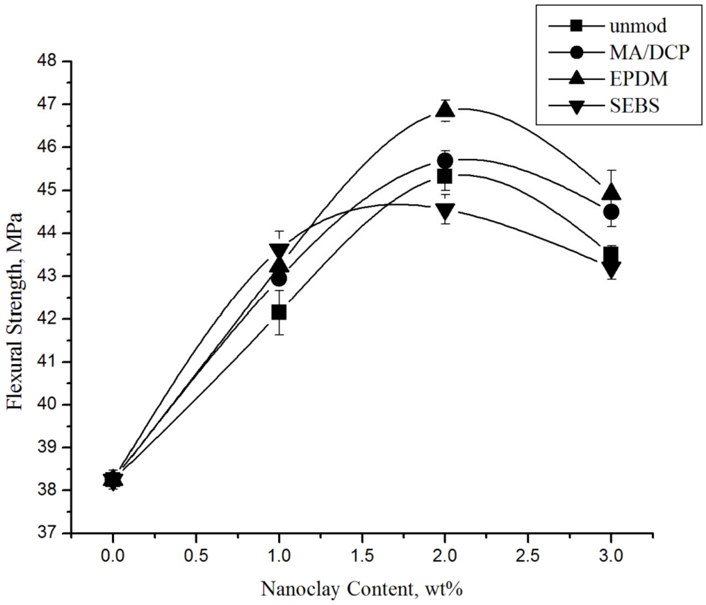


Figure 3.51 Effect of compatibilizers on the flexural strength of PP/HDPE/N100 composites

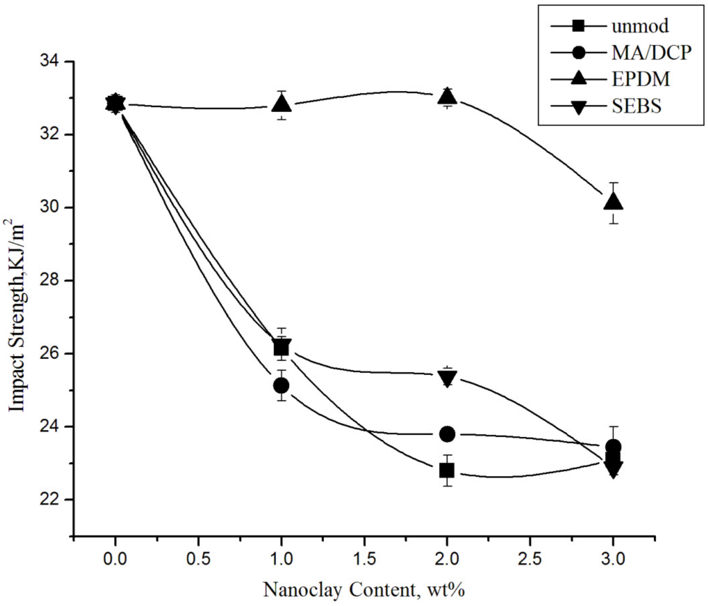


Figure 3.52 Effect of compatibilizers on the impact strength of PP/HDPE/N100 composites

The impact strength of the nanocomposites with and without different compatibilisers are shown in figure 3.52. The impact strength of composites with MA/DCP and SEBS are lower than composites containing nanoclay alone. This may be due to increase in crystallinity of the resultant composites. But for composites containing EPDM the impact strength is slightly increased.

Similar studies were conducted by several researchers and they report an increase in mechanical properties on the addition of compatibilizers[156-158].

3.4 Conclusions

- Surface modification of nanoclay affects the structure and properties of PP/HDPE/ nanokaolinite clay composites.
- Enhancement in properties is maximum in nanocomposites with amino modified and unmodified nanoclay due to better filler matrix interaction and dispersion.
- Blend composition affects the composite properties and optimum blend composition is 80PP/20HDPE by wt%.
- Melt compounding temperature of 150°C – 170° C is suitable for the preparation of PP/HDPE nanocomposites by melt compounding.
- Thermal stability and dynamic mechanical properties are increased in PNC compared to pure blend due to reinforcement effect.

- Good phase morphology is attained in the case of surface modified nanocomposites with amino modified nanoclay.
- Although addition of compatibilizers like EPDM increases the mechanical properties of unmodified nanoclay composites slightly, the surface modified nanoclay composites show superior properties.
- There is no considerable increase in impact strength on the addition of nanoclay.

References

[1]. Giannelis E.P (1996) "Polymer layered silicate nanocomposites". Adv. Mater., Vol. 8: 29–35.

[2]. Jordan J, Jacob K. I, Tannenbaum R, Sharaf M. A & Jasiuk I (2005) "Experimental trendsin polymer nanocomposites-a review". Mater. Sci. Eng. A, Vol. 393: 1-11.

[3]. Hussain F, Hojjati M, Okamoto M, & Gorga R.E (2006)"Review article: Polymer-matrix nanocomposites, processing, manufacturing, and Application". An Overview Journal of Composite Materials, Vol. 40, No. 17: 1511-1565.

[4]. Usuki A, Kawasumi M, Kojima Y, Okada A, Kurauchi T, & Kamigaito O. J (1993) "Swelling behaviour of montmorillonite cation exchanged for V-amino acids by Ecaprolactam".Mater. Res., Vol. 8, No.5: 1174.

[5]. Paul D.R&Robeson L.M (2008)"Polymer nanotechnology: Nanocomposites". Polymer, Vol.49: 3187-3204.

[6]. Kumar A.P, Depan D, Tomer N.S & Singh R.P (2009) "Nanoscale particles for polymer degradation and stabilization-Trends and future perspectives". Prog. Polym. Sci., Vol. 34: 479-515.

[7]. Armentano I, Dottori M, Fortunati E, Mattioli S, & Kenny J.M (2010) “Biodegradable polymer matrix nanocomposites for tissue engineering”. A review. Polym. Degrad. Stab., In Press.

[8]. Cosoli P, Scocchi G, Pricl S, & Fermaglia M, (2008) “Many-scale molecular simulation for ABS-MMT nanocomposites”. Upgrading of industrial scraps. Microporous and Mesoporous Materials, Vol. 107: 169-179.

[9]. Ma H, Xu Z, Tong L, GuA& Fang Z (2006) “Studies of ABS-graft-maleic anhydride/ clay nanocomposites: Morphologies, thermal stability and flammability properties”. Polym. Degrad. Stab., Vol. 91: 2951-2959.

[10]. Pandey J.K, Reddy K.R, Kumar A.P & Singh R.P (2005)“An overview on the degradability of polymer nanocomposites”. Polym. Degrad. Stab., Vol. 88: 234-250.

[11]. Sheng N, Boyce M.C, Parks D.M, Rutledge G.C, Abes J.I & Cohen R.E (2004) “Multiscale micromechanical modeling of polymer/clay nanocomposites and the effective clay particle”. Polymer, Vol. 45: 487-506.

[12]. Le Baron P.C, Wang Z & Pinnavaia T.J (1999) “Polymer-layered silicate nanocomposites: an overview”. Appl. Clay Sci., Vol. 15: 11-29.

[13]. Thostenson E.T, Li C & Chou T.W (2005) “Nanocomposites in context”. Compos. Sci.Technol., Vol. 65: 491-516.

[14]. Kawasumi M, Hasegawa N, Kato M, Usuki A& Okada A (1996) “Preparation and mechanical properties of polypropylene-clay hybrids”. Macromolecules 30 (20): 6333-338.

[15]. Kornmann X, Lindberg H & Berglund L.A (2001)“Synthesis of epoxy-clay nanocomposites: Influence of the nature of the clay on structure”. Polymer 42 (4): 1303-310.

[16]. Hasegawa N, Kawasumi M, Kato M, Usuki A & Okada A (1998) “Preparation and mechanical properties of polypropylene-clay hybrids using a maleic anhydride modified polypropylene oligomer”. J. Appl. Polym 67(1): 87-92.

[17]. Kornmann X, Lindberg H & Berglund L.A(2001) “Synthesis of epoxy-clay nanocomposites. Influence of the nature of the curing agent on structure”. Polymer42(10): 4493-499.

[18]. Xu W.B, Ge M.L & He P (2002)“Nonisothermal crystallization kinetics of polypropylene/montmorillonite nanocomposites. J. Polym. Sci. Pt B: Polym. Phys 40(5): 408.

[19]. Pavlidou S & Papaspyrides C.D (2008) “A review on polymer-layered silicatenanocompopsites”. Prog. Polym. Sci., Vol. 32: 1119-1198.

[20]. Ahmad M.B, Hoidy W.H, Ibrahim N.A.B & Al-Mulla E.A.J (2009)“Modification of montmorillonite by new surfactants”. J. Eng. Appl. Sci., Vol.4, No. 3: 184-188.

[21]. Chigwada G, Wang D, Jiang D.D & Wilkie C.A (2006) “Styrenic nanocomposites sprepared using a novel biphenyl-containing modified clay”. Polym. Degrad. Stab., Vol. 91: 755-762.

[22]. ASTM D 638-94b (1995) Tensile properties of plastics. Annual book of American Society for Testing and Materials (ASTM) standards

[23]. ASTM D790-92 (1995) Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials. Annual book of American Society for Testing and Materials (ASTM) standards

[24]. ASTM D 256-10 (1995) Standard test method for determining Izod pendulum impact resistance of plastics. Annual book of American Society for Testing and Materials (ASTM) standards

[25]. ASTM D 1238-10. Standard test method for melt flow rates of thermoplastics by extrusion plastometer, volume 08.01. ICS number code 83.080.20 (thermoplastic material)

[26]. Jiang L, Lam Y.C, Tam K.C, Chua T.H, Sim G.W & Ang L.S (2005) “Strengthening acrylonitrile-butadiene-styrene (ABS) with nano-sized and micron-sized calcium carbonate”. Polymer, Vol. 46: 243-252.

[27]. Tortora M, Vittoria V,Galli G, Ritrovati S, & Chiellini E (2002) "Transport properties of modified montmorillonite/ poly(caprolactone) nanocomposites". Macromol. Mater. Eng., Vol. 287: 243-249.

[28]. Gorrasi G, Tortora M, Vittoria V, Pollet E, Lepoittevin B & Alexandre M(2003) "Vaporbarrier properties of polycaprolactonemontmorill onitenanocomposites: effect ofclay dispersion". Polymer, Vol. 44: 2271–2279.

[29]. Fornes T.D, Yoon P.J, Keskkula H, & Paul D.R (2001)"Nylon 6 nanocomposites: the effect of matrix molecular weight". Polymer, Vol. 42: 9929–9940.

[30]. Shelley J.S, Mather P.T & DeVries K.L (2002)"Reinforcement and environmental degradation of nylon 6/clay nanocomposites". Polymer, Vol. 42: 5849–58.

[31]. Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T & Kamigaito O (1993) "Sorption of water in nylon 6–clay hybrid". J. Appl. Polym. Sci., Vol. 49: 1259–1264.

[32]. Alexandre M & Dubois P (2000)"Polymer–layered silicate nanocomposites: preparation, properties and uses of a new class of materials". Mater. Sci. Eng. R Rep., Vol. 28: 1–63.

[33]. Finnigan B, Martin D, Halley P, Truss R & Campell K (2004)"Morphology and properties of thermoplastic polyurethane nanocomposites incorporating hydrophilic layered silicates". Polymer, Vol. 45: 2249-2260.

[34]. Wang S.J, Long C.F, Wang X.Y, Li Q, & Qi Z.N (1998)"Synthesis and properties of silicon rubber organo-montmorillonite hybrid nanocomposites". J. Appl. Polym. Sci., Vol. 69: 1557-1561.

[35]. Osman M.A, Rupp J.E.P & Suter U.W (2005)"Effect of non-ionic surfactants on the exfoliation and properties of polyethylene-layered silicate nanocomposites". Polymer, Vol. 46: 8202-8209.

[36]. Mittal V (2008) "Mechanical and gas permeation properties of compatibilized polypropylene–layered silicate nanocomposites". J. Appl. Polym. Sci., Vol. 107: 1350-1361.

[37]. Fornes T.D & Paul, D.R (2003) "Modeling properties of nylon 6/clay nanocomposites using composite theories". Polymer, Vol. 44: 4993-5013.

[38]. Mittal V (2007) "Polypropylene-layered silicate nanocomposites: Filler matrix interactions and mechanical properties". J. Thermoplast. Compos. Mater., Vol. 20: 575-599.

[39]. Ray S.S & Okamoto M (2003)"Polymer/layered silicate nanocomposites: a review from preparation to processing". Prog. Polym. Sci., Vol. 28: 1539-1641.

[40]. Yao K.J, Song M, Hourston D.J &Luo D.Z (2002)"Polymer/layered clay nanocomposites: 2 polyurethane nanocomposites. Polymer, Vol. 43: 1017-1020.

[41]. Zhang Q, Fu Q, Jiang L& Lei Y (2000)"Preparation and properties of polypropylene/montmorillonite layered nanocomposites". Polym. Int., Vol. 49: 1561-1564.

[42]. Oya A, Kurokawa Y & Yasuda H (2000)"Factors controlling mechanical properties of clay mineral/polypropylene nanocomposites". J. Mater. Sci., Vol. 35: 1045-1050.

[43]. Phang I.Y, Liu T, Mohamed A, Pramoda K.P, Chen L, Shen L, Chow S.Y, He C, Lu X & Hu X (2005)"Morphology, thermal and mechanical properties of nylon12/organoclaynanocomposites prepared by melt compounding". Polym. Int., Vol. 54: 456-464.

[44]. Blumstein A (1965)"Polymerization of adsorbed monolayers: II. Thermal degradation of the inserted polymers". J. Polym. Sci. A, Vol. 3: 2665-2670.

[45]. Vyazovkin S, Dranka I, Fan X & Advincula R (2004)"Kinetics of the thermal and thermo-oxidative degradation of a polystyrene–clay nanocomposite". Macromol. Rapid Commun., Vol. 2: 498-503.

[46]. K Hariprasad, M Senthilkumar "Dynamic Mechanical properties of PP/MMT/OMMT Nanocomposites".

[47]. Nam P.H, Maiti P, Okamoto M, Kotaka T, Hasegawa N &Usuki A (2001)"Ahierarchical structure and properties of intercalated polypropylene/claynanocomposites". Polymer, Vol. 42: 9633-9640.

[48]. Laus M, Francesangeli O & Sandrolini F (1997)“New hybrid nanocomposites based on an organophilic clay and poly(styrene-b-butadiene) copolymers”. J. Mater. Res., Vol. 12: 3134-3139.

[49]. Krikorian V & Pochan D (2003)“Poly(l-lactide acid)/layered silicate nanocomposite: fabrication, characterization, and properties”. Chem. Mater., Vol. 15: 4317-4324.

[50]. Ray S.S, Maiti P, Okamoto M, Yamada K & Ueda K (2002) “New polylactide/ layeredsilicate nanocomposites. 1. Preparation, characterization and properties”. Macromolecules, Vol. 35: 3104-3110.

[51]. Martuscelli E, Pracella M, Avella M, Greco R and Ragosta G (1980) "Properties of polyethylene-polypropylene blend-Crystallization behaviour," Macromol. Chem., 181, pp 957.

[52]. Vaia RA &Giannelis EP (1997) Vaia, R. A. and Giannelis, E. P. (1997) Lattice model of polymer melt intercalation in organically-modified layered silicates, Macromolecules, 30, 7990-9;

[53]. Vaia, R. A. and Giannelis, E. P. (1997) Polymer melt intercalation in organically-modified layered silicates: model predictions and experiment, Macromolecules, 30, 8000.

[54]. Lee JY, Baljon ARC, Lorin RF (1990) J ChemPhys111(21):9754–60.

[55]. Manias E, Chen H, Krishnamoorti R, Genzer J, Kramer EJ & Giannelis EP (2000) Intercalation Kinetics of Long Polymers in 2 nm Confinements. Macromolecules 33:7955–66.

[56]. Hunter DL, Kamena KW & Paul DR (2007). Processing and properties of polymers modified by clays MRS Bull 32:2806.

[57]. Cho JW & Paul DR (2001) Nylon 6 nanocomposites by melt compounding. Polymer 42:1083.

[58]. Fornes TD, Yoon PJ, Keskkula H & Paul DR (2001) Nylon 6 nanocomposites: the effect of matrix molecular weight. Polymer 42:9929.

[59]. Krishnamoorti R (2007). Strategies for dispersing nanoparticles in polymers. MRS Bull 32:341.

[60]. Zhu J &Wilkie CA(2007)"Intercalation compounds and clay nanocomposites". In: KICKELBICK, G. (ed.) Hybrid Materials: Synthesis, Characterization, and Applications. John Wiley & Sons.

[61]. Morgan AB & Gilman JW(2003) "Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and X-ray diffraction: A comparative study". Journal of Applied Polymer Science 87:1329-1338.

[62]. Kodgire P, Kalgaonkar R, Hambir S, Bulakh N, Jog JP (2001) "PP/clay nanocomposites: effect of clay treatment on morphology and dynamic mechanical properties". J Appl PolymSci; 81(7):1786.

[63]. Maiti P, Nam PH, Okamoto M, Hasegawa N, Usuki A (2002) "Influence of crystallization on intercalation, morphology and mechanical properties of polypropylene/clay nanocomposites". Macromolecules; 35:2042.

[64]. Zanetti M, Lomakin S & Camino G (2000)"Polymer layered silicate nanocomposites". Macromolecular Materials and Engineering, 279**:**1-9.

[65]. Krikorian V and Pochan, DJ(2003)"Poly (l-lactic acid)/layered silicate nanocomposite: fabrication, characterization, and properties. Chemistry of materials, 15**:**4317-4324.

[66]. Okamoto M, Morita S, Kim YH, Kotaka T and Tateyama H. (2001)a. "Dispersed structure change of smectic clay/poly(methyl methacrylate) nanocomposites by copolymerization with polar comonomers". Polymer, 42**:**1201-1206.

[67]. Chin IJ, Thurn-Albrecht T, Kim HC, Russell TP and Wang J(2001)"On exfoliation of montmorillonite in epoxy'. Polymer, 42**:**5947-5952.

[68]. B.C Poon, S.P Chum AHiltner& E Baer (2004) "Adhesion of polyethylene blends to polypropylene". Polymer 45: 893-903.

[69]. Abdalla M.O, Dean D, Campbell S (2002). "Viscoelastic and Mechanical Properties of Thermosetting PMR-type Polyimide Nanocomposites" Polymer 43, 5483-5491

[70]. Lin J.C, Chang L.C, Nien M.H, Ho H.L (2006) "Mechanical behavior of various nanoparticle filled composites at low-velocity impact "Composite Structures, 74:30-36

[71]. Isik I, Yilmazer U, Bayram G, (2003) Impact modified epoxy / montmorillonite nanocomposites : Synthesis and characterization. Polymer, 44, No. 20:6371

[72]. Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O (1993). Synthesis of nylon 6–clay hybrid by montmorillonite intercalated with ϵ-caprolactam. J Polym Sci Part A Polym Chem. 31:983–6.

[73]. Kawasumi M (2004). "The discovery of *polymer*-clay hybrids". J Polym Sci Part A Polym Chem42:819–24.

[74]. Fukushima Y, Inagaki S (1987). "Synthesis of an Intercalated Compound of Montmorillonite and 6-polyamide". J Inclusion Phenom5:473–82.

[75]. Kojima Y, Usuki A, Kawasumi M, Okada A, Kurauchi T, Kamigaito O (1993). One-pot synthesis of nylon 6–clay hybrid**.** J PolymSci Part A PolymChem 31:1755–8.

[76]. Biasci L, Aglietto M, Ruggeri G, Ciardelli F (1994). Functionalization of motmrillonite by methyl kethacrylate polymer containing side-chain ammonium cations. Polymer 35(15):3296–309.

[77]. Huang X, Lewis S, Brittain WJ (2000). Synthesis of polycarbonate- layered silicate nanocomposites via cyclic oligomers. Macromolecules 33:2000–4.

[78]. Zhou Q, Fan X, Xia C, Mays J, Advincula R (2001). Living anionic surface-initiated polymerization (LASIP) of styrene from clay surfaces. Chem Mater 13:2465–7.

[79]. Albrecht M, Ehrler S, Muhlebach A (2003). Nanocomposites from Layered Silicates: Graft Polymerization with Intercalated Ammonium Peroxides. Macromol Rapid Commun 24:382–7.

[80]. Kiersnowski A, Piglowski J (2004). Polymer-layered silicate nanocomposites based on poly(ε-caprolactone). EurPolym J 40:1199–207.

[81]. Ray SS, Okamoto M (2003). Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog Polym Sci. 28:1539–641.

[82]. Hussain F, Hojjati M (2006) Review article: Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. J Compos Mater 40(17):1511–65.

[83]. Goldberg HA, Feeney CA, Karim DP, Farrell M (2002).. Rubber World 226:1–17.

[84]. Takahashi S, Goldberg HA, Feeney CA, Karim DP, Farrell M, O'Leary K, *et al.* (2006) Gas barrier properties of butyl *rubber*/vermiculite nanocomposite coatings Polymer 47:3083–93.

[85]. Vaia RA, Ishii H, Giannelis EP (1993) Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates. Chem Mater 5:1694.

[86]. Vaia RA, Teukolsky RK, Giannelis EP (1994) "Interlayer structure and molecular environment of alkylammonium layered silicates" Chem Mater 6:1017–22.

[87]. Vaia RA, Jandt KD, Kramer EJ, Giannelis EP (1995) Kinetics of Polymer Melt Intercalation Macromolecules 28:8080–5.

[88]. Giannelis EP (1996). Polymer Layered Silicate Nanocomposites. Adv Mater 8(1):29.

[89]. Vaia RA, Jandt KD, Kramer EJ, Giannelis EP (1996) Microstructural Evolution of melt intercalated polymer-organically modified layered silicates nanocomposites. Chem Mater 8:2628–35.

[90]. Anastasiadis SH, Karatasos K, Vlachos G (2000). "Nanoscopic-confinement effects on local dynamics", Phys Rev Lett84(5):915–8.

[91]. Vaia RA, Giannelis EP (2001). "Liquid crystal polymer nanocomposites: direct intercalation of thermotropic liquid crystalline polymers into layered silicates." Polymer 42:1281–5.

[92]. Dennis HR, Hunter DL, Chang D, Kim S, White JL, Cho JW, *et al.* (2001). Dennis HR, Hunter DL, Chang D, Kim S, White JL, Cho JW, *et al.* (2001) Polymer 42:9513.Polymer 42:9513.

[93]. Fornes TD, Yoon PJ, Hunter DL, Keskkula H, Paul DR (2002) Effect of organoclay structure on nylon 6 nanocomposite morphology and properties. Polymer 43:5915.

[94]. Yoon PJ, Fornes TD, Paul DR (2002). Thermal expansion behavior of nylon 6 nanocomposites. Polymer 43:6727.

[95]. Fornes TD, Paul DR (2003) Crystallization behavior of nylon 6 nanocomposites', Polymer 44:3945.

[96]. Yoon PJ, Fornes TD, Paul DR(2003). "Polycarbonate Nanocomposites: 1.Effect of Organoclay Structure on Morphology and Properties, Polymer44:5323.

[97]. Yoon PJ, Hunter DL, Paul DR (2003). "Polycarbonate Nanocomposites: 2.Degradation and Color Formation." Polymer 44:5341.

[98]. Fornes TD, Yoon PJ, Paul DR (2003). "Polymer Matrix Degradation and Color Formation in Melt Processed Nylon 6-Clay Nanocomposites," Polymer 44:7545.

[99]. Fornes TD, Hunter DL, Paul DR (2004). "Effect of Sodium Montmorillonite Source on Nylon 6/Clay Nanocomposites," P Polymer 45:2321.

[100]. Shah RK, Paul DR(2004). "Nylon 6 nanocomposites prepared by a melt mixing masterbatch process" Polymer 45:2991.

[101]. Chavarria F, Paul DR (2004). "Comparison of Nanocomposites Based on Nylon 6 and Nylon 6,6," Polymer 45:8501.

[102]. Fornes TD, Paul DR(2004). "Nylon-6 Nanocomposites from Alkylammonium-Modified Clay: The Role of the Alkyl Tails on Exfoliation," Macromolecules 37:7698.

[103]. Bourbigot S, Vanderhart D, Gilman J, Stretz HA, Paul DR(2004). "Solid State NMR Characterization and Flammability of Styrene-Acrylonitrile Copolymer Montmorillonite Nanocomposites,"Polymer 45:7627.

[104]. Hotta S, Paul DR.(2004). "Nanocomposites Formed from Linear Low Density Polyethylene and Organoclays," Polymer 45:7639.

[105]. Ibanes C, David L, Seguela R, Rochas C, Robert G (2004). Structure and mechanical behavior of nylon 6 fibres filled with organic and mineral nanoparticles. II. In situ study of deformation mechanisms. J PolymSci Part B PolymPhys42:2633–48.

[106]. Vlasveld DPN, Groenewold J, Bersee HEN, Mendes E, Picken SJ (2005). Analysis of the modulus of polyamide-6 silicate nanocomposites using moisture controlled variation of the matrix properties Polymer46:6102–13.

[107]. Stretz HA, Paul DR, Li R, Keskkula H, Cassidy PE (2005) Structure and mechanical behavior of nylon 6 fibres filled with organic and mineral nanoparticles. II. In situ study of deformation mechanisms. Polymer 46:2621.

[108]. Shah RK, Hunter DL, Paul DR (2005). Structure and mechanical behavior of nylon 6 fibres filled with organic and mineral nanoparticles. II. In situ study of deformation mechanisms. Polymer 46:2646.

[109]. Stretz HA, Paul DR, Cassidy PE (2005). Poly(styrene-co-acrylonitrile)/ Montmorillonite organoclay Mixtures: A Model System for ABS Nanocomposites, Polymer 46:3818.

[110]. Zeng QH, Yu AB, Lu GQ, Paul DR (2005). Clay based polymer nanocomposites-research and commercial development. J Nanosci. Nanotechnol. 46:3818.

[111]. Lee H-S, Fasulo PD, Rodgers WR, Paul DR (2005). TPO based nanocomposites. Part 1. Morphology and mechanical properties, Polymer 46:11673.

[112]. Ahn YC, Paul DR (2006). Rubber toughening of nylon 6 nanocomposites, Polymer 47:2830.

[113]. Shah RK, Paul DR (2006). “Comparison of nanocomposites prepared from sodium, zinc and lithium ionomers pf ethylene/methacrylic acid copolymers. Macromolecules 39:3327.

[114]. Lee H-S, Fasulo PD, Rodgers WR, Paul DR (2006). TPO based nanocomposites. Part 1. Morphology and mechanical properties, Polymer 47:3528.

[115]. Shah RK, Paul DR (2006). "Organoclay degradation in melt processed polyethylene nanocomposites." Polymer 47:4074.

[116]. Shah RK, Krishnaswarmy RK, Takahashi S, Paul DR (2006). Blown film of nanocomposites prepared from low density polyethylene and a sodium ionomer of poly (ethylene co-methacrylic acid).Polymer 47:6187.

[117]. Chavarria F, Paul DR (2006). Morphology and properties of thermoplastic polyurethane ... Effect of organoclay structure Polymer 47:7760.

[118]. Stretz HA, Paul DR (2006). Properties and morphology of nanocomposites based on styrenic polymers. Part I: Styrene-acrylonitrile copolymers Polymer 47:8123.

[119]. Stretz HA, Paul DR (2006) Polymer 47:8527.

[120]. Shah RK, Cui L, Williams KL, Bauman B, Paul DR (2006) J Appl PolymSci 102:2980.

[121]. Shah RK, Kim DH, Paul DR (2007). Morphology and properties of nanocomposites formed from ethylene/methacrylic acid copolymers and organoclays. Polymer 48:1047

[122]. Cui L, Paul DR (2007) Polymer 48:1632.

[123]. Chavarria K, Nairn K, White P, Hill AJ, Hunter DL, Paul DR (2007). Morphology and properties of nanocomposites from organoclays with reduced cation exchange capacity J ApplPolymSci105:2910.

[124]. Yoo Y, Shah RK, Paul DR (2007). Fracture behavior of nanocomposites based on poly(ethylene-co- methacrylic acid) ionomers. Polymer 48:4867.

[125]. Kim DH, Fasulo PD, Rodgers WR, Paul DR (2007). Structure and properties polypropylene-based nanocomposites: effect of PP-g-MA to organoclay ratio. Polymer 48:5308.

[126]. Kim DH, Fasulo PD, Rodgers WR, Paul DR (2007).Effect of the ratio of maleated polypropylene to organoclay on the structure and properties of TPO based nanocomposites-Part 1: Morphology and mechanical properties. Polymer 48:5960.

[127]. Cui L, Ma X, Paul DR (2007). Morphology and properties of nanocomposites formed from ethylene-vinyl acetate copolymers and organoclays. Polymer 48:6325.

[128]. Chavarria K, Shah RK, Hunter DL, Paul DR (2007). Effect of Melt Processing Conditions on the Morphology and Properties of Nylon 6 Nanocomposites. Polym Eng Sci 47:1847.

[129]. Liu L, Qi Z, Zhu X (1999). Studies on Nylon 6/clay nanocomposites by melt-intercalation process. J ApplPolymSci 71:1133–8.

[130]. Heinemann J, Reichert P, Thomann R, Mulhaupt R (1999). “Polyolefine nanocomposites formed by melt compounding and transir=tion metal catalyzed ethane homopolymerization and copolymerization in the presence of layered silicates”. Macromol Rapid Commun20:423–30.

[131]. Garce’ s JM, Moll DJ, Bicerano J, Fibiger R, McLeod DG (2000). Polymeric nanocomposites for automotive applications. Adv Mater 12(23):1835–9.

[132]. Varlot K, Reynaud E, Kloppfer MH, Vigier G, Varlet J (2001) Clay–reinforced polyamide:

[133]. preferential orientation of the montmorillonite sheets and the polyamide crystalline lamellae. J PolymSci Part B PolymPhys 39:1360–70.

[134]. Reichert P, Hoffmann B, Bock T, Thomann R, Mulhaupt R, Friedrich C (2001). Morphological stability of polypropylene nanocomposites. Macromol Rapid Commun 22(7):519–23.

[135]. Kim SW, Jo WH, Lee MS, Ko MB, Jho JY (2002). Effects of shear on melt exfoliation of clay in preparation of nylon 6/organoclay nanocomposites Polymer 34(3):103–11.

[136]. Ray SS, Yamada K, Ogami A, Okamoto M, Ueda K (2002). "New Polylactide/ Layered Silicate Nanocomposite: Nanoscale Control Over Multiple Properties. "Macromol Rapid Commun23:943–7.

[137]. Ray SS, Yamada K, Okamoto M, Fujimoto Y, Ogami A, Ueda K. (2003) New polylactide- layered silicate nanocomposites-Designing of material with desired properties. Polymer .44:6633–46.

[138]. Ray SS, Okamoto K, Okamoto M (2003) Structure –Property relationship in biodegradable Poly(butylenes succinate)/Layered Silicate Nanocomposites Macromolecules 36:2355–67.

[139]. Yalcin B, Valladares D, Cakmak M (2003) Amplification effect of platelet type nanoparticles on the orientation behaviour of injection moulded nylon 6 nanocomposites. Polymer.44:6913–25.

[140]. Yalcin B, Cakmak M (2004) Polymer.45:2691–710.

[141]. Konishi Y, Cakmak M (2005) Structural hierarchy developed in injection molding of nylon 6/clay/carbon black nanocomposites. Polymer 46:4811–26.

[142]. Hsieh AJ, Moy P, Beyer FL, Madison P, Napadensky E (2004) “Mechanical response and rheological properties of polycarbonate layered-silicate nanocomposites”, Polym Eng Sci.44(5):825–37.

[143]. Weon J-I, Sue H-J (2005). . Effects of clay orientation and aspect ratio on mechanical behavior of nylon-6 nanocomposite. P Polymer.46:6325–34.

[144]. Vermogen A, Masenelli-Varlot K, Se’gue’ la R, Duchet-Rumeau J, Boucard S,Prele P. (2005)Macromolecules .38:9661–9.

[145]. Kim Y, White JL (2005). Formation of*polymer* nanocomposites with various organoclays. JPolym Sci.96:1888–96.

[146]. Morgan AB (2006). Flame retarded polymer layered silicate nanocomposites: a review of commercial and open literature systems PolymAdv Technol. 17:206–17.

[147]. Masenelli-Varlot K, Vigier G, Vermogen A, Gauthier C, Cavaille’ JY (2007) J PolymSci. Part B-PolymPhys 45:1243–51.

[148]. Picard E, Vermogen A, Gerard J-F, Espuche E (2007) J MembrSci 292:133–44.

[149]. Lee H, Fasulo P.D, Rodgers W.R, Paul D.R (2005) TPO based nanocomposites-Part1: Morphology and mechanical properties. Polymer, 46, No. 25:11673

[150]. Okada A, Fukushim Y, Kawasumi M, Inagaki S, Usuki A, Sugiyama S, *et al.* (1988) USPatent 4,739,007.

[151]. Pluta M, Jeszka JK, Boiteux G (2007) "Polylactide/montmorillonite nanocomposites: Structure, dielectric, viscoelastic and thermal properties." Eur. Polym J 43:2819–35.

[152]. Xu H, Yang B, Wang J, Guang S, Li C (2007) J PolymSci Part A Polym Chem.45:5308–17.

[153]. Park J.H, Jana S.C (2003) The relationship between nano- and micro-structures and mechanical properties in PMMA–epoxy–nanoclay composites, Polymer, 44:2091

[154]. NRR. Anbusagarand P.K. Giridharan (2013) "Influence of Nanoparticles on Impact properties of Polystyrene Foam Sandwich GFRP Composites". International Journal of Research in Engineering and Technology (IJRET) Vol. 2, No. 2,ISSN 2277 – 4378.

[155]. JavadMoftakharianEsfahani, MasoudEsfandeh, Ali Reza Sabet (2011) "High-Velocity Impact Behaviour of Glass Fiber-Reinforced Polyester Filled with Nanoclay". DOI 10.1002/app.36605.

[156]. Runzhou Huang , XinwuXu , Sunyoung Lee , Yang Zhang , Birm-June Kim and Qinglin Wu (2013) "High Density Polyethylene Composites Reinforced with Hybrid Inorganic fillers: Morphology, Mechanical and Thermal Expansion Performance". Materials 6. 4122-4138.

[157]. Vesna Rek, Nina Vranjes, Miroslav SˇLouf, Ivan Fortelny "Morphology and Properties of SEBS Block Copolymer Compatibilized PS/HDPE Blends", Journal of Elastomers and Plastics Vol. 00–Month 2007.

[158]. Merlin Thomas , Atul D. Kamble and Neetha John, "Investigations of the influence of compatibilizer and clay filler on the properties of thrmoplastic polyurethane/polyolefins blends", Archives of Applied Science Research, 2012, 4 (2):1191-1202.

[159]. H. Salmah, C.M. Ruzaidi and A.G. Supri, "Compatibilisation of Polypropylene/Ethylene Propylene Diene Terpolymer/Kaolin Composites: The Effect of Maleic Anhydride-Grafted-Polypropylene", Journal of Physical Science, Vol. 20(1), 99–107, 2009 99.

……

Chapter 4

MECHANICAL PROPERTIES OF PP/HDPE/NANOKAOLINITE CLAY COMPOSITES

Contents

4.1 Introduction

Polymers are widely used owing to their ease of production, light weight and ductile nature. However, compared to metals and ceramics, they are inferior in mechanical properties. One way to improve their mechanical properties is to reinforce them with particulate fillers like talc, mica, calcium carbonate, kaolin, fused silica or fibres of glass, nylon etc. Nanofillers have now emerged as the ultimate reinforcing agents for polymers for improving their mechanical properties without affecting density, transparency and processibility[1-4]. Polymer nanocomposites is a new class of composite materials derived from nanoparticles, with at least one dimension in the nanometer range. These nanoparticles are dispersed in the polymer matrix at a relatively low loading (often under 5% by weight). Because the nanoparticles (such as nanoclays, nanofibers , carbon nanotubes etc.) are so small and their aspect ratios (largest dimension/smallest dimension) are very high, even at such low loadings, certain polymer properties can be greatly improved while maintaining their light weight and processability[5-6]. The size of the nanoclay particles, the modifications incorporated and the amount of nanofiller used play a major role in the development of properties of polymer blend[7]. Polypropylene (PP) and High density polyethylene (HDPE) are the most widely used commodity plastics owing to their light weight, ease of production and process ability. Blending and incorporation of nanofiller can uplift the applicability of PP and HDPE as a strategic material. Generally every 1 wt% of nanoclay loaded into polymer creates a 10% property enhancement.

Polymer layered silicate nanocomposites are currently prepared in four ways- in situ polymerization[8], intercalation from a polymer solution[9-10], direct intercalation by molten polymer[11-12] and sol gel technology[13]. According to Ray and Okamato[14] direct intercalation by molten polymer method of preparation of nanocomposites has a greater advantage over other methods as this method is environmentally benign owing to absence of organic solvents and is compatible with current industrial process, such as extrusion and injection moulding. Polymer nanocomposites made of silica, montmorillonite clay and other nanoparticles are extensively studied and reported in earlier studies[15-23]. However, scarce amount of literature is available on effect of nanokaolinite clay as reinforcing agent on thermoplastics. Kaolinite clay is a 1:1 aluminosilicate that has wide variety of applications in industry, particularly as filler in paper, plastics, paints and rubber. It was observed in a recent report that the china clay based polymer nanocomposites give better oxygen barrier and water transport property than that from montmorillonite based nanoclay. Kaolinite has the potential to an ideal precursor for the preparation of polymer nanocomposites since it is cheaper when compared to montmorillonite clays.

Since the pioneering work of Toyota research group[24], polymer nanocomposites (PNC) have shed a light on the replacement of conventional fibre-reinforced composites by using a small proportion of nanofillers, composed of inorganic layered silicates. When well dispersed into neat polymers, those nanofillers can dramatically enhance their mechanical, thermal, barrier and flame retardant properties[25-28]. Natural clay silicates are made up of several hundred thin platelet layers stacked into orderly particles or tactoids in the size of 8-10μm. Each of the disc-like clay platelets, has a very large aspect ratio about 100-1000, and they are easily agglomerated due to the interlayer van der Waal's forces. The enhanced reinforcement mainly benefits from the much greater surface to volume ratio of these high aspect ratio nanofillers since many important chemical and physical interactions are governed by surfaces (or interfaces) between fillers and the polymer matrix. Consequently, clay particles should be uniformly dispersed and exfoliated as individual platelets within the polymer matrix in order to achieve excellent property enhancement. In addition, lower clay content (≤ 5wt%) has also been found essential for accomplishing the large contact surface areas and alleviating the clay agglomeration to obtain a better dispersion[29].

Nanoparticle filled polymers can enhance the material properties than conventional filled polymers even at a low loading range of 1-5% by weight. This can happen only if nano dispersion of clay in the matrix is realized[30]. The main challenge facing the preparation of PNCs using nanoclay is that clay is naturally hydrophilic whereas PP and HDPE have no polar groups in their backbone and are two of the most hydrophobic polymers. The result is usually a low level of dispersion of the clay platelets in the polymer matrix and a poor interfacial bonding between clay surface and polymer matrix. In order to overcome this difficulty and to ensure proper dispersion, either compatibilisers are used to provide a bridge between clay and polymer[11,16,17,20,22,23,31-33] or clay surface modifiers are used to replace the inorganic cations in the surface of clay (Na+) with organic cations like dialkyl ammonium, alkyl amine etc.[21,34,35]. In the case of surface modifiers, the clay surface is treated with a long organic alkyl or amine chain and are known as organo modified layered silicate (OMLS) or briefly, organoclay[36]. Much work has been carried out on organo modified montmorillonites as they have high cation exchange capacity. Since kaolinites have very low cation exchange capacity (<0.1) and have no interlayer cations, a very little has been used on nanokaolinite polymer composites for study.

While many studies on nanocomposites focus on the importance of chemical surface modification of the clay and grafting with compatibilisers in order increase the compatibility between clay and host polymer, the role and importance of processing conditions are not extensively studied. Modesti. *et al.* [36] has studied the influence of processing parameters and clay content in PP/organo modified monmorillonite nanocomposites and reported that the mechanical and thermal properties of the PNCs are affected by the processing parameters.

Depending on nano filler types the obtained nanocomposites can offer[3,37-39.]

- better mechanical properties
- lower permeability against the gases
- higher heat deflection temperature
- higher flame retardancy.

To achieve all the aforesaid improvements, the presence of full exfoliation or intercalation and well dispersion of nanofillers in polymer matrix is necessary. In the melt intercalation method for production of nanocomposite, the most important parameters which lead to gain this morphology are surface modification of nanofiller by surfactants and proper processing conditions[40.] Demirkol and Kalyon[41] studied different methods (batch and continuous) to produce the nanocomposite. Their results point to the difficulty of the generation of nanocomposites using melt compounding when the interfacial properties between the polymer melt binder and the organoclay are not favourable. The effect of shear field on the morphology of nanocomposite has been reported by Homminga *et al.*[42]. They found the shear forces can facilitate the break-up of large-sized agglomerates, whereas the extent of further exfoliation of the mineral layers is determined by the compatibility between the polymer matrix and the mineral layers rather than shear forces. To ensure this organoclay can be used as nanofiller to produce polymer nanocomposite by melt compounding technique.

Design of Experiments (DoE) is a structured statistical technique used for analyzing the behaviour of a product, process, or simulation by changing multiple design parameters in a specific manner and recording the response. Applications of DoE include choosing between alternatives, selecting the key factors affecting a response, response surface modelling, regression modelling, etc. The interpretation of results consists of determining the set of factors that are statistically significant for each response measured in the experiment, quantifying the relationship between each measured response and the statistically significant factors and determining the ranges of the statistically significant factors ("process windows" or "process set points") that lead to certain optimal/desired ranges for the measured responses.

Response surface methodology (RSM) is a statistical technique that is useful for modelling and optimization of processes in which the response of interest is influenced by several variables. The RSM has important applications not only in the design, development, and formulation of new processes, but also in the improvement of existing designs. It defines the effect of independent variables on the process either individually or collectively. The technique is employed extensively for optimization studies in recent years. RSM involves three steps: performing the statistically designed experiments, estimating coefficients in the proposed model and predicting the response of the process, and checking the validity of the model.

Cheng and Wu [43] introduced a novel method for exploring a response surface using only one design. This is in contrast to the common practice in response surface optimization, which is to use a sequential experimentation process that consists of beginning with a screening experiment in order to identify important factors, moving to a new region using steepest ascent if main effects indicate such an opportunity for improvement, and finally fitting a response surface model based on a second-order design in the new region. Rather, they proposed to use 3-level orthogonal arrays in order to first screen a large number of factors and then project from the larger factor space onto a smaller space to perform response surface exploration reusing the initial design. Assuming that all factors are quantitative and are denoted by x_1;x_2; ::::;xi , the second-order model is given by

$$y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i<j=1}^{3} \beta_{ij} x_i x_j \text{ ....} (1)$$

where y is the response, xi and xj are the uncoded independent variables and β_0, βi, βii and βij are intercept, linear, quadratic and interaction constant coefficients respectively. In general all RSM problems use either one or the mixture of the both of these models (second order model).In each model, the levels of each factor are independent of the levels of other factors. In order to get the most efficient result in the approximation of polynomials the proper experimental design must be used to collect data.

Method of Least Square is used to estimate the parameters in the polynomials. The response surface analysis is performed by using the fitted surface. The response surface designs are types of designs for fitting response surface. Therefore, the objective of studying RSM can be accomplished by

1) understanding the topography of the response surface (local maximum, local minimum, ridge lines), and
2) finding the region where the optimal response occurs. The goal is to move rapidly and efficiently along a path to get to a maximum or a minimum response so that the response is optimized.

The one-step approach to RSM is also described in Lawson [44]. The sequential nature of RSM is usually viewed as advantageous, as it gives the experimenter an opportunity to learn from each experiment, Cheng and Wu mentions the case in which experimental preparation is time-consuming or its duration long as a disadvantage to the sequential framework. According to research conducted by Myers, Khuri, and Carter [45], the orthogonal design was motivated by Box and Wilson [46] in the case of the first-order model. For the second-order models, many subject- matter scientists and engineers have a working knowledge of the central composite designs (CCDs) and three-level designs by Box and Behnken[47].

The Box-Behnken design (BBD) is the most popular class of second-order designs of RSM. This design is well suited for fitting quadratic surfaces and usually works well for process optimization. The design of experiments using BBD was successfully employed for the optimization of process parameters by some researchers in their studies like polystyrene/ montmorillonite composites[48], styrene / butadiene / rubber / organoclay composites[40], natural-butyl-rubber-layered silicate nanocomposites[49] and PP / nanoclay / $CaCO_3$ nanocomposites .

The Box-Behnken design was chosen as an experimental design for finding the exact quantitative relationship between properties of nanocomposite as the responses and different mixing conditions and content of nanoclay in the formulations. This design is rotatable which means that all the points in design area are at equal distance from the centre points[50].
The number of design points (N) is calculated by

$$N = 2^k + 2k + m \quad \text{..} (2)$$

where k and m are the number of factors and the number of replicates of the centre points respectively. The replicate of centre points is due to checking the reproducibility of the samples. The multiple linear regression analysis was used and the data are fitted as linear or second order equations. The orders of equations are specified based on the lack of fit test and maximizing simultaneously three parameters viz. R^2. A computer analysis has been done using commercially available package (MINITAB IV) to compute the equation constants.

In this part of research work the combined influence of melt compounding parameters and nanoclay content on the mechanical properties of PP/HDPE/modified nanoclay composites are analysed using Box-Behnken method of response surface methodology. As discussed in Chapter 3, amino silane modified nanoclay and unmodified nanoclay is used for upgrading PP/HDPE blend.

4.2 Methodology

Blends of PP and HDPE in the weight ratio 4:1 was melt compounded in an internal mixer- Thermo Haake Rheocord 600 with roller type rotors. When the polymers melted and torque stabilised nanoclay was added and mixing was continued for a predetermined time given by Box Behnken method of DoE. The total weight of material per batch was 40 g which gives a suitable volume for the rheocord. Amino silane modified nanoclay (N100A) was used as the nanofiller. All the four process variables (temperature, rpm and nanoclay loading) were varied in three levels suggested by three level-four factor BBD as shown in Table 4.1. The mixing parameters and nanoclay content were varied according to a predetermined set of 27 experiments as specified by Box-Behnken experimental design as shown in Table 4.2.

According to Gupta and Bhattacharya[51], melt intercalation is the most widely used method in PNC preparation and it has the tremendous potential for industrial application and is compatible with current industrial process, such as extrusion and injection moulding. The melt blending process involves mixing the kaolin sheets by annealing, statically or under shear, with polymer pellets while heating the mixture above the softening point of the polymer. During the annealing process, the polymer chains diffuse from the bulk polymer melt into the galleries between the kaolin sheets. Giannelis[25] use the direct polymer melt method to intercalate PEO by heating the polymer and silicate at 80°C for 6 h. A range of nanocomposites with structures from intercalated to exfoliated can be obtained, depending on the degree of penetration of the polymer chains into the silicate galleries. The nanoclay was dried in an oven at 70°C for 1 hour before mixing. After mixing the melt is hot pressed in a hydraulic press into thin sheet and cut into small pieces. Dumb bell and rectangular shaped specimens were prepared using Model JIM 1H series-4508 semi automatic plunger type injection moulding machine with a barrel temperature of 180°C.

Tensile strength and modulus were tested as per ASTM standards D638 in an AGX-10KN series Autograph UTM from Schimadzu Corporation. Flexural testing was done as per ASTM D790 in the same UTM with a crosshead speed of 5 mm/min. Impact testing was done in pendulum type Resil Impact tester from CEAST Technologies, Italy according to ASTM D256. Tensile samples are injection-moulded, dumbbell-shaped specimens with an overall length of 115 mm, a width in the gauge section of 8 mm and thickness of 3.2 ± 0.4 mm. Flexural and impact specimens are rectangular bars of dimensions 40x12x3.2 mm. A minimum of five samples were tested in each nanocomposites and the average results were recorded.

Based on regression analysis, data from the experiments were used to fit mathematical models of the general form as given by Equation 1.

The quality of fit of the polynomial model equation is expressed by the coefficient of determination, R^2. R^2 value is determined for each response and model is validated using data from experiment conducted from a different combination of variables than used in the Box-Behnken experimental design points. Further statistical verifications were conducted to check the goodness and applicability of the developed model in to the real time situations. The steps involved in the analysis are:

- Estimating regression coefficients for each mechanical property
- Conducting p test and ANOVA test to estimate the significance of each parameter in the model.
- Calculating the statistical parameters : Coefficient of correlation R, average absolute relative error (AARE), average root-mean-square error (RMSE), normalized mean-biased error (NMBE) and scatter index (SI)

In this section statistical checks were performed for the models developed for both PP/HDPE/unmodified clay nanocomposites and PP/HDPE/modified clay nanocomposites.

4.3 Results and discussion

In this section mechanical properties of PP/HDPE/N100A composites and PP/HDPE/N100 composites are analysed using Box-Behnken method and the response equations are developed for tensile strength, tensile modulus, % elongation at break (break strain), flexural strength, flexural modulus and impact strength. The mechanical properties are optimized for the variables- nanoclay content and temperature, time and shear of melt mixing. The variables of interest- melt compounding temperature, time of mixing, mixing torque and nanoclay content are varied in three levels based on the design table suggested by Box-Behnken method of DoE. The 27 combinations of variables are selected and mixing is carried out in all combinations with both modified and unmodified nanoclay. The experimental results obtained are tabulated. Model equations are developed based on the regression analysis conducted on these set of data. Response surface and contour plots are drawn to visualise how each response varied in the selected design space. Main effects and interaction effects plots are drawn to illustrate the effect of each variable on the responses. Finally the developed model is validated with confirmatory experiments. The variables are varied in three levels based on the preliminary experiments as shown in Table. 4.1.

Table 4.1 Variables in Box– Behnken design

Variables	Levels used, actual (coded)		
	Low(-1)	Medium(0)	High(1)
Mixing Temperature(^{o}C)	150	160	170
Mixing shear(rpm)	30	50	70
Mixing Time(min)	4	8	12
Nano clay content(%)	1	2	3

4.3.1 Mechanical properties of PP/HDPE/N100A nanocomposites

The variables of interest- temperature, time and shear rate of mixing, and nanoclay content are varied in three levels based on the design table suggested by Box-Behnken method of DoE. The variables are varied in three levels based on the preliminary experiments as shown in Table. 4.1. The 27 combinations of variables, together with the respective responses are listed in Table 4.2.

Table 4.2 Box–Behnken experimental design table with experimental response values of mechanical properties

Sl. No	Temp ^{o}C	time Min	rpm	clay wt%	TS	BS	IS	FS	FM	TM
1	160	12	50	1	39.1	9.5	22.78	45.95	1517	1351
2	170	4	50	2	31.6	11.2	24.78	44.85	1439.25	1259
3	150	8	70	2	36.2	10.1	23.75	44.28	1482.73	1289.2
4	160	12	30	2	37.5	9.8	22.83	44.95	1525.41	1320.65
5	150	8	50	3	37.25	10.3	23.54	43.6	1489.21	1296.58
6	170	12	50	2	34.6	11.2	24.12	43.14	1418.65	1222.2
7	150	8	30	2	36.5	10.1	23.65	44.76	1476.21	1313.15
8	160	12	70	2	37.3	9.7	22.25	45.55	1529.58	1328.14
9	160	4	50	1	38.2	9.9	22.64	45.55	1501.3	1310.5
10	160	8	50	2	39.22	8.2	22.01	47.1	1561.09	1392.44
11	160	4	30	2	38.5	10	22	45.65	1530.75	1310.68
12	170	8	30	2	35.7	11.5	22.33	44.86	1391.82	1298.32
13	160	4	50	3	38.4	10.1	22.43	45.05	1511.41	1309.5
14	160	8	50	2	39.9	8.2	22.55	47.31	1556.66	1391
15	160	8	30	1	38.57	9.5	23.01	45.45	1532	1321.52
16	150	12	50	2	36.5	9.3	23.66	45.135	1448	1301
17	160	4	70	2	37.8	9.2	22.54	46.15	1542.75	1352.32
18	160	8	30	3	38.6	9.2	22.56	45.05	1521.36	1331.45
19	160	8	70	3	38.5	9.9	22.64	45.65	1521.2	1322.71
20	160	8	70	1	38.1	9.6	22.24	45.65	1515.23	1311.54
21	160	12	50	3	38.6	9.8	22.35	44.955	1511.98	1305.3
22	150	4	50	2	35.7	10.2	23.12	44.05	1428	1247.36
23	170	8	50	3	34.6	11.5	24.64	44.15	1415.89	1261.14
24	170	8	70	2	35.1	11.5	24.91	44.05	1435.12	1248.72
25	170	8	50	1	35.2	11.9	24.25	44.6	1424.52	1252.05
26	150	8	50	1	36.1	10.3	23.45	43.2	1492.45	1283.52
27	160	8	50	2	39.56	8.2	22.34	48.3	1570.44	1390.25

Tensile strength, tensile modulus, flexural strength and flexural modulus has a trend of increasing initially with the temperature, time, shear and nanoclay content, reach a maximum and then decreases whereas impact strength and break strain show a reverse trend. The results show that all the variables have an effect on the properties of nanocomposite and the optimum properties are obtained at the middle levels. There is an increase of 22.5% in tensile strength and 19.1% increase in flexural strength, also tensile and flexural modulus increases by 62.9% and 28.6% respectively, but the impact strength decreases by 31%. The mechanical properties increase at 2 wt% nanoclay content as there may be good dispersion and proper interfacial adhesion at this loading rate between nano clay and polymer matrix.

Hauldin[52] indicated that an increase in composite modulus and mechanical properties is due to filler matrix interaction capability for micro filled systems and in the case of nanoclay filled systems, the increased interaction is a result of extremely high surface area generated by the high aspect ratio of the nanoclay.

The tensile and flexural properties first increase, reaches a maximum at the middle level settings of variables, ie., 160°C mixing temperature, 8 minutes of compounding time and 50 rpm shear rate, and then decreases. Residence time and mixing efficiency as affective parameters in nanocomposite morphololology have been considered by many research groups. Borse and Kamal [53] reported that the larger residence time and higher mixing efficiency lead to higher degree of exfoliation and better mechanical properties of polyamide nanocomposites while Zhu and Xanthos[54] reported that the mixing time is a dominant factor in producing satisfactory polypropylene nanocomposite in an extruder and that coupling of long mixing time and high shear rate might result in poor exfoliation of nano filler.

The enhancement of properties can be ascribed to the resistance exerted by clay sheets against plastic deformation of the polymer[55,56]. The insertion of polymer chains inside the kaolinite sheets leads to an increase in the surface area of interaction between the clay and polymer matrix, thereby resulting in an increase in strength and modulus. The decrease in the mechanical properties after the critical loading may be due to the agglomeration of clay particles[57-60]. When the clay agglomerates are present, the stress acting on a small part of the material surface would be much greater than the average stress applied to the test specimen. Even though there is a slight decrease in impact strength, this can be attributed to the increase in crystallinity on the addition of nanoparticles. Liu *et al*.[61] has reported similar effects. The increase in mechanical properties on increasing temperature and mixing shear can be attributed to proper mixing and dispersion of nanoclay sheets in the polymer matrix and better compatibilization of PP and PE blend [62-64]. Above critical temperature and mixing shear, the material degrades resulting in the decrease of mechanical properties.

The experimental data were analysed by the response surface regression procedure using the following second order polynomial equation given by equation 1. Each coefficient in the equation estimates the change in the mean response per unit increase in ‘X’ when all other predictors are held constant. The equations for all responses are listed in Table 4.3, where X_1, X_2, X_3 and X_4 are mixing temperature, mixing time, mixing torque and nanoclay loading in coded variables.

Table 4.3 Statistical data and equations for different responses

Response	R^2 %	Adjusted R^2 %	Model Equations (in coded form)
Tensile Strength	92.2	83.0	$39.9-0.95\ X_1+0.28X_2-0.19X_3+0.06X_4-3.66X_1^2-1.32X_2^2-0.75X_3^2-0.39X_4^2+0.55X_1X_2-0.08X_1X_3-0.44X_1X_4+0.13X_2X_3-0.18X_2X_4+0.09X_3X_4$
Flexural Strength	90.5	79.5	$47.24+0.05\ X_1-0.14X_2+0.05X_3-0.16X_4-2.13X_1^2-0.84X_2^2-0.71X_3^2-1.1X_4^2-0.69X_1X_2-0.08X_1X_3-0.21X_1X_4+0.02X_2X_3-0.12X_2X_4+0.1X_3X_4$
Tensile Modulus	92.2	83.2	$1390.65-12.78\ X_1+0.24X_2-3.6X_3-0.29X_4-81.11X_1^2-37.93X_2^2-26.09X_3^2-37.54X_4^2-31.61X_1X_2-6.41X_1X_3-0.99X_1X_4-8.54X_2X_3-11.18X_2X_4+0.31X_3X_4$
Flexural Modulus	93.2	85.2	$1561.09-24.28\ X_1-0.24X_2+4.09X_3-0.95X_4-96.22X_1^2-25.94X_2^2-13.43X_3^2-19.76X_4^2-10.15X_1X_2+9.19X_1X_3-1.35X_1X_4-1.96X_2X_3-3.78X_2X_4+4.15X_3X_4$
% Strain at Break	95.4	90.0	$8.2+0.7\ X_1-0.1X_2-0.01X_3-0.008X_4+1.8X_1^2+0.69X_2^2+0.69X_3^2+0.84X_4^2+0.23X_1X_2+0X_1X_3-.09X_1X_4+0.19X_2X_3+0.05X_2X_4+0.16X_3X_4$
Impact Strength	87.2	78.3	$22.01+0.3\ X_1+0.04X_2+0.16X_3-0.01X_4+1.587X_1^2+0.2X_2^2+0.14X_3^2+0.37X_4^2-0.3X_1X_2+0.62X_1X_3+0.075X_1X_4-0.28X_2X_3-0.055X_2X_4+0.21X_3X_4$

Each coefficient estimates the change in the mean response per unit increase in X when all other predictors are held constant. MINITAB software package was used for regression analysis. The factors with positive coefficients have a positive effect on the property and vice versa. The R^2 values for all responses are obtained in the range of 0.78–0.97. Although, R^2 closer to 1 means that the model is more valid. But the range achieved for

R^2 in this study is an indication of a very good fitting of the experimental data by the response surface method in the models.

The adequacy of the model can be checked with R^2 and R^2adjusted. R^2 is the coefficient of determination which is found out by the formula:

$$R^2 = 1 - \frac{SS_E}{SS_T} \tag{3}$$

Where SS_E= Total sum of squares, which is defined by the following equation:

$$SS_T = \sum_{i=1}^{n} y_i^2 - \frac{(\sum_{i-1}^{n} y_i^2)}{n} \tag{4}$$

Sum of squares of errors or residuals is given by the equation:

$$SS_E = \sum_{i=1}^{n} e_i^2 \tag{5}$$

where y_i is the value of response and e_i is the difference between experimental and predicted values.

$$R_{adj}^2 = \frac{SS_E/(n-p)}{SS_T/(n-1)} \tag{6}$$

where n is the number of observations and p is the number of regression coefficients

R^2 adjusted is considered rather than solely relying on R^2 value because R^2 value can be easily increased by adding more variables, regardless of whether these factors are statistically significant or not [77]. The R^2 and R^2 adjusted values for the above regression model are 92.2 % and

83 %, respectively. For general rule of thumb, the R-squared or adjusted R-squared should be higher than 0.80 to produce a good linear model. If R-squared is less than 0.5, it is recommended to consider other type of model rather than linear model [78]. These values indicating that the model fits the data reasonably well. In general, the higher the R^2, the better the model fits our data.

Contour plots of the mechanical properties of the nanocomposites prepared by varying the process parameters and modified clay content are shown in figures 4.1 and 4.2.(a &b). The circular nature of the figure proves that there is a maximum/minimum property encircled by the contour lines and the range of experiments chosen was appropriate. The actual value of the property encircled by each contour line is shown in the column in the right hand side of the figure.

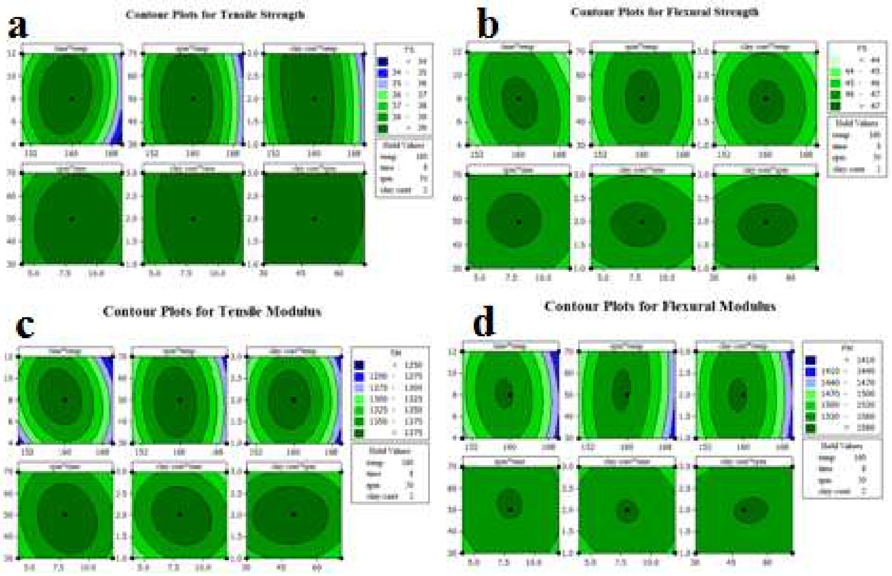


Figure 4.1 **(a) Contour plots for tensile strength (b) Contour plots for flexural strength (c) Contour plots for tensile modulus (d) Contour plots for flexural modulus**

The maximum value of the tensile strength obtained is displayed in the figure as >39, flexural strength obtained is > 47 and so on. Contour plots of impact strength and break strain illustrate a reverse trend on the other hand. The nature of contours show that there is minimum encircled by the centre portion and the properties show a slight decrease on the addition of modified nano kaolin clay. Kurokawa[65]and Chavarria[66] studied the mechanical properties of polypropylene nanocomposite with low cation capacity clays with and without modification and reported similar observations.

The contour plots for tensile strength, flexural strength, impact strength and break strain are overlaid to find the feasible region having desired properties and shown in fig. 4.2 (c&d). The feasible region is obtained at the centre region where all the contour lines keep encircling.

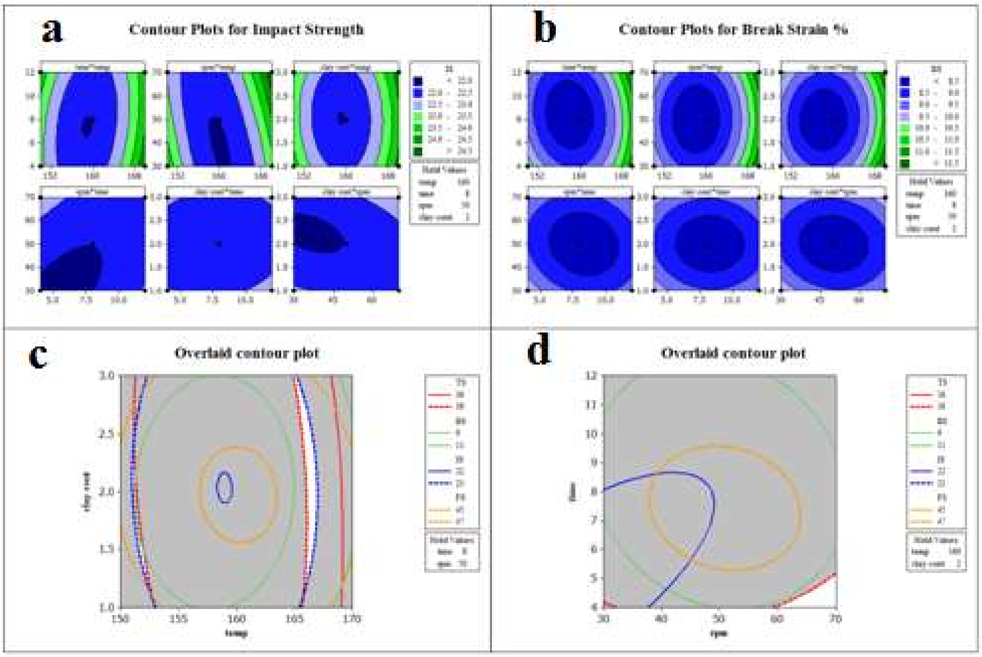


Figure 4.2 (a) Contour plots for impact strength (b) Contour plots for break strain (c) &(d) Overlaid contour plots

The desired values of all these properties can be obtained at any given combination within the optimized region. For the purpose of overlaying, nanoclay content and temperature are chosen as variables keeping the value of mixing time and rpm at mid point in fig.4.2.c and vice versa in 4.2.d.

Main effects plots of the responses are plotted in fig.4.3 and 4.4 (a&b), where it is seen that melt intercalation temperature is the most important determining factor for the properties of the nanocomposites. As the temperature increases the properties increase, reaches a maximum and then decreases. The initial increase may be due to better mixing and intercalation of polymer chains in between the clay sheets and further increase may cause the deterioration due to thermal decay of the polymer matrix. Similar observations were reported by Mohammed Salleh *et al.* [67] and Fabio Bertini *et al.*[68]

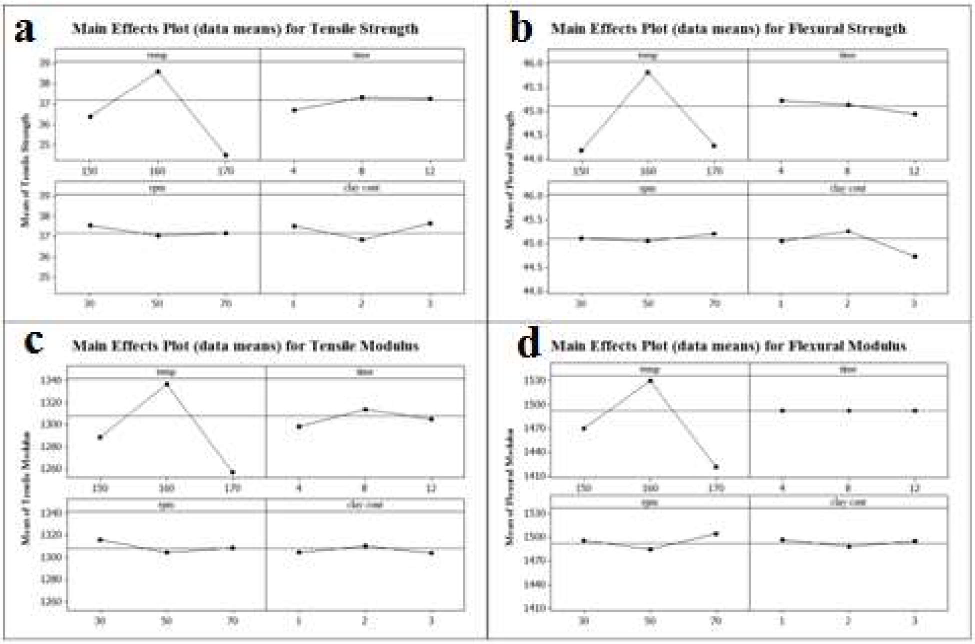


Figure 4.3 **(a) Main effects plot for tensile strength (b) Main effects plot for flexural strength (c) Main effects plot for tensile modulus (d) Main effects plot for flexural modulus**

Interaction plots are used to visualise the interaction effect of factors on the responses and to compare the relative strength of effects If the change in the mean of response from a one level of factor to another depends on the level of another factor, the two factors are said to have interaction effects. Parallel lines represent the absence of interaction between the factors. The greater the deviation from parallel, greater is the interaction between the factors. As seen from Fig. 4.4 (c) for tensile strength, the interaction between the factors was more significant than impact strength. A similar trend is obtained for other mechanical properties.

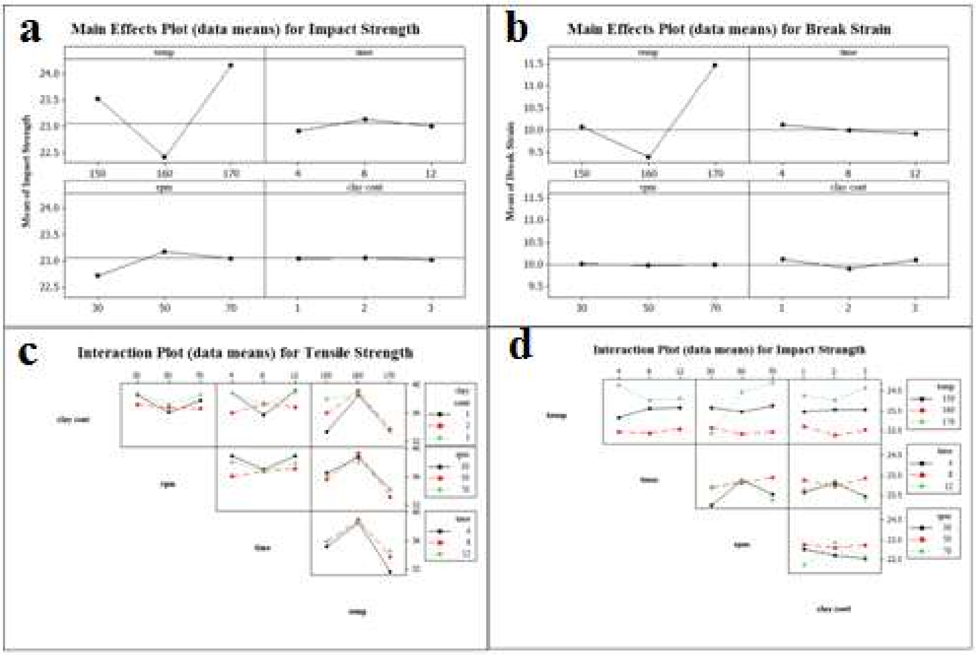


Figure 4.4 (a) Main effects plot for impact strength (b) Main effects plot for break strain (c) Interaction plot for tensile strength (d) Interaction plot for impact strength

Response surface plots of tensile strength and % elongation at break are illustrated in fig. 4.5 (a&b). As seen in the figure, the response navigates smoothly in the design space with only one maximum/minimum and without any saddle points. This suggests that the response can be optimized and the conditions for best nanocomposite can be found using DoE. Flexural strength and modulus and tensile modulus followed the same trend as tensile strength.

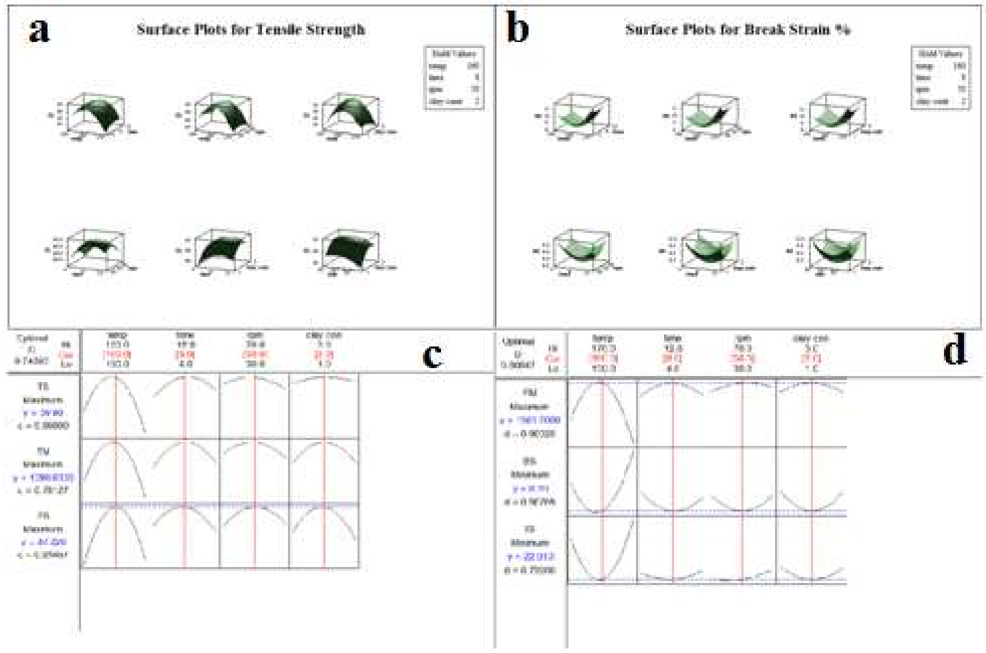


Figure 4.5 **(a) Surface plots for tensile strength (b) Surface plots for break strain (c) Response optimization plots for tensile strength, tensile modulus, and flexural strength (d) Response optimization plots for flexural modulus, break strain, and impact strength**

The optimisation of processing conditions and nanoclay loading for maximum properties of nanocomposites is done using response optimiser of Minitab IV. The optimum conditions are obtained by taking the top summit point of the response surface plots. The optimum conditions obtained for all properties remain almost same. The optimisation plot for mechanical properties is shown in Fig.4.5 (c&d). Response optimisation is useful to determine optimum operating conditions. It helps to identify the combination of input variable settings that jointly optimise a single response or a set of responses. This is useful when we need to evaluate the impact of multiple inputs on a response. Once an optimisation plot has been created, the input variable settings can be changed. For response surface designs, the factor levels can be adjusted. Input variable settings on the optimisation plot can be changed for many reasons (Minitab Inc, 2007), includes:

- search for input variable settings with a higher composite desirability
- search for lower-cost input variable settings with near optimal properties
- explore the sensitivity of response variables to changes in the design variables
- calculate the predicted responses for an input variable setting of interest
- explore input variable settings in the neighbourhood of a local solution

From figures 4.5 (c&d), it is evident that the optimum processing conditions are mixing temperature- 160°C, mixing time-8 min, mixing torque-50 rpm and nanoclay loading-2 wt.% i.e., 0.8 g/batch. The predicted properties for this condition are given below:

Tensile strength: 39.96 MPa, tensile modulus: 1,390.65 MPa, flexural strength: 47.24 MPa, flexural modulus: 1,561.09 MPa, % elongation at break: 8.19, and impact strength: 22 kJ/m^2.

Confirmatory experiments were carried out to validate the equations, using combinations of independent variables, which were not part of the original experimental design but were within the experimental region.

Conditions of verification experiments are:

Run 1: mixing temperature- 155°C, mixing time-8 min, mixing torque- 60 rpm and nanoclay loading-3 wt.%.

Run 2: mixing temperature- 165°C, mixing time-12 min, mixing torque- 30 rpm and nanoclay loading-2.5 wt.%

Table. 4.4 Comparison of predicted and observed values for verification experiment

Properties	Predicted		Observed		% Change from actual	
	Run1	Run2	Run1	Run2		
Tensile Strength	39.13	36.79	35.96	37.01	−8.82	0.59
Flexural Strength	45.44	44.14	45.76	45.01	0.69	1.9
Tensile Modulus	1332.86	1284.22	1336.72	1256.06	0.28	−2.24
Flexural Modulus	1527.60	1463.77	1582.12	1405	3.45	−4.18
%strain at break	9.442	10.36	9.83	10.12	3.95	−2.3
Impact strength	22.66	22.61	20.75	23.83	−9.2	5.1

The results of verification experiments are provided in Table 4.4. The percentage deviation obtained for all responses prove that the model fits reasonably well with experimental data.

Hydrophilic nature of nanokaolinite clay and organophilic nature of polymer matrix introduces difficulty in proper dispersion and compatibility of the polymer matrix and nanoclay, which results in poor mechanical and thermal properties of the resultant nanocomposites. This difficulty can be overcome either by adding different compatibilizers[11-17-19, 22, 62, 69-70.] (which act as a bridge between the polymer chains and clay layer) or by modifying nanoclay [21, 56, 60, 71-72]. Here the properties of unmodified nanoclay composites are compared with the commercially available modified nanoclay, produced by guest displacement method. Dimethyl sulfoxide or urea is initially used as a guest intercalant to force in between clay platelets. Then, it is again treated with required organic molecule and the guest is displaced. The mechanical properties of nanocomposites with both types of nanoclay at optimum processing conditions are compared with PP/HDPE pure blend and are illustrated in Table 4.5. It is evident from the table that the nanocomposites have better mechanical properties such as tensile strength, tensile modulus and flexural strength than PP/HDPE pure blend. Surface modification of nanoclay further increases the mechanical properties. This can be attributed to better dispersion of nanofiller on the polymer matrix. This is evident in the morphological characterization using SEM which is discussed later.

Table.4.5 Effect of surface modification of nanokaolinite clay on mechanical properties

Property	PP/HDPE	PP/HDPE/N100	PP/HDPE/N100A
Tensile Strength, MPa	32.01	36.84	39.22
Tensile Modulus, MPa	854.02	1248.00	1392.00
Flexural Strength, MPa	39.61	45.785	47.16
Impact Strength, KJ/m^2	32.38	24.43	22.13

There is 6.4% increase in tensile strength, 3.9 % increase in flexural strength and 11.5% increase in tensile modulus for PP/HDPE/modified nanoclay composites compared to PP/HDPE unmodified clay nanocomposites as a result of surface modification of nanokaolinite clay.

4.3.2 Mechanical properties of PP/HDPE/unmodified nanokaolinite clay composites

As suggested by Box Behnken Design 27 experimental combinations of nanocomposites are prepared and the mechanical properties are found out for each combination (Table 4.6). Tensile strength, tensile modulus, flexural strength and flexural modulus have a trend of increasing initially with the temperature, time, shear and nanoclay content, reach a maximum and then decrease whereas impact strength and break strain show a reverse trend. The results show that all the variables has an effect on the properties of nano composite and the optimum properties are obtained at the middle levels. There is an increase of 13.8% in tensile strength and 15.5% increase in flexural strength, also tensile and flexural modulus increases by 41% and 22% respectively, but the impact strength decreases by 24%. The mechanical properties increase at 2 wt% nanoclay content as there may be good dispersion and proper interfacial adhesion at this loading rate between nano clay and polymer matrix. The decrease in impact strength may be attributed to the fact that inclusion of nanoclay affects the crystallinity of the polymer blend.

Yu Dong *et al.*[73] in their paper studied the mechanical properties of PP nanocomposites with organo clays and they also observed that tensile and flexural properties increased while there was a reduction in impact strength of the polymer nanocomposites with organoclays.

Table 4.6 Box–Behnken experimental design table with experimental response values of mechanical properties

Temp °C	Time min	Rpm	Clay wt%	TS	TM	BS	IS	FS	FM
160	8	30	3	33.9	1177.23	12.4	26.4	44.6	1324.55
160	4	50	3	33.6	1160.15	12.4	25.5	44.1	1350.88
160	8	50	2	36.6	1207.41	11.6	24.3	45.7	1490.55
170	12	50	2	33.4	980.13	13.3	26.8	44.1	1313.36
160	4	50	1	34.8	1145.65	12.1	25.7	44.7	1339.71
160	8	70	3	35.9	1190.59	12.5	25.6	44.3	1400.86
160	12	70	2	35.1	1131.2	12.9	26.4	44.6	1393.54
170	8	30	2	34.6	1165.34	14.0	25.7	44.5	1351.22
170	8	50	1	34.7	1139.46	13.6	25.6	44.3	1334.96
170	4	50	2	34.9	1207.64	13.5	25.1	43.9	1356.73
150	12	50	2	35.6	1165.91	12.8	26.5	44.2	1341.92
160	12	30	2	34.6	1148.58	12.2	25.9	44.8	1369.46
160	4	30	2	34.5	1183.56	13.3	25.6	44.8	1354.78
160	12	50	1	34.7	1148	12.4	25.5	44.9	1351.92
170	8	70	2	35	1159.56	13.4	25.9	42.4	1292.75
170	8	50	3	34.2	1124.2	13.05	26.1	43.4	1265.46
160	8	30	1	35.6	1216.78	12.9	25.3	45	1363.15
150	8	30	2	34.9	1156.15	13.3	27.1	43.7	1289.48
160	8	70	1	35.9	1183.77	12.3	26.1	44.7	1352.66
160	8	50	2	36.8	1208.44	11.1	24.5	44.2	1488.65
150	8	70	2	35.4	1143.54	13.5	26.8	44.1	1396.6
150	8	50	1	35.3	1127.34	12.8	26.9	43.7	1273.13
160	12	50	3	34.4	1071.51	12.12	25.7	44.6	1367.53
150	4	50	2	33.5	995.41	13.2	27.9	43.4	1344.99
160	8	50	2	36.5	1207.41	11.5	24.7	45.2	1487.84
150	8	50	3	34.2	1109.86	13.2	27	43.8	1369.41
160	4	70	2	34.9	1167.27	12.1	25.6	44.2	1379.35

The experimental data were analysed by the response surface regression procedure using the following second order polynomial equation given as equation1 (page 189).

The equations for all responses are listed in Table 4.7, where X_1, X_2, X_3 and X_4 are mixing temperature, mixing time, mixing torque and nanoclay loading in coded variables. The factors with positive coefficients have a positive effect on the property and vice versa. The variables which have coefficients with larger magnitude have greater effect on the response. From the responses it can be seen that tensile and flexural properties first increase, reach a maximum and then decrease as the process parameters and nanoclay loading increase. The tensile and flexural properties are influenced by the dispersion of nanoclay in the matrix and interfacial interaction between the matrix and nanoclay. The improvement in tensile and flexural properties can be attributed to the dispersion of nanoclay in the matrix, rigidity of nanoclay and affinity between the polymer and organo–modified nanoclay. Optimum processing conditions lead to better dispersion and thereby better performance of nanocomposites. On further increase of temperature, torque and time of mixing, beyond optimum, material is degraded and this results in inferior mechanical properties. When nanoclay loading is increased beyond optimum, agglomeration and inadequate wetting results. This leads to inferior properties. The impact strength and elongation at break on the other hand show the reverse behaviour. This can be attributed to the crystallinity of polymer nanocomposites. The crystallinity is increased on the addition of nanocomposites which led to the decrease in the value of impact strength and elongation at break[90].

Table 4.7 Statistical data and equations for different responses

Response	R^2 %	Adjusted R^2 %	Model Equations (in coded form)
Tensile Strength	97.2	93.9	$36.64-0.06X_1+0.13X_2+0.34X_3-0.38X_4-1.1X_1^2-1.29X_2^2-0.5X_3^2-0.88X_4^2-0.89X_1X_2-0.02X_1X_3+0.15X_1X_4+0.02X_2X_3+0.25X_2X_4+0.45X_3X_4$
Flexural Strength	94.8	87.1	$45.08-0.03X_1+0.17X_2-0.3X_3-0.2X_4-1.05X_1^2-0.19X_2^2-0.28X_3^2-0.22X_4^2-0.12X_1X_2-0.62X_1X_3-0.28X_1X_4+0.11X_2X_3-0.06X_2X_4$
Tensile Modulus	99.6	99.1	$1207.76+6.51X_1-17.86X_2-5.98X_3-10.62X_4-61.18X_1^2-57.37X_2^2+7.45X_3^2-21.18X_4^2-99.5X_1X_2+1.71X_1X_3+0.55X_1X_4-0.27X_2X_3-22.75X_2X_4+11.59X_3X_4$
Flexural Modulus	98.3	96.4	$1489.01-8.42X_1+0.94X_2+13.59X_3+5.26X_4-98.19X_1^2-56.42X_2^2-55.89X_3^2-77.66X_4^2-10.07X_1X_2-41.4X_1X_3-41.45X_1X_4-0.13X_2X_3+1.11X_2X_4+21.7X_3X_4$
% Strain at Break	98.3	96.2	$11.44+0.16X_1-0.07X_2-0.13X_3-0.05X_4+1.4X_1^2+0.46X_2^2+0.75X_3^2+0.36X_4^2+0.02X_1X_2-0.19X_1X_3-0.22X_1X_4+0.49X_2X_3-0.1X_2X_4+0.16X_3X_4$
Impact Strength	96.7	92.8	$24.99-0.59X_1+0.12X_2+0.04X_3+0.09X_4+1.29X_1^2+0.65X_2^2+0.7X_3^2+0.57X_4^2+0.78X_1X_2+0.105X_1X_3+0.0825X_1X_4+0.13X_2X_3+0.08X_2X_4-0.38X_3X_4$

R-square value is the percentage of response variable variation that is explained by its relationship with one or more predictor variables. The R^2 values for all responses are obtained in the range of 0.8–1(Table.4.7). When R^2 is closer to one it means that the model is more valid and the range achieved for R^2 in this study is an indication of very good fitting of experimental data by the response surface methodology. Significantly high

R^2 suggests that the final model can satisfactorily account for the variations in the process response.

Response surface plots and contour plots are based on the model equations obtained in the regression analysis and are shown in fig. 4.6 and fig 4.7. The two dimensional contour plots are a series of curves that identify different combinations of variables for which the response is constant. The circular shapes of contour plots indicate that a maximum lies in the selected range of operation and the selected range of process parameters and nanoclay loading is appropriate. Contour plots illustrate the change in properties when two or more variables vary together and allow predictions to be made for combinations not actually evaluated. The response surface plot is a three dimensional graph that represents the functional relationship between the response and two variables, while the other variables are held at constant levels. The plot is used to visualise how a response reacts to changes in variables. The response surface plots of the mechanical properties indicate that the response passes through a maximum and then decreases for tensile strength and vice versa for impact strength. The trend followed by other properties is similar to that of tensile strength.

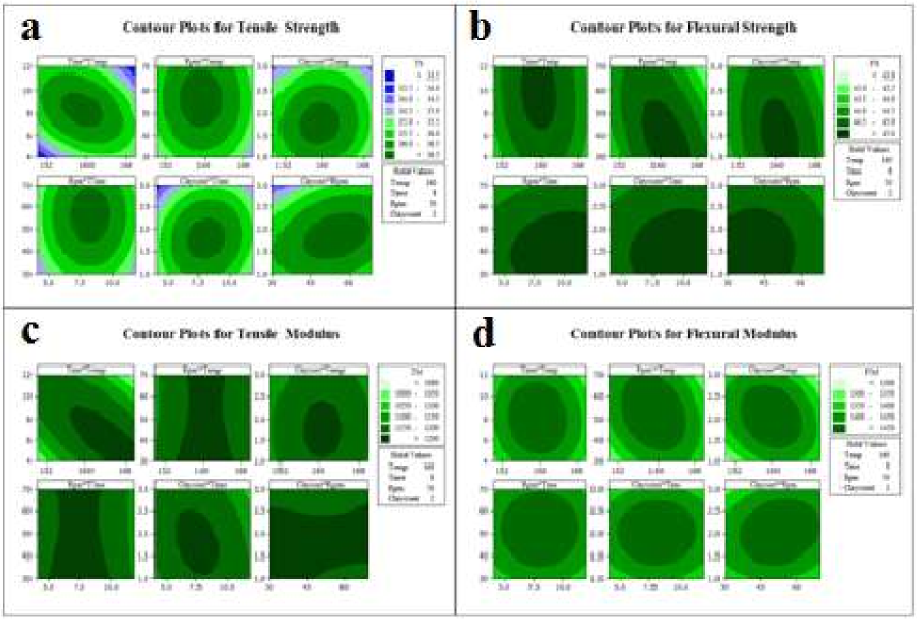


Figure 4.6 (a) Contour plots for tensile strength (b) Contour plots for flexural strength (c) Contour plots for tensile modulus (d) Contour plots for flexural modulus

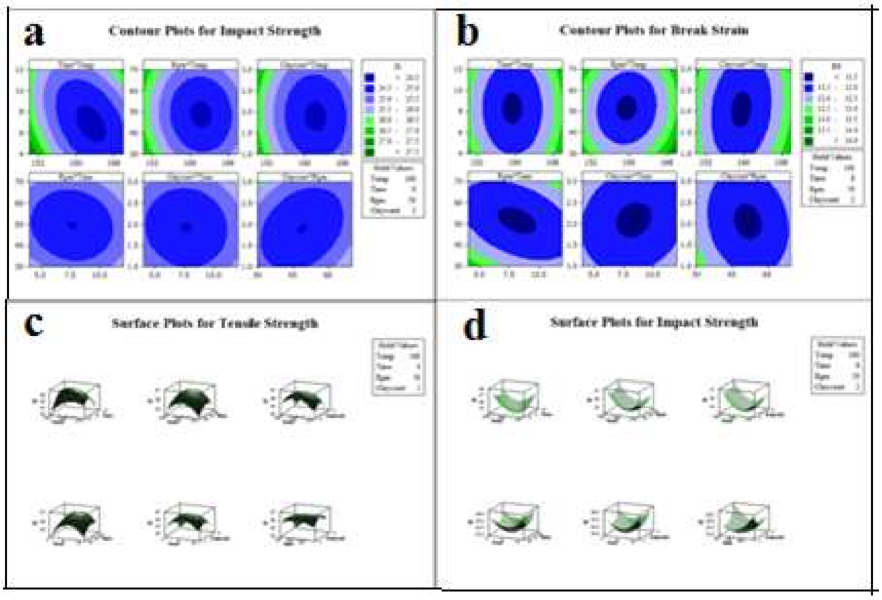


Figure 4.7 (a) Contour plots for impact strength (b) Contour plots for break strain (c) Surface plots for tensile strength (d) Surface plots for impact strength

The inclusion of fillers in the matrix leads to a significant increase in mechanical properties. Zhao *et al.* [74] observed the increase in tensile performance by the incorporation of nanofiller. Svehlova *et al.* [75] has mentioned that better filler dispersion leads to a higher modulus. Hence a higher mechanical performance of PNC is an indication of better filler dispersion.

Main effect plots are used to visualise the effect of the factors on the responses and to compare the relative strength of the effects. When the change in the mean response across the levels of a factor is significant, a main effect is present. The slope of the line indicates the strength of the effect. A horizontal line (slope=0) indicates absence of main effect. The greater the slope of the main effect, stronger is the effect of those process variables. The main effect plots of mechanical properties are illustrated in fig. 4.8 and fig 4.9 (a&b). From the main effect plots, it is evident that the temperature of mixing is the most determining factor for the increase in properties of nanocomposites. Increasing temperature first improves the properties, reaches a maximum and then decreases. The initial increase can be attributed to proper mixing and thereby better dispersion. Further increase in temperature led to degradation of polymer which can be the reason for decrease in properties. Increase of nanoclay loading also initially increases the properties of nanocomposites and then higher levels of loading decreases the properties. The horizontal nature of main effect plots suggests that mixing torque and time has comparatively less effect on the responses. Also it is evident from the fig. 4.9 that nanoclay loading was not the only factor responsible for the decrease in the impact strength. The decrease in impact strength with the addition of clay to PP/HDPE for impact tests may be ascribed to the interaction between nanoclay particles and polymer matrix. During mechanical deformation, in the nanocomposite, the micro-voids from the presence of clay nanoparticles trigger large scale plastic deformation with consequent tearing of matrix ligaments between micro-voids and result in stretching of fibrils (fibrillation) inter dispersed with micro-voids. Thus, there is a clear relationship between the fracture mode and impact strength of neat PP/HDPE blend and clay–reinforced nanocomposites.

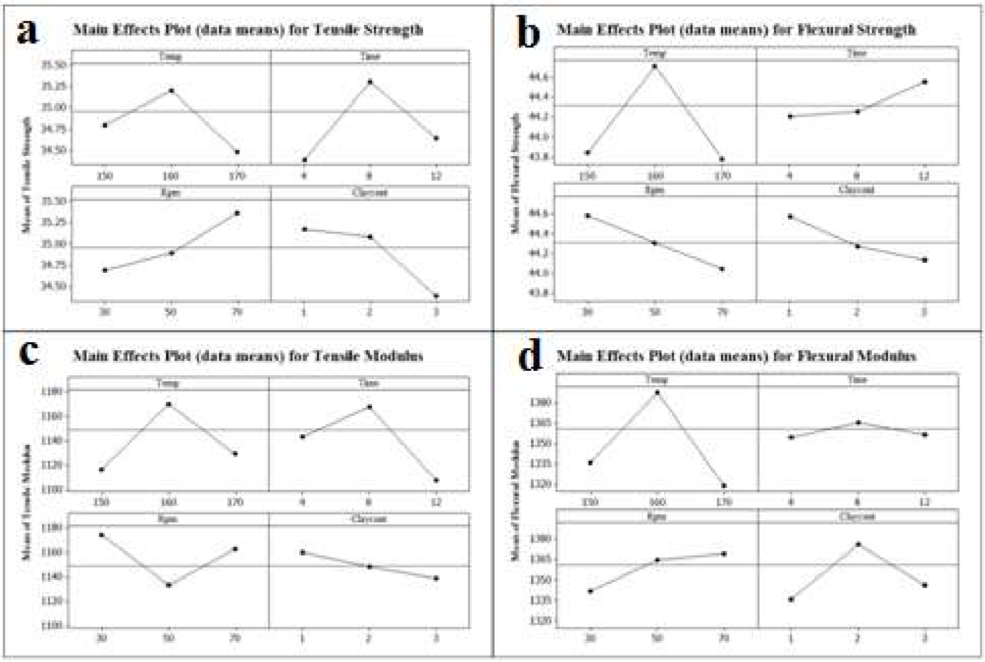


Figure 4.8 (a) Main effects plot for tensile strength (b) Main effects plot for flexural strength (c) Main effects plot for tensile modulus (d) Main effects plot for flexural modulus

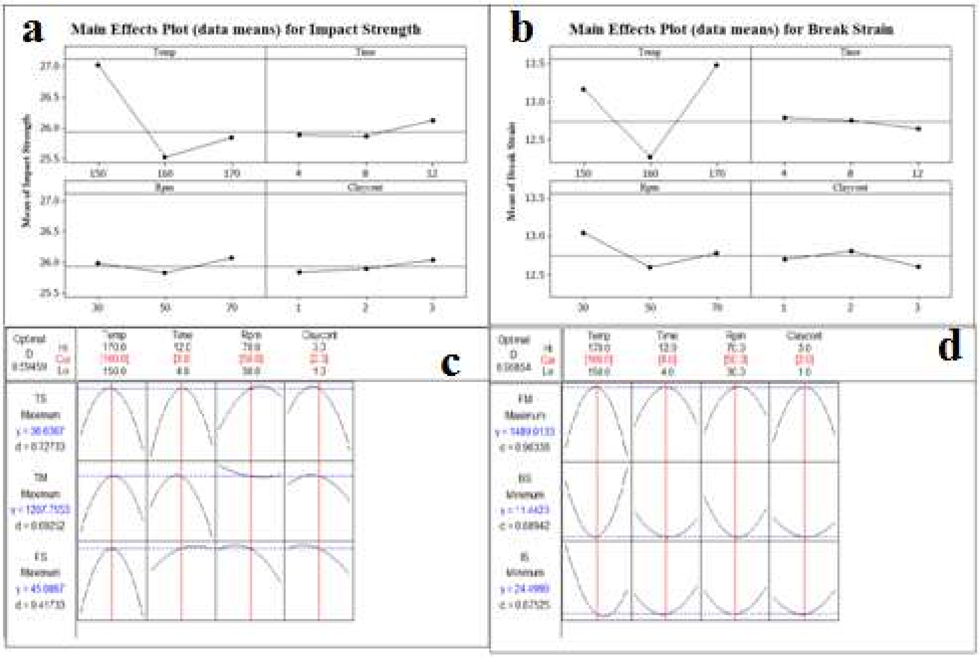


Figure.4.9 (a) Main effects plot for impact strength (b) Main effects plot for break strain (c) Response optimization plots for tensile strength, tensile modulus & flexural strength (d) Response optimization plots for flexural modulus, break strain & impact strength

The optimisation of processing conditions and nanoclay loading for maximum properties of nanocomposites are done using response optimiser of Minitab. The optimum conditions are obtained by taking the top summit point of the response surface plots. The optimum conditions obtained for all properties remain almost same. The optimisation plot for mechanical properties is shown in fig.4.9 (c&d). From fig., it is evident that the optimum processing conditions are mixing temperature- 160°C, mixing time-8 min, mixing torque-50 rpm and nanoclay loading-2wt% i.e., 0.8 g/batch. The predicted properties for this condition are given below:

Tensile strength: 36.62MPa, tensile modulus: 1207.41MPa, flexural strength: 45.78MPa, flexural modulus: 1490.55MPa, % elongation at break: 11.667, and impact strength: 24.32 kJ/m^2.

4.3.3 Statistical analysis of PP/HDPE/nanoclay composites

4.3.3.1 Statistical analysis of PP/HDPE/N100A composites

The first step in the analysis involves finding the significant parameters. The analysis in this study was done using uncoded units. Use of uncoded units helps to eliminate any spurious statistical results due to different measurement scales of the factors and makes them easier to interpret [76]. The significant parameters along with the results of p tests for the mechanical properties of PP/HDPE/N100A nanocomposites are given on Table. 4.8. A confidence level of 95% is chosen for setting up the DoE experimental design which suggested an ‘α’ value of 0.05. Probability of occurrence (p-value) that quantifies the significance of terms in the polynomial model should ideally be less than the chosen α-level, such as 0.05, for the term to be significant. From the analysis on mechanical properties as shown in Table 4.8, the p-values for the estimated coefficients of temperature and nanoclay content indicate that they are the most determining factor in the analysis. p-values of quadratic terms are less than 0.05, indicating that they are significantly related to tensile modulus. Interestingly, other coefficients such as rpm, time and interaction coefficients are higher than 0.05, hence not considered to have a significant effect for the range of conditions studied in this DoE.

Table 4.8 p value and significance level of each process variable affecting the mechanical properties

Term	Tensile Strength		Tensile Modulus		Flexural Strength		Flexural Modulus		Impact Strength		Break Strain	
	p value	Significance level%	p value	Significance level%	p value	Significance level	p value	Significance level%	p value	Significance level%	p value	Significance level%
Constant	0	100	0	>100	0	100	0	>100	0	>100	0	>100
Temp	0.001	>99	0.01	>99	0.021	>97.9	0.001	>99.9	0.037	>96.3	0	>100
Time	0.247	>75.3	0.542	> 45.8	0.363	>63.7	0.967	>3.3	0.776	>22.4	0.282	>71.8
Rpm	0.412	>58.8	0.5	>50	0.728	>27.2	0.474	>52.6	0.259	>74.1	0.914	>8.6
Clay cont	0.812	>18	0.057	>94.3	0.278	>72.2	0.166	>83.4	0.081	>91.9	0.029	>97.1
Temp*Temp	0	100	0	>100	0	100	0	>100	0	>100	0	>100
Time*Time	0.003	>99.7	0	>100	0.002	>99.8	0.009	>99.1	0.254	>74.6	0	>100
Rpm*Rpm	0.054	>94.6	0.008	>99.2	0.007	>99.3	0.129	>87.1	0.487	>51.3	0	>100
Clay cont*Clay cont	0.285	>71.5	0.001	>99.9	0	100	0.034	>96.6	0.093	>90.7	0	>100
Temp*Time	0.197	>80	0.027	>97.3	0.015	>0.985	0.31	>69	0.231	>76.9	0.17	>83
Temp*Rpm	0.855	>14	0.488	>51.2	0.744	>25.6	0.356	>64.4	0.023	>97.7	1	>0
Temp*Clay cont	0.299	>70	0.914	>8.6	0.406	>59.4	0.89	>11	0.758	>24.2	0.548	>45.2
Time*Rpm	0.762	>23	0.359	>64.1	0.921	>7.9	0.841	>15.9	0.261	>73.9	0.251	>74.9
Time*Clay cont	0.672	>32.8	0.236	>76.4	0.625	>37.5	0.7	>30	0.821	>17.9	0.745	>25.5
Rpm*Clay cont	0.822	>17.8	0.973	>2.7	0.693	>30.7	0.672	>32.8	0.389	>61.1	0.33	>67

Temperature: Decreasing temperature moved mechanical properties towards its maximum. This effect is attributed to polymer matrix, because it was found to be highly sensitive to heat, especially at temperatures higher than 190 °C [80-81]. For the effect of temperature on nanocomposites, the results reported in the literature are relatively controversial. Kwak *et al.* [82] reported a better dispersion of organoclay in polyethylene at higher temperature (230 °C instead of 170 °C). Modesti *et al.* [36,83] obtained better results at lower temperature (170 °C instead of 200 °C). But for polypropylene, as temperature increases, viscosity decreases, and thus the stress necessary to break the clay aggregates decreases. At the same time, diffusion is improved, which can help to intercalate and exfoliate the platelets. In addition, a temperature too high could cause a degradation of the organoclay intercalants, leading to a collapse of the interlayer galleries and decreased intercalation[84].

Speed: Increasing rotor speed moved mechanical properties towards its maximum. Generally speaking, it is well admitted in the literature that an increase in screw speed leads to a better dispersion. This effect has been observed on different systems, including nanocomposites based on polyamide [85-86], polyethylene [82], and polypropylene [36 83, 87]. It can be explained by the fact that a higher shear rate allows the breakage of large agglomerates to small aggregates, enhancing polymer–clay interactions by making the entire surface of layers available for the polymer[88]. This suggests that the optimum speed at these factor conditions is above the range trials in this study.

Time: Increasing time first increases then decreases mechanical properties. The properties reach a maximum within the range of times trialled, so the optimum is around 8 minutes for these factor conditions. Denault and coworkers[89] reported that long compounding time and high compounding temperature can lead to organoclay degradation in a polymer nanocomposite. Bourbigot *et al.* [90] also reported that longer times accompanied by higher shear lead to the re-agglomeration of the platelets.

Nanoclay content: Yu Dong and coworkers [73] reported that the clay content is the second significant factor in the preparation of PP/organoclay composite, first being temperature. They stated that the tensile and flexural properties are greatly improved at low nonoclay concentration while impact properties reduce, and that can be improved by addition of MAPP. Similar results are envisaged by more researchers [91-94].

The statistical analysis of the experimental and model results was further carried out by analysis of variance (ANOVA) test. The sum of squares represents a measure of variation or deviation from the mean. It is calculated as a summation of the squares of the differences from the mean. The calculation of the total sum of squares considers both the sum of squares from the factors and from randomness or error. In analysis of variance (ANOVA), the total sum of squares helps express the total variation that can be attributed to various factors.

The total sum of squares = regression sum of squares (SSR) + sum of squares of the residual error (SSE)

Sequential sums of squares (Seq SS) depend on the order the factors are entered into the model. For example, if we have a model with three factors, X_1, X_2, and X_3, the Seq SS for X_2 shows how much of the remaining variation X_2 explains, given that X_1 is already in the model. To obtain a different sequence of factors, repeat the regression procedure entering the factors in a different order. Adjusted sum of squares (Adj SS) does not depend on the order the factors are entered into the model. It is the unique portion of regression analysis explained by a factor, given all other factors in the model, regardless of the order they were entered into the model. For example, if we have a model with three factors, X_1, X_2, and X_3, the adjusted sum of squares for X_2 shows how much of the remaining variation X_2 explains, given that X_1 and X_3 are also in the model. Mean squares represent an estimate of population variance. It is calculated by dividing the corresponding sum of squares by the degrees of freedom.

For significance check, coefficient of fit (F) value given in ANOVA table is used. Probability of occurrence of F value greater than calculated F value due to noise is indicated by p value. If p value is less than 0.05, significance of corresponding term is established. For lack of fit p value must be greater the 0.05. An insignificant lack of fit is desirable as it indicates anything left out of model is not significant so we can develop model fits. Based on analysis of variance (ANOVA) test full quadratic model was found to be suitable for tensile strength, flexural strength and impact strength with regression p-value less than 0.05 and lack of fit more then 0.05. The ANOVA table for tensile modulus is shown in Table.4.9. Here the p values of regression, linear and square terms are less than 0.05 and this indicates that these terms are significant in the model.

Table.4.9 Analysis of Variance for tensile modulus

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	45826	45826	3273.3	10.19	0
Linear	4	3271.1	40445.4	10111.3	31.49	0
Square	4	39550.1	39550.1	9887.5	30.79	0
Interaction	6	3004.7	3004.7	500.8	1.56	0.241
Residual Error	12	3853.2	3853.2	321.1		
Lack-of- Fit	10	3850.8	3850.8	385.1	310.87	0.003
Pure Error	2	2.5	2.5	0.2		
Total	26	49679.2				

For lack of fit the p value is 0.003, which is less than 0.05 and this indicates the model does not fit well with experimental data. This result was a deviation from the above ANOVA results and this indicates that the developed model is not well suited for tensile modulus and further modelling of tensile modulus with available micromechanical model and selection of a best fit model is carried out in Chapter 8. The p value for interaction term is 0.241 which implies that there is no interaction effects present between melt compounding parameters in the preparation of PNC. In the case of tensile strength, flexural strength and flexural modulus, lack of fit the p value is more than 0.05 and this indicates very good fit of the model with experimental data.

The ANOVA table for impact strength is shown in table.4.10. Here the p values of regression, linear and square terms are less than 0.05 and this indicates that these terms are significant in the model. For lack of fit the p value is 0.034, which is somewhat less than 0.05, indicates that model is inadequate for properly estimating the values of impact strength and this may be due to the decrease in the value of impact strength as the nanoclay is added to the polymer matrix. The p value for interaction term is 0.205 which is more than the chosen degree of confidence level and this implies that the interaction effects are not significant in the preparation of polymer-clay nanocomposites by melt compounding technology.

Table 4.10 Analysis of Variance for impact strength

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	16.88	16.8	1.2	5.07	0.004
Linear	4	1.58	12.78	3.19	13.43	0
Square	4	12.87	12.87	3.2	13.52	0
Interaction	6	2.42	2.42	0.40	1.7	0.205
Residual Error	12	2.85	2.85	0.23		
Lack-of-Fit	10	2.70	2.70	0.27	6.65	0.034
Pure Error	2	0.14	0.14	0.07		
Total	26	19.74				

A final statistical analysis of the experimental results was carried out by calculating statistical parameters as coefficient of correlation (R), average absolute relative error (AARE), average root-mean-square error (RMSE), normalized mean-biased error (NMBE) and scatter index (SI) whose equations are given below:

$$R = \frac{\sum_{i=1}^{N}(E-\overline{E})(P_i-\overline{P})}{\sqrt{\sum_{i=1}^{N}\left(E_i-\overline{E}\right)^2\sum_{i=1}^{N}\left(P_i-\overline{P}\right)^2}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

$$AARE(\%) = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{(E_i-P_i)}{E_i}\right| X100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(P_{ij}-E_{ij}\right)^2\right]^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$NMBE(\%) = \frac{\frac{1}{N}\sum_{i=1}^{N}(E_i - P_i)}{\frac{1}{N}\sum_{i=1}^{N}E_i} X100 \quad \dots\dots\dots\dots(10)$$

$$SI = \frac{RMSE}{\overline{E}} \quad \dots\dots\dots\dots(11)$$

where E is the experimental finding and P is the predicted value obtained from the model. $\overline{E}$ and $\overline{P}$ are the mean values of E and P respectively. N is the total number of data points employed in the investigation. The values of the statistical terms are presented in Table 4.11. The correlation coefficient is a commonly used statistical parameter and provides information on the strength of the linear relationship between experimental and predicated values. The closeness of R towards unity indicates better fitting of the model towards experimental data. The AARE and RMSE are computed through a term-by-term comparison of the relative error and therefore are unbiased statistics for measuring the predictability of a model. The NMBE provides information on the mean bias in predictions from a model. A positive NMBE indicates over prediction, whereas a negative NMBE indicates under prediction from a model. It can be seen from the table that NMBE for all mechanical properties except tensile modulus are low values and sufficiently able to predict the corresponding responses with better levels of accuracy [60]. The scatter index provides deviation from a linear behaviour and small value indicates better performance of the model. Low values of SI indicate that the model fits with the experimental data without much scattering. From the statistical evaluation, it is clear that the model fits with the experimental data very well for all mechanical properties except tensile modulus.

Table 4.11 Standard statistical evaluation during validation of the model performance

	R	AARE	NMBE	RMSE	SI
TS	0.96	1.17	0.03	0.545	0.014
FS	0.95	0.7	-0.02	0.37	0.008
IS	0.924	1.1	-5.7E-14	0.33	0.014
TM	0.6	67.7	892.5	67.58	0.679
FM	0.96	0.71	0.0009	12.9	0.009
BS	0.98	1.59	0.037	0.21	0.021

4.3.3.2 Statistical analysis of PP/HDPE/N100 composites

Multivariate optimization of polymeric systems can be carried out using the following procedure

1) Choose a statistical design to investigate the experimental region of interest.
2) Perform the experiments in random chronological order.
3) Perform analysis of variance (ANOVA) on the regression results so that the most appropriate model with no evidence of lack of fit can be used to represent the data.

Here in this section, regression analysis, ANOVA test and statistical parameters evaluation are conducted for PP/HDPE/unmodified clay nanocomposites.

The significant parameters along with the results of p tests for the mechanical properties of PP/HDPE/N100A nanocomposites are given on Table. 4.12.

Table 4.12 p value and significance level of each process variable affecting the mechanical properties

Term	Tensile Strength		Tensile Modulus		Flexural Strength		Flexural Modulus		Impact Strength		Break Strain	
	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %
Constant	0	>100	0	>100	0	>100	0	>100	0	>100	0	> 100
Temp	0.03	>97	0.001	>99.9	0.044	>95.6	0.021	>97.9	0	>100	0.001	>99.9
Time	0.07	>93	0	>100	0.137	>86.3	0.771	>22.9	0.087	>91.3	0.093	>90.7
Rpm	0	>100	0.002	>99.8	0.083	>91.7	0.101	>89.9	0.492	>50.8	0.075	>92.5
Clay cont	0	>100	0	>100	0.071	>92.9	0.021	>97.9	0.151	>84.9	0.024	>97.6
Temp*Temp	0	>100	0	>100	0	>100	0	>100	0	>100	0	>100
Time*Time	0	>100	0	>100	0.288	>71.2	0	>100	0	>100	0	>100
Rpm*Rpm	0	>100	0.008	>99.2	0.115	>88.5	0	>100	0	>100	0	>100
Clay cont*Clay cont	0	>100	0	>100	0.21	>79	0	>100	0	>100	0	>100
Temp*Time	0	>100	0	>100	0.542	>45.8	0.09	>91	0	>100	0.775	>22.5
Temp*Rpm	0.842	>15.8	0.541	>45.9	0.007	>99.3	0	>100	0.361	>63.9	0.017	>98.3
Temp*Clay cont	0.194	>80.6	0.841	>15.9	0.17	>83	0	>100	0.47	>53	0.007	>99.3
Time*Rpm	0.851	>14.9	0.922	>7.8	0.574	>42.6	0.982	>1.8	0.243	>75.7	0	>100
Time*Clay cont	0.044	>95.6	0	>100	0.738	>26.2	0.842	>15.8	0.505	>49.5	0.05	>95
Rpm*Clay cont	0.002	>99.8	0.001	>99.9	1	>0	0.002	>99.8	0.005	>99.5	0.031	>96.9

A confidence level of 95% is chosen for setting up the DoE experimental design which suggested an 'α' value of 0.05. Probability of occurrence (p-value) that quantifies the significance of terms in the polynomial model should ideally be less than the chosen α-level, such as 0.05, for the term to be significant. From the analysis on mechanical properties as shown in Table 4.11, the p-values for the estimated coefficients of temperature and nanoclay content indicate that they are the most determining factor in the analysis. p-values of quadratic terms are less than 0.05, indicating that they are significantly related to tensile modulus. Interestingly, other coefficients such as rpm, time and interaction coefficients are higher than 0.05, so are not considered to have a significant effect for the range of conditions studied in this DOE.

Further statistical analysis of the model developed for all the mechanical properties of PP/HDPE/N100 nanocomposites are done by ANOVA tests. The representative ANOVA results of are given in Table.4.13 and Table.4.14.

Table.4.13 Analysis of Variance for tensile modulus

Source	**DF**	**Seq SS**	**Adj SS**	**Adj MS**	**F**	**P**
Regression	14	85319	85319	6094.2	207.32	0
Linear	4	6120.3	66576.4	16644.1	566.23	0
Square	4	36975.3	36975.3	9243.8	314.47	0
Interaction	6	42223.4	42223.4	7037.2	239.41	0
Residual Error	12	352.7	352.7	29.4		
Lack-of-Fit	10	352	352	35.2	100.13	0.01
Pure Error	2	0.7	0.7	0.4		
Total	26	85671.7				

Table.4.14 Analysis of Variance for impact strength

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	17.18	17.18	1.23	25.09	0
Linear	4	4.49	11.9	2.98	60.95	0
Square	4	9.5	9.5	2.38	48.58	0
Interaction	6	3.17	3.17	0.53	10.83	0.06
Residual Error	12	0.58	0.58	0.048		
Lack-of-Fit	10	0.5	0.5	0.053	1.81	0.407
Pure Error	2	0.05	0.058	0.03		
Total	26	17.773				

As illustrated in the above tables, the regression, linear and square terms are important in determining the, tensile modulus and impact strength of PNC since the p value is less than 0.05. The p value for interaction term is more than 0.5 for impact strength and hence the interaction term is not significant while preparing the PNC using melt compounding. In the case of probability of occurrence of lack of fit the value is more than 0.05 in the above mentioned properties and this indicates a good fit of the model with the experimental data. Tensile strength and flexural strength follows similar pattern as the ANOVA result of impact strength. But the p value for lack of fit in the cases of tensile modulus and flexural modulus are less than 0.05 (0.01 for tensile modulus and 0.013 for flexural modulus) and hence we can conclude that the developed model is somewhat inadequate for predicting the modulii of PNC. This problem is addressed in Chapter 8.

A final statistical analysis of the capability of the developed model to predict the properties of the PNC is carried out by evaluating the statistical parameters like correlation coefficient (R), average absolute relative error (AARE), average root-mean-square error (RMSE), normalized mean-biased error (NMBE) and scatter index (SI) and illustrated in Table 4.15 as shown below.

Table 4.158 Standard statistical evaluation during validation of the model performance

	R	AARE	NMBE	RMSE	SI
TS	0.98	0.3	0.01	0.14	0.004
FS	0.92	0.36	-0.01	0.25	0.005
IS	0.98	0.46	-0.02	0.14	0.005
TM	0.99	0.24	10.2	3.61	0.3
FM	0.99	0.4	0.48	7.29	0.5
BS	0.99	0.45	0	0.09	0.007

The statistical parameters like NMBE, RMSE and SI are high for tensile and flexural modulus and this indicates that the developed model is not very suitable for simulating modulii in the design space.

4.4 Conclusions

- PP/HDPE blend can be effectively modified by cheap and abundantly occurring nanokaolinite clay by environmentally benign melt compounding method.
- The mechanical properties of PP/HDPE blend like tensile and flexural strength and modulus can be significantly increased by the inclusion of nanokaolinite clay
- Box Behnken method of Response surface methodology can be effectively applied for combined optimization of melt mixing parameters and nanoclay content.
- Organomodified nanoclay can act as a molecular bridge between the non polar polymer matrix. Nanokaolinite clay can be converted to organoclay by guest displacement method.

- Modified nanoclay on incorporation into the polymer matrix increases the tensile strength by 22.5% and there is 19.1% increase in flexural strength. Also tensile and flexural modulus increases by 62.9% and 28.6% respectively, but the impact strength decreases by 31%.
- Response equations are developed for all the mechanical properties. Contour and surface plots illustrates the behaviour of the mechanical properties as the variables change from low to high level of the experimental range.
- The main effects plots show that melt compounding temperature and nanoclay content are the most important determining factors affecting the properties of PP/HDPE nanokaolinite clay composites. Interaction plots suggest that there is certain extent of interaction between process parameters and nanoclay content on the responses.
- The overlaid contour plots show that there is a region in the design space where all the mechanical properties are optimum values.
- The R^2 value obtained in the range of 0.8-1 and the results of verification experiments indicates that the model fits well with the experimental data within the entire range of experiments.
- The optimum mechanical properties are obtained with melt compounding parameters of $160^{\circ}C$ temperature, 8 min of mixing time, 50 rpm shear rate and 2 wt% of nanokaolinite clay N100A by response optimization technique.

- The validation of model equations are done using confirmatory experiments and the results prove that the model can navigate the design space very well.
- The statistical analysis of the model developed for the mechanical properties of PP/HDPE nanokaolinite clay composites with and without surface modification was carried out using regression analysis, ANOVA test and by evaluating statistical parameters.
- While examining the results of regression analysis the following conclusions can be drawn out-
  a) The p values and significance levels obtained deduce that the melt compounding temperature and nanoclay content are the most determining factors in the formulation of PNC by melt compounding technique, while the effect of compounding time and shear rate are less so that they can be screened out from further analysis if necessary.
  b) The p values obtained for interaction terms are high and this suggests that there is not much interaction effect between melt compounding parameters and nanoclay content in the preparation of PNC.
  c) The R^2 statistics deduce that the developed model fits reasonably well with the experimental data.
- The results of the ANOVA test conducted for PP/HDPE/nano kaolinite clay composites can be summarized as follows-
  a) The p values obtained for the terms like regression, linear and square indicated that these terms are significant in the model.

The p value obtained for interaction terms is more than 0.5, for the ANOVA results of most of the mechanical properties and this suggests that interaction effects are nil for such properties.

b) The F value which corresponds for the fit of the model should be greater than the tabulated F value for the selected level of confidence. The results show that this condition is satisfied and the model fits with the experimental data.

c) Finally the p value for lack of fit should be more than α value for the selected level of confidence, i.e., 0.5 for the model to be significant. This condition is satisfied for all properties except tensile and flexural modulii.

- A further statistical evaluation is conducted by evaluating the statistical coefficients as correlation coefficient (R), average absolute relative error (AARE), average root-mean-square error (RMSE), normalized mean-biased error (NMBE) and scatter index (SI). These coefficients are calculated using experimental values and predicted properties by the developed model. The evaluation proved that the developed model fits suitably well with the experimental data and can navigate smoothly in the entire design space except for tensile modulus.
- Statistical evaluation suggests that Box-Behnken experimental design can be used to optimize complex processes like preparation of PNC whose response is affected by a large number of variables, effectively with a minimum number of experiments.

References

[1] Oya A, Kurokawa Y, Yasuda H (2000) "Factors controlling mechanical properties of clay mineral/ polypropylene nanocomposites". J Mater Sci 35:1045.

[2] Peter R, Hansjorg N, Stefen K, Rainer B, Ralf T, Rolf M (2000) "Polypropylene/organoclay nanocomposite formation: influence of compatibilizer functionality and organoclay modification". Macromol Mater Eng 275:8.

[3] Pegoretti A, Dorigato A, Penati A (2007) "Tensile mechanical response of polyethylene-clay nanocomposites". Express PolymLett 1(3):123–131.

[4] Lei SG, Hoa SV, Ton That M-T (2006) "Effect of clay types on the processing and properties of polypropylene nanocomposites". Compos SciTechnol 66:1274–1279.

[5] Alexandre M, Dubois P (2000) "Polymer – Layered silicate nanocomposites: preparation, properties and uses of a new class of materials". Mater Sci Eng;28:1.

[6] Dennis HR, Hunter DL, Cho JW, Paul DR, Cheng D, Kim S, *et al.* May (2000). "Guidelines for the production of polypropylene nanocomposites". In: Proceeings of SPE ANTEC, Orlando, Florida, USA.

[7] Meera Balachandran, Lisha Stanley, R Muraleekrishnan, S S Bhagawan. "Modeling NBR-Layered Silicate Nanocomposites". A DoE Approach Wiley Inter Science, in press.

[8] Baniasadi H, Ramazani SA, Nikkhah JS (2010) "Investigation of in situ prepared polypropylene/clay nanocomposites properties and comparing to melt blending method". Matter Des 31:76–84.

[9] Gilman JW, Jackson CL, Morgan AB, Harris R (2000) "Flammability properties of polymer- layered silicate nanocomposites". Polypropyl/Polystyr/ Nanocomposites. Chem Matter 12:1866–1873.

[10] Vaiziri HS, Omaraei IA, Abadyan M, Mortezaei M, Yousefi N (2011) "Thermophysical and rheological behaviour of polystyrene/silica nanocomposites: investigation of nanoparticle content". Mater Des 32:4537–4542.

[11] Venkatesh GS, Deb A, Ajay K, Shakti SC (2012) "Effect of nanoclay content and compatibilizer on viscoelastic properties of montmorillonite/ polypropylene nanocomposites". Mater Des 37:285–291.

[12] Hejazi I, Sharif F, Garmabi H (2011) "Effect of material and processing parameters on mechanical properties of polypropylene/ethylene-propylene-diene-monomer/clay nanocomposites". Mater Des 32:3803–3809

[13] Hernandez JCR, Sanchez MS, Ribelles LG, Pradas M (2007) "Polymer-silica nanocomposites prepared by sol–gel technique; nanoindentation and tapping mode AFM studies". EurPolym J 43:2775–2783.

[14] Ray SS, Okamato M (2003) "Polymer/layered silicate nanocomposites: a review from preparation to processing". ProgPolymSci 28:1539–1544.

[15] Hui S, Chathopadhyay S, Chaki TK (2010) "Thermal and thermo-oxidative degradation study of a model LDPE/EVA based TPE system: effect of nano silica and electron beam irradiation". Polym Compos 31(8):1387–1397.

[16] Akhlaghi S, Sharif A, Kalaee M, Elahi A, Pirzadeh M, Mazinani S, Afshari M (2012) "Effect of stabilizer on the mechanical, morphological and thermal properties of compatibilized high density polyethylene/ethylene vinyl acetate copolymer/organoclay nanocomposites". Mater Des 33:273–283.

[17] MoslehShirazi S, Janghorban K (2012) "Investigation of physical and chemical properties of polypropylene hybrid nanocomposites". Mater Des 34:474–478.

[18] Dayama N, Bhabani KS (2012) "Microstructural correlation to micromechanical properties of polyamide- 6/low density polyethylene-grafted-maleic anhydride/nanoclay ternary nanocomposites". Mater Des 33:510–522.

[19] LV Z, Yang Y, Wu R, Tong Y (2012) “Design and properties of a novel nucleating agent for isotactic polypropylene”. Mater Des 37:73–78.

[20] Zare Y, Garmabi H, Sharif F (2011) “Optimization of mechanical properties of PP/nanoclay/CaCO3 ternary nanocomposite using response surface methodology”. J ApplPolymSci 122:3188–3200.

[21] Qiu Z-C, Zhang J–J, Huang C-L, Niu Y, Yang K–K, Wang Y-Z (2012) “The influence of the surface character of the clays on the properties of poly (p-dioxanone)/fibrous clay nanocomposites”. J ApplPolymSci 125:E247–E259.

[22] Gunning MA, Istrate OM, Geever LM, Lyons JG, Blackie P, Chen B, Higginbotham CL (2012) “The effect of maleic anhydride grafting efficiency on the flexural properties of polyethylene composites”. J ApplPolymSci 124:4799–4808.

[23] Mandal S, Alam S (2012) “Studies on the mechanical, thermal and morphological properties of poly(ether ether ketone)/poly(ether sulfone)/ barium titanate nanocomposites: correlation of experimental results with theoretical predictive models”. J ApplPolymSci 126:724–733.

[24] A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi and O. Kamigaito, (1990), “Synthesis and properties of nylon-6/clay hybrids in: Polymer based molecular composites”, edited by D. W. Schaefer, J. E. Mark, MRS Symposium Proceedings, Pittsburgh, 171 ,p.45-50.

[25] E. P. Giannelis, (1996), “Polymer layered silicate nanocomposites”, Adv. Mater. 8 p.29-35.

[26] R. A. Vaia, G. Price, P. N. Ruth, H. T. Nguyen and J. Lichtenhan, (1999), “Polymer/layered silicate nanocomposites as high performance ablative materials”, Appl. Clay Sci. 15 p.67-92.

[27] E. P. Giannelis, (1998), “Polymer-layered silicate nanocomposites: synthesis, properties and applications”. Appl. Organomet. Chem. 12 p.675-680.

[28] P. B. Messersmith and E. P. Giannelis, (1995), “Synthesis and barrier properties of poly(ε-caprolactone)-layered silicate nanocomposites”, J. Polym. Sci. Part A 33 p.1047-1057.

[29] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito,(1993), “Mechanical properties of nylon 6-clay hybrid”, J. Mater. Res. 8 p.1185-1189.

[30] Alexandre, M and Dubois, P (2000) “Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials.” Mater. Sci. Eng. .R., 28:pp 1-63.

[31] Vijayalakshmi NS, Murthy RAN (1992), “Modification of polyethylene by unsaturated compounds”. J ApplPolymSci 44:1377–1382.

[32] Dennis HR, Hunter DL, Chang D, Kim S, White JL, Cho JW, Paul DR (2001), “Effect of melt processing condition on the extend of exfoliation in organo-clay based nanocomposites”. Polymer 42:9513–9522.

[33] Vaia RA, Giannelis EP (1997), “Lattice of polymer melt intercalation in organically modified layered silicates”. Macromolecules 30:7990–7999.

[34] Yu ZZ, Yang M, Zhang Q, Zhao C, Mai YWD (2003), “ Dispersion and distribution of organically modified montmorillonite in nylon-66 matrix”. J PolymSciPolymPhys 41:1234–1243.

[35] Chrissopoulou K, Anastasidis SH (2011), “Polyolefin/layered silicate nanocomposites with functional compatibilizers”. EurPolym J 47:600–613.

[36] M. Modesti ,A.Lorenzetti, D. Bon, S. Besco (2006) “Thermal behavior of compatibilised polypropylene nanocomposites: Effect of processing conditions”.Polymer Degradation and Stability 91:672-680.

[37] TjongS.C:(2006) “Structural and mechanical properties of polymer nanocomposites”. Material Science and Engineering Report,73:53-64.

[38] Arroyo M., Lopez-Manchado M.A., Valentin J.L., Carettero(2007) “Morphology/behavior relationship of nanocomposites based on natural rubber/eppoxidized natural rubber blends”. Composites Science and Technology, 67: 1330-1347.

[39] Hussain F., Hojjati M., Okamoto M., Gorga R.E (2006), "Reviearticle: Polymer-matrix nanocomposites, processing, manufacturing, and application". An overview Journal of Composite Material,17: 40-53.

[40] I.Ghasemi, M. karrabi, M. Mohammadi, H. Azizi (2010), "Evaluating the effect of processing conditions and organoclay content on the properties of styrene-butaiene rubber/organoclay nanocomposites by response surface methodology". Express Polymer Letters Vol 4, No.2 62-70.

[41] Demirkol E.A, Kalyon D.M, (2007), "Batch and continous processing of polymer layered organoclay nanocomposites". Journal of Applied Polymer Science, 104: 1391-1402.

[42] Homminga D, Goderis B, Hoffman H, Reynaers H, Groeninckx G (2005), "Influence of shear flow on the preparation of polymer layered silicate nanocomposites". Polymer 46: 9941-9957.

[43] Cheng, S. and Wu, C. (2001). "Factor Screening and Response Surface Exploration (with comment)". Statistica Sinica 11, pp. 553–604.

[44] Lawson, J. (2003). "One-Step Screening and Process Optimization". The American Statistician 57, 1, pp. 15–20.

[45] Myers, Raymond H., Khuri, Andre I. and Carter, Walter H., Jr (1989). "Response surface methodology": 1966-1988. Technometrics31 (2): 137-153

[46] Box, G. and Behnken, D. (1960). "Some New Three Level Designs for the Study of Quantitative Factors". Technometrics 2, 4, pp. 455–475.

[47] ErdemYalcInkaya S, Yildiz N, Sacak M, Calimli A (2010) "Preparation of polystyrene/montmorillonite nanocomposites: optimization by response surface methodology". Turk J Chem 34:1–12.

[48] Balachandran M, Lisha PS, Mulaleekrishnan R, Bhagawan SS (2010) "Modeling NBR- layered silicate nanocomposites: a DoE approach". J ApplPolymSci 118:3300–3310.

[49] Montgomery D.C.M (2001), “Design and analysis of experiments”. Wiley, New York.

[50] R.K. Gupta and S.N.Bhattacharya (2008), “Polymer-clay Nanocomposites: Current Status and Challenges”. Indian Institute of Chemical Engineers Vol. 50 No. 3 July-September, pp. 242-267.

[51] Hauldin J.M (1982), “Plastic Deformation of Semi-crystalline Polymer”. In Plastic Deformation Of Amorphous and Semi-crystalline Materials. B. Escaig and C. G’Sell (Eds), Les Edition de Physique, EDP sciences, Le Ulis, France. p.291.

[52] Borse K.N., Kamal M.R (2006), “Melt processing effects on the structural and mechanical properties of PA-6/clay nanocomposites”. Polymer Engineering and Science, 46: 1094-1108.

[53] Zhu L, Xanthos M (2004), “Effects of process conditions and mixing protocols on structure of extruded polypropylene nanocomposites”. Journal of Polymer Applied Science,93:1891-1899.

[54] ASTM D638-94b (1995), “Tensile properties of plastics. Annual book of American Society for Testing and Materials (ASTM) standards”.

[55] Nayak SK, Mohanty S, Sushanta KS (2009), “Effect of clay types on the mechanical, dynamic mechanical and morphological properties of polypropylene nanocomposites”. Polym. Plast. Tech Eng 48:976–988.

[56] ASTM D790-92 (1995), “Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials”. Annual book of American Society for Testing and Materials (ASTM) standards.

[57] ASTM D 256-10 (1995), “Standard test method for determining Izod pendulum impact resistance of plastics”. Annual book of American Society for Testing and Materials (ASTM) standards.

[58] ASTM D 1238-10. Standard test method for melt flow rates of thermoplastics by extrusion plastometer, volume 08.01. ICS number code 83.080.20 (thermoplastic material).

[59] Asha KK, George TS, Anjana R, Joseph N, George KE Effect of modified kaolin clays on the mechanical properties of polypropylene/polystyrene blends. J ApplPolymSci doi:10.1002/app. 38043.

[60] Liu SL, Lu XH, Liew FY, Lim SH, Yong MS. “Melt processing and properties of intercalated polypropylene/organoclaynanocomposites”. STR/04/004/FT.

[61] Kallel T, Massardier-Nageotte V, Jaziri M, Gerard J-F, Elleuch B (2003), “Compatibilization of PE/PS and PE/PP blends. Effect of processing conditions and formulation”. J Appl. Polym. Sci 90:2475–2484.

[62] Homminga D, Goderis B, Hoffman S, Reynaers H, Groeninckx G (2005), “Influence of shear flow on the preparation of polymer layered silicate nanocomposites”. Polymer 46:9941–9954.

[63] Zhang M, Lin B, Sundararaj U (2012), “Effects of processing sequence on clay dispersion, phase morphology and thermal and rheological behaviours of PA6-HDPE-clay nanocomposites”. J ApplPolymSci 125:E714–E724

[64] Kurokawa Y, Yasuda H, Oya, A (1996), “Preparation of a nanocomposites of polypropylene and smectite”. J. Mater. Sci. Lett. 15(17) 1481-1483.

[65] Chavarria F, Naim K, White P, Hill A.J, Hunder D.L, Paul D.R (2003), “Morphology and properties of nanocomposites from organoclays with reduced cation exchange capacity”. J. Appl. Polym. Sci. 105(5),2910-2924.

[66] M.A.Mohd. Salleh, J.Abd.Razak, N.A.Ibrahim, A.Fakhru’lRazi, A.R.Suraya (2008), “The influence of melt compounding parameters on the tensile properties of low filler loading of untreated-MCNTs-polyproplene(pp) nanocomposites”. Journal of Engineering Science and Technology Vol. 3 No.1 97-108.

[67] Fabio Bertini, Maurizio Canetti, Guido Audisio, Giovanna Costa, Luciano falqui (2006), ”Characterization and thermal degradation of polypropylene-montmorillonite nanocomposites”. Polymer Degradation and Stability 91, 600-605.

[68] George TS, Krishnan A, Joseph N, Anjana R, Geroge KE (2012), “ Effect of maleic anhydride grafting on nanokaolin clay reinforced polystyrene/high density polyethylene blends”. Polym Compos. doi:10. 1002/pc.22276.

[69] Banalia K, Aicha S (2012), "Properties of polypropylene/polyamide nanocomposites prepared by melt processing with a PP-g-MAH compatibilizer”. Mater Des 34:313–318.

[70] Anjana R, George KE, George TS, Krishnan A (2012), “Optimisation of processing conditions of PP/ HDPE/nanokaolinite clay composites by response surface methodology”. Int J PlastTechnol 16(2):136–149.

[71] Gholamian F, Ghariban-Lavasani S, Garshasbi MM, Ansari M, Bataghv F, Moraveji A, Ranjbar Z.” The effects of water absorption and surface treatment on mechanical properties of epoxy nanocomposite using response surface methodology”. Polym Bull. doi: 10.1007/s00289-013-0938-8.

[72] Yu Dong, Debes Bhattacharyya (2008) “Effects of clay type, clay/ compatibiliser content an matrix viscosity on the mechanical properties of polypropylene/organoclay nanocomposites". Composites; Part A 39; 1177-1191.

[73] Zhao K, Li R KY (2006). 'A study on the photo-degradation of zinc oxide (ZnO) filled polypropylene nanocomposites. Polymer 47:3207

[74] Svehlov V, Polouek E (1994) Mechanical properties of talc-filled polypropylene. Influence of filler content, filler particle size and quality of dispersion. Angew Makromol Chem 214,1:91-99.

[75] Malik ZA., Malik M. H, Hussain T. &Arain FA. (2011). “Development of Models to Predict Tensile Strength of Cotton Woven Fabrics”. Journal of Engineered Fibers and Fabrics, 6.

[76] Montgomery, Douglas C. (2005). “Design and Analysis of Experiments: Response surface method and designs”. New Jersey: John Wiley and Sons, Inc.

[77] Termonia Y. (2007).” Structure–property relationships in nanocomposites”. Polymer, 48, 6948-6954.

[78] Myers, Raymond H. and Montgomery, Douglas C. (1995). “Response Surface methodology: process improvement with steepest ascent, the analysis of response Surfaces experimental designs for fitting response surface”. 183-351, New York: John wiley and Sons, Inc.

[79] Jamshidi K., Hyon SH. &Ikada Y. (1988). “Thermal characterization of polylactides”. Polymer, 29, 2229-2234.

[80] Garlotta D. (2001). “A literature review of poly (lactic acid)”. Journal of Polymers and the Environment, 9, 63-84.

[81] Kwak M., Lee M. & Lee BK. (2002). SPE ANTEC Tech. Papers. San Francisco.

[82] Modesti M., Lorenzetti A, Bon, D. &Besco S. (2005). “Effect of processing conditions on morphology and mechanical properties of compatibilized polypropylene nanocomposites”. Polymer, 46, 10237-10245.

[83] Muzny CD., Butler BD., Hanley H. J. M., Tsvetkov F. &Peiffer DG. (1996). “Clay platelet dispersion in a polymer matrix”. Materials Letters, 28, 379-384.

[84] Cho J W. & Paul DR (2001). “Nylon 6 nanocomposites by melt compounding”. Polymer, 42, 1083-1094.

[85] Incarnato L., Scarfato P., Russo GM., Di Maio L., Iannelli P. &Acierno D. 2003. Preparation and characterization of new melt compounded copolyamidenanocomposites. Polymer, 44, 4625-4634.

[86] Lertwimolnun W. &Vergnes, B. (2005). “Influence of compatibilizer and processing conditions on the dispersion of nanoclay in a polypropylene matrix. Polymer, 46, 3462-3471.

[87] Beyer G. (2002).”Nanocomposites: a new class of flame retardants for polymers. Plastics,additives and compounding”, 4, 22-28.

[88] Denault J., Ton-That M.-T. & Bloch J. 2006. “Poly(lactic acid) Nanocomposites: Fabrication Microstructure and Performance. Design, Applications of Composites Proceedings of the Sixth Joint Canada-Japan Workshop on Composites”, 11-19.

[89] Bourbigot S., Fontaine G., Bellayer S. &Delobel R. (2008).” Processing and nanodispersion: A quantitative approach for polylactide nanocomposite”. Polymer Testing, 27, 2-10.

[90] Lei SG. (2003) “Formulation and mechanical properties of polypropylene nanocomposites. M.Asc thesis, Concordia University, Department of Mechanical and Industrial engineering”.

[91] Hasegawa N, Kawasumi M, Kato M, Usuki A, Okada A, (1998) “Preparation and mechanical properties of polypropylene-clay hybrids using a maleic anhydride- modified polypropylene oligomer”. J ApplPolym Sci,67: 87-92.

[92] Wang Y, Cheng Fb, Wu KC (2004) “Twin screw extrusion compounding of polypropylene/organoclaynanocomposites modified by maleated polypropylenes”. J ApplPolym Sci,93:100-12.

[93] Perrin Sarazin F, Ton-That M-T, Bureau MN, Denault J. (2005) “micro and nano structure in polypropylene/clay nanocomposites. Polymer,46:11624-34.

* * *

Chapter 5

CHARACTERIZATION OF PP/HDPE/KAOLINITE CLAY NANOCOMPOSITES

Contents

5.1 Introduction

Polyolefins are particularly well-known for their wide range of applications in automotive and packaging industries. PP and HDPE are especially used as commodity polymers because of their economic advantage and superior performance. In the automotive sector, components for the exterior, interior and the under hood, are increasingly replacing metal parts by reinforced composites due to their weight reduction, improved performance, added aesthetic appearance and reliability. In the present scenario PP is the most widely used polyolefin which account for more than half of all the plastic materials used in automobiles. Polyethylene is a cheap and highly processible commodity plastic used in enormous amounts in packaging industries. It is also used in the production of pipes and fittings for the transportation of water or gas under pressure [1]. These two polymers are cheap and can be reprocessed several times without significant loss of properties and can be modified to achieve specific requirements. An important invasion of PP an HDPE in the field of engineering plastics is that it is now conquering the market formerly occupied by engineering plastics like ABS or polyamides. Jeon *et al.* [2] reported that HDPE can be easily intercalated in between the clay galleries. Later these results were extended to PP also by other researchers [3-6]. Blending of two or more polymers offers a good possibility to modify thermoplastic material so as to improve their properties. The blends of these polymers can be prepared by optimizing thermal, mechanical and processing behaviour. Blending of PP and HDPE would impart synergistic effect as HDPE act as impact modifier, while PP improves tensile and flexural properties. In order to compete with metals, ceramics and other engineering materials in strength and durability, PP/HDPE blend has to be reinforced. Nanokaolinite clay is the material used for reinforcing purpose.

Polymer/clay nanocomposites are a class of hybrid materials composed of organic polymer matrix in which layered inorganic particles with nanoscale dimension are distributed with self-assembled pattern uniformly[7]. The development of PNC that contain ultrafine, delaminated or exfoliated phyllosilicates is increasing every day. Minerals of high aspect ratio provide large interfacial area between the mineral particles in polymer chains which result in improvement of mechanical properties [8]. These nanocomposites synergistically integrate the advantages of organic polymers with excellent process properties and inorganic materials which have the characteristics like high modulus and strength. Among polymer nanocomposites, those based on PP/HDPE and nanoclay have attracted considerable interest, because PP and HDPE are the most widely used and fastest growing class of thermoplastics, while nanoclay is one of the most widely accepted and effective nano reinforcement [9-19]. However, scientists and engineers are faced with several challenges. Nanoclay is naturally hydrophilic whereas PP and HDPE are the most hydrophobic polymers. The result is usually a low level of dispersion of clay platelets in the polymer matrix and a poor interfacial bonding between clay surface and polymer matrix. Attempts to resolve these problems involve two strategies: either to add compatibilizers while PNC being prepared or to modify the nanoclay surface with organic cations prior to the preparation process. Usuki *et al.*[20] first reported a novel approach to prepare PP nanocomposites using a functional oligomer with polar telechilic OH groups as compatibilizer. Akhlaghi *et al.* [21] investigated the effect of compatibilizers on HDPE nanoclay composites and reported that high tensile, thermal and calorimetric properties are obtained in the presence of compatibilizers. Venkatesh and coworkers[22] reported that in the presence of compatibilizers, the mechanical and thermal properties of PP/nanoclay composites are enhanced. Similar studies were conducted and reported by other researchers also [23-32]. Lei *et al.* [33] studied the effect of six different types of nanoclays modified with alkyl amine or alkyl ammonium ion on the reinforcement of PP and reported good enhancement in mechanical and dynamic mechanical properties. Nayak and coworkers [34] reported the effect of quaternary ammonium modified organoclays on PP and found that the organoclays are well dispersed in the polymer matrix. Similar studies were conducted by other researchers also[23,26,35-36]. In this aspect several types of commercial organoclay are currently available. The main difference among them concerns the organic modifiers (intercalants), whose organic cations can replace the cations (Na^+) on the clay surface and are tailored to the polymer in which the clay would be incorporated. Therefore intercalants are widely used to improve the compatibility of nanoclay with the matrix.

While many studies on nanocomposites focus on the importance of chemical surface modification of the clay in order to increase the compatibility between clay and host polymer, the role and importance of processing conditions have not been extensively studied. Mohammed Salleh and co-workers[37] reported that the melt mixing parameters play a crucial role in determining the properties of PP/Carbon nanotube composites. Modesti *et al.* [38] studied the effect of processing parameters and clay composition on the properties of PP nanocomposites and found that apart from nanoclay content, melt compounding temperature is a determining factor for the properties of nanocomposites. According to them lower processing temperature is very important to promote exfoliation due to increased melt viscosity and shear stress. Similar studies were reported in other literatures [25,29,39] also.

Nanoclay reinforced PP and HDPE is found to be scratch resistant, has low density and higher stiffness compared to other mineral reinforced plastics and virgin polymers. It has wide application in textile, automotive industry, space and aerospace industry, packaging etc.

The analysis of mechanical properties and statistical analysis using Design of Experiments in Chapter-4 suggests that the most important determining variables in the preparation of PP/HDPE/nanoclay composites are the melt mixing temperature, nanoclay content and type of surface modification of nanoclay. In this section effect of the above parameters on thermal and morphological properties are analysed to find out the applicability of the composite in sophisticated applications.

5.2 Methodology

Polypropylene (PP), high density polyethylene (HDPE) and both modified nanokaolinite clay(N100A) and unmodified nanokaolinite clay (N100) are the materials use for the preparation of nanoclay reinforced blends. The nanoclay was pre-dried before mixing by keeping in a vacuum oven at 70°C for 1 hour.

The nanocomposites were prepared by melt mixing of PP and HDPE in the ratio 80/20 by weight with nanoclay in an internal mixer, Thermo Haake Rheocord for 8 min and 50 rpm rotor speed. For evaluating the effect of nanoclay content the composites were prepared by varying both N100 and N100A clay content from 1 to 3% by wt at a mixing temperature of 160°C. To study the effect of surface modification PNC were prepared with both type nanokaolinite clay at 2 wt% nanoclay content and compared with pure blend of PP and HDPE. To study the effect of melt compounding temperature, the mixing was carried out at three different temperatures- 150°C, 160°C and 170°C. The variation of torque with time of mixing was monitored. The torque was stabilized to a constant value in a mixing time of 8 minutes. The resultant compound was hot pressed into thin sheets and cut into pieces. Rectangular specimens for dynamic mechanical analysis were prepared by injection moulding in a semiautomatic injection moulding machine.

Melt flow index (MFI) was determined using CEAST Modular Line Melt Flow Indexer according to ASTM D 1238[40] .Thermal stability of PP/HDPE (80/20) blend, unmodified and modified clay nanocomposites was analysed. Thermal analysis was done in a TA-Q 600 series instrument in nitrogen atmosphere for samples of 5–7 mg size and temperature range of

400–1,020°C at 20°C/min. The dynamic mechanical properties were determined using dynamic mechanical thermal analyzer [DMTA; Model 2980 supplied by TA Instrument (USA)]. The test sample is a rectangular strip of dimension 40x12x3.2 mm. The dual-cantilever mode of deformation was used under the test temperature range from 40 to 110° C with a heating rate of 30°C/min at a constant frequency of 10Hz. The crystallization behaviour was analysed using DSCQ100 (TA Instruments). The rheology study was carried out in Anton Paar Rheometer (MCR 102) at a temperature of 210°C, in a plate type geometry (PP50). Frequency sweep tests were carried out on pure blend, nanocomposites and hybrid composites to investigate the time dependent shear behaviour of the composites. In frequency sweep tests the materials were subjected to varying angular frequencies of 100 rad/s to 0.1 rad/s, at a constant strain of 5%. The data analysis was carried out using Rheoplus software.

The morphology of the tensile fractured cross section was examined using a scanning electron microscope JEOL-JSM-6390 with an accelerator voltage of 20 kV in a vacuum atmosphere. The samples were subjected to gold sputtering prior to electron microscopy to give necessary conductivity. The samples were also analyzed in a Bruker AXS D8 Advance X-Ray Powder Diffractometer (Cu Ka radiation) to find the basal spacing of nanocomposites. The samples were scanned in the range of 3°–80°at incremental step of scanning 0.02° at a wavelength of 1.5406 A°.

5.3 Results and discussion

In this section, final characterization of PNC was carried out by verifying the thermal, dynamic mechanical, crystallization and morphological properties.

The major parameters considered were the effects of surface modification of nanoclay, nanoclay content and melt compounding temperature.

5.3.1 Effect of surface modification of nanoclay

Effectively, polyolefins are difficult to intercalate in the interlayer space of hydrophilic non-swelling clays without chemical modification of one of the two pristine components. In order to solve the problem of the lack of interfacial adhesion between non-polar PP/HDPE blend and polar kaolinite sheets, the surface modification of kaolinite clay by guest displacement method was carried out. Here the properties of unmodified nanoclay composites are compared with the commercially available modified nanoclay. Dimethyl sulfoxide or urea is initially used as a guest intercalant to force in between clay platelets. Then, it is again treated with required organic molecule and the guest is displaced. In this section in order to study the effect of surface modification of nano kaolinite clay, composites with both modified nanoclay (N100A) and unmodified nanoclay (N100) are prepared with 2wt% filler content and compared with pure PP/HDPE blend. The materials for testing are prepared at identical conditions of processing as 160°C mixing temperature, 8 rpm mixing shear and 8 minutes of processing time

Melt flow index (MFI)

The presence of interactions between the polymer chains and clay surface may affect the mobility and rheological properties of the polymer chains. Therefore, nanoclay addition should decrease the MFI in polymers. The MFI values of PP/HDPE blends with and without different surface modifications of nanoclay are given in fig. 5.1. The results reveal that penetration of polymer chains into the interlayer space of the amino-modified organoclay is greater compared to others. Consequently, the interaction between the polymer chains and the clay sheets should be stronger in it compared to others. The presence of interactions between the polymer chains and the surface may affect the mobility and the rheological properties of the polymer chains. These values appear to be decreasing with increase in filler loading particularly for amino-modified clay at 2wt% of the filler. Increased amount of surface modified nanoclay may impart plasticising effect and this may be the reason for increase in MFI after optimum filler content.

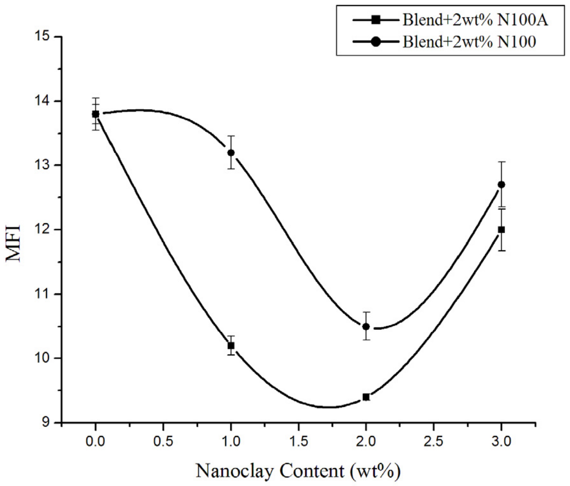


Figure 5.1 Melt flow index curves of PP/HDPE/N100 and PP/HDPE/N100A at various filler loadings.

As shown in fig. 5.1, the polymer MFI reduced significantly at filler loading of 2 wt%. These results prove that the penetration of the polymer chains into the interlayer space of the organoclay is greater in clay nanocomposites compared to pure blends at 2wt% filler loading. Consequently, the interaction between the polymer chains and the sheets should be stronger in composites and this may be the reason for decrease in MFI and enhancement in mechanical properties. The findings of Abbas-Abadi and co-workers[41] support the above results.

Thermal stability

In most cases, the incorporation of nanoclay into the polymer matrix is found to enhance the thermal stability. The thermal stability of the nanocomposites has been investigated using TGA. Table 5.1 represents the results of TGA of PP/HDPE nanocomposites. The nanocomposites were prepared with both modified and unmodified nanokaolinite clay containing 2wt% nanoclay content. The temperature at which degradation begins (onset), the temperature at which 10 % degradation occurs, the temperature at which 50% degradation occurs (which is the midpoint of degradation process), and the temperature at which 80% degradation occurs, (which is a measure of complete degradation) are recorded. It can be observed that both types of PNC show higher degradation temperature than pure PP/HDPE. Pure blend shows an onset degradation temperature of 353°C. For unmodified clay, this temperature shifts to 364°C, and the corresponding value for amino-modified clay nanocomposite is 402°C. The temperatures at which weight loss reaches 50 and 80 % drastically shift to higher temperatures upon the addition of nanokaolinite clay. TGA thermograms of neat PP/HDPE (80/20) nanocomposites with two different modified nanoclays are illustrated in fig.5.2 Improved thermal stability of nanocomposites can be attributed to the decreased permeability of oxygen caused by the partial exfoliation of the clay sheets in the nanocomposites. This may result in the formation of highly charred carbonaceous ash cumulating on the nanocomposites surface.

The charred surface layer formed during decomposition shields the thermal shock due to heat penetration to the underlying material; on the other hand, such cumulative char layer tends to retard diffusion of O_2 and volatile products through nanocomposites [35,42-47].

Table. 5.1 TGA results of PP/HDPE clay nanocomposites

Samples	T_{onset} (°C)	10% Weight loss(°C)	50% Weight loss (°C)	80% Weight loss (°C)
Pure Blend	353	400	459	482
Blend+2wt% N100	384	444.85	482	654
Blend+2wt% N100 A	410	446.61	486.66	780

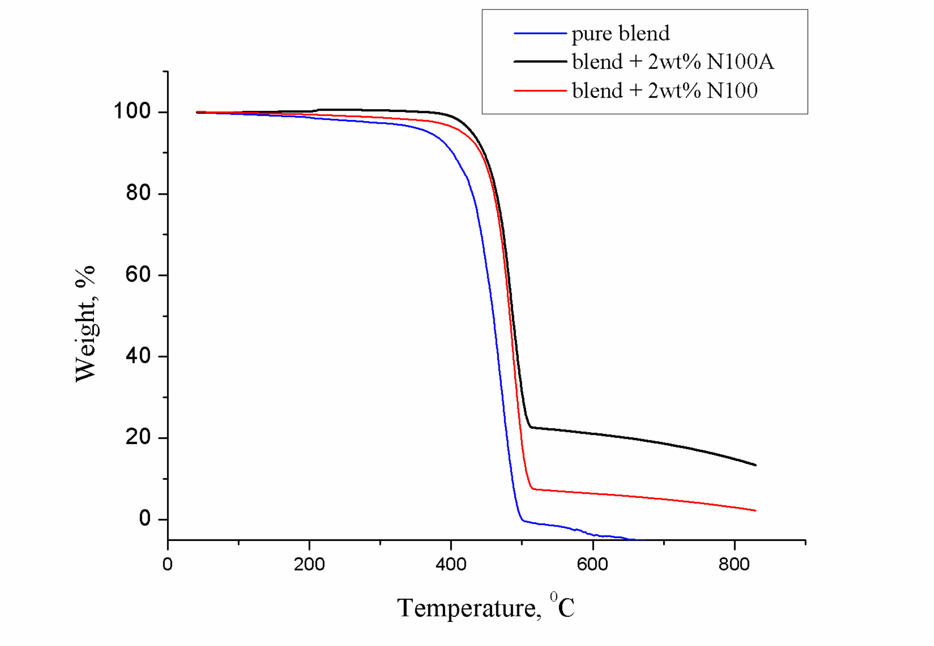


Figure. 5.2 TGA thermograms of pure PP/HDPE, PP/HDPE/N100, PP/HDPE/N100A

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis is used to study the relaxation in polymers. The DMA measurement consists of the observation of time-dependent deformation behaviour of a sample under periodic, mostly sinusoidal deformation force with small amplitudes. Thus, it is possible to calculate storage modulus (E') as a function of temperature and deformation frequency. The analysis of storage modulus curve is very useful in ascertaining the performance of the sample under cyclic stress and temperature. Fig. 5.3 compares dynamic storage modulus curves of nanocomposites with two different modifications of nanoclay with PP/HDPE pure blend. PNC exhibit higher storage moduli over the entire temperature range of study (40–110°C) than pure blend. As can be seen from the figure, the nanocomposites with amino silane-modified clay (N100A) show noticeably higher values of storage modulus over the entire range of temperature. This further proves the overall superiority of modified clay in improving the mechanical behaviour of the blend. This observation clearly illustrates the effect of surface modification of nanoclay in the intercalation of the polymer in clay sheets, leading to dispersion of clay platelets in the polymer matrix. The enhancement of storage modulus strongly depends on the aspect ratio of the dispersed clay particles and the intercalation of polymer chains inside the clay sheets [35,43-44,48].When a polymer matrix is reinforced with rigid filler particles, the polymer interface adjacent to the clay particle is highly restrained mechanically. Active surface area of the filler increases because of the intercalation of the polymer chains inside the clay galleries. Polymer chains inside the clay galleries are immobilized and the effective immobilization of these chains is responsible for the enhancement of the hydrodynamic storage modulus. To clarify the effect of clay on E' the storage modulus of PNC relative to that of pure blend at different temperatures is enumerated in Table 5.2 (relative modulus=E'nanocomposites/E'pureblend). Apparently, the relative modulus of the clay composites is higher than unity over the entire range of temperature, which is considered the real reinforcing effect of nanoclays. It is observed that the reinforcing effect of nanoclay on the storage modulus is significant at higher temperature ranges[44].

Table 5.2 Relative storage modulus (E' nanocomposites/E' pure blend)

Sample	**$E'_{nanocompsites}/E'_{pureblend}$**			
	40°C	**60°C**	**80°C**	**100°C**
Pure blend + 2 wt% N100A	1.12	1.19	1.26	1.30
Pure blend + 2 wt% N100	1.06	1.18	1.23	1.25

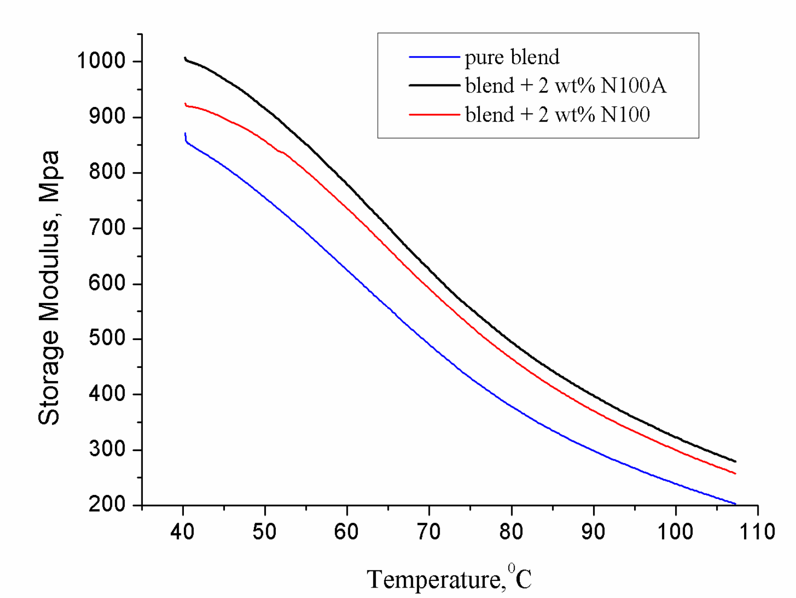


Figure 5.3 Storage modulus of PP/HDPE, PP/HDPE/N100 and PP/HDPE/N100A

The damping coefficient curves of PP/HDPE, PP/HDPE/N100A and PP/HDPE/N100 composites are shown in fig. 5.4. The results indicate that much more reinforcement is obtained in the presence of modified nanoclay when compared to pure blend. The damping is affected by the incorporation of the filler in a composite system due to shear stress concentrations at the filler ends in association with the additional energy dissipation in the matrix material.

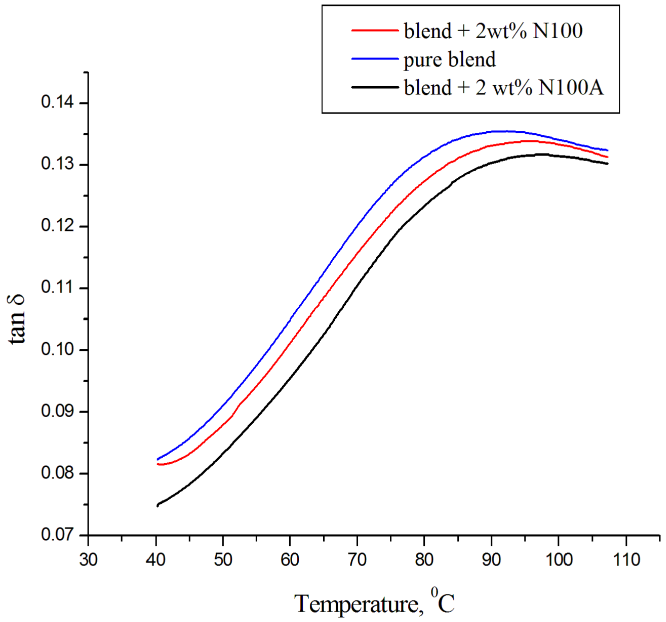


Figure 5.4 tanδ curves for PP/HDPE, PP/HDPE/N100, PP/HDPE/N100A

Differential scanning calorimetry (DSC)

Differential scanning calorimetry is one of the most widely accepted methods of thermal analysis for studying the crystallization behaviour of polymers and their composites. As they undergo temperature changes, the materials' chemical and physical properties are also changed, which are detected by transducers and convert the changes into electrical signals that are collected and analyzed to give thermograms. In non-isothermal DSC, the crystallization characteristics are studied from the heat flows associated with the corresponding transitions as a function of time and temperature.

The effect of nanoclay as nucleating agent on PP/HDPE nanocomposites, was investigated using non isothermal crystallization studies. The crystallization temperature (Tc), the apparent melting temperature(Tm) and the corresponding enthalpies (ΔHc and ΔHm) for all the samples are reported in table 5.3. It is observed that nanoclay can act as nucleating agent as inclusion of 2 wt% nanoclay has enhanced the crystallization temperature of PP/HDPE blend by 10°C. This shows that the nucleating effect increases with surface area and good dispersion of fillers. In Fig. 5.5 the heat flow vs temperature in the cooling scan mode is illustrated. The enhancement of crystallization temperature on addition of modified nanoclay is seen in the graph.

Table 5.3 Thermal characteristics of PP/HDPE/nanoclay composites

Sample	Tc, °C	Tm1, °C	Tm2, °C	ΔHc (J/g)	ΔHm1 (J/g)	ΔHm2 (J/g)
Pure blend	117..5	131.2	163.5	81.69	17.84	32.56
PP/HDPE/2wt% N100A	122.61	131.5	162	105.1	21.42	38.24
PP/HDPE/2 wt% N100	120.22	129.2	160.2	100.61	18.12	30.35

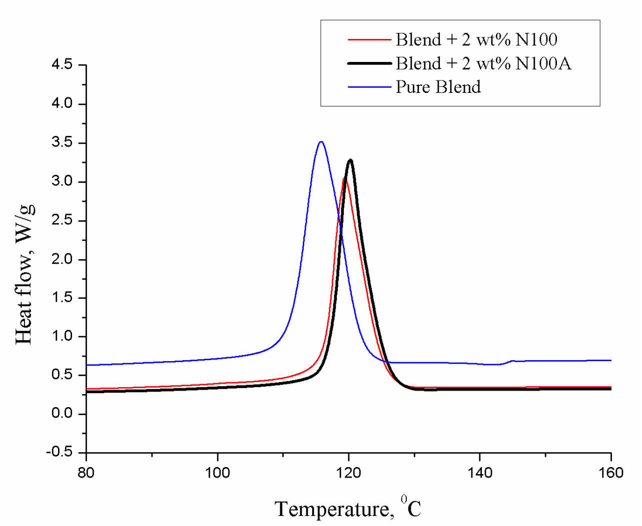


Figure 5.5 DSC cooling scan curves of pure PP/HDPE, PP/HDPE/N100, PP/HDPE/N100A

In the DSC heating scan curves (fig.5.6) it is seen that the melting temperature of PP/HDPE/N100A and PP/HDPE/N100 are slightly more when compared with the pure blend. This may be the reason for enhanced thermal stability of PNC.

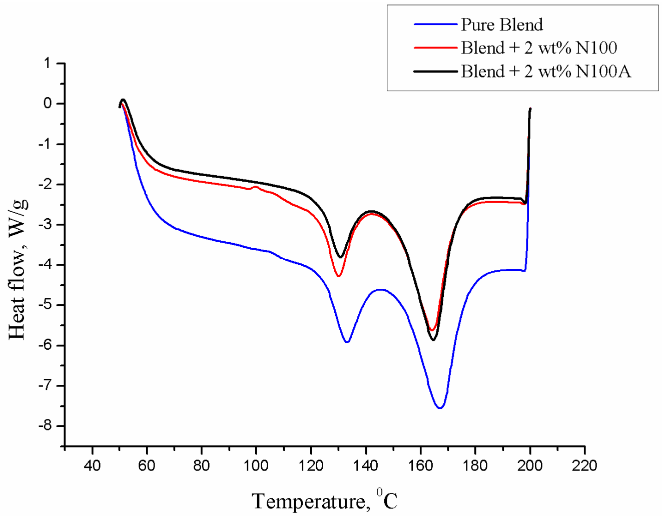


Figure 5.6 DSC heating scan curves for pure PP/HDPE, PP/HDPE/N100, PP/HDPE/N100A

Dynamic rheological analysis (DRA)

Rheology is a branch of physics that deals with the deformation and flow of matter under stress. It is particularly concerned with the properties of matter that determine its behaviour when a mechanical force is exerted on it. Rheology is distinguished from fluid dynamics because it is concerned with the three traditional states of matters rather than only liquid and gases. Applications of rheology are important in many areas of industries involving metal, plastic, and many other materials. The results from rheological investigations provide the mathematical description of the viscoelastic behaviour of matter. An understanding of the rheology of a material is important in the processing of composites, whether the task is designing an injection moulded part or a weldline. It is the rheological properties that govern the flow behaviour of polymers when they are processed in the molten state.

Rheological properties of a two-phase system depend, not only on the rheological behaviour of the components, but also the size, size distribution and the shape of discrete phase droplets dispersed in a continuous matrix phase[49]. Rheological properties of multiphase systems are strongly influenced by the morphology, which depends on the thermodynamic interactions between the constituent polymers and flow history. Therefore, rheological properties are essential in order to relate the morphology of the phase-separated state to the processing of multiphase systems

In order to measure a material's rheology, five criteria must be met:- geometric boundary conditions, stress, strain, strain rate and mode of deformation. For a good comprehension of the rheological properties of materials, it is essential to either measure the deformation resulting from a given force or measure the force required to produce a given deformation. As a measure of force, one can use the stress which is defined as the ratio of applied force to the cross sectional area on which the force acts. Deformation can be described in term of strain or rate of strain[50-56].

The variations of storage modulus (E') with frequency for the pure blend as well as blend containing different surface modified nanokaolinite clays are shown in fig 5.7. The composites are prepared at uniform melt compounding conditions and contain 2 wt% nanoclay. All the composites containing nanokaolinite clays show a higher storage modulus than pure blend. The enhancement in storage modulus is observed for composites containing unmodified and amino modified clays. This is expected as nanoclay has higher storage modulus than polymer and its addition increases the overall storage modulus of the composite.

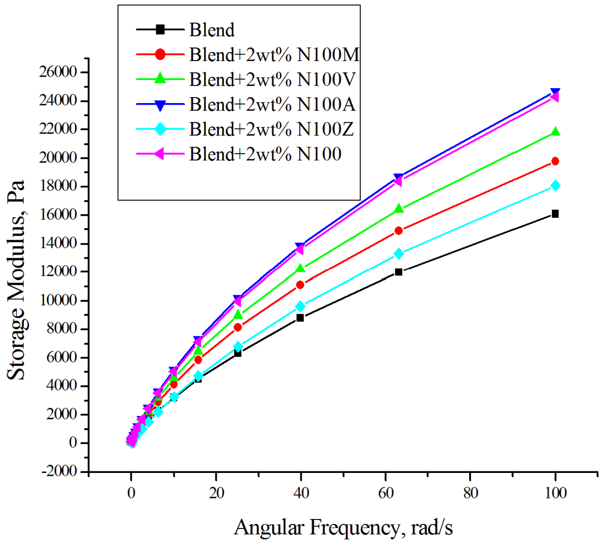


Figure 5.7 Storage modulus vs angular frequency of blend containing different types of surface modified nanoclay

In Fig 5.8 the variations of complex viscosity (η) with frequency on a log scale for the blend as well as different nanocomposites containing 2 wt% nanokaolinite clay is plotted. As it can be seen, for all nanocomposites, complex viscosity is decreasing with increasing frequency. For composites containing nanoclay, the complex viscosity is above that of pure blend. This is attributed to particle-particle interaction as an important parameter in increasing the viscosity[57]. The amino silane modified and unmodified nanocomposites show highest complex viscosity, indicating more particle-polymer interaction and better dispersion of clay particles in the polymer matrix.

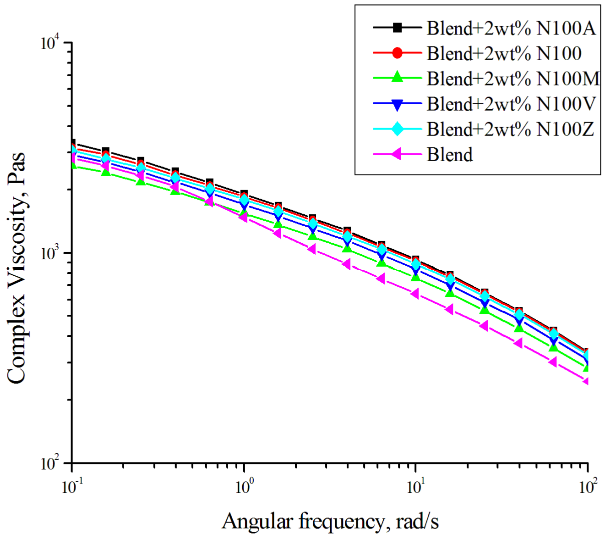


Figure 5.8 Complex viscosity vs angular frequency of blend containing various surface modified nanoclay

X-ray diffraction (XRD)

X-ray diffraction is extremely useful to study the structure and morphology of polymer nanocomposites. It provides information on the changes of the interlayer spacing of the clay upon the formation of nanocomposites. Clays and organoclays show a characteristic peak in XRD analysis due to their regular layered structures. The peak is indicative of the platelet separation or d-spacing in clay structure. Any change in the interlayer or d-spacing of a clay lattice by organic modification or polymer intercalation causes the change in the position, broadness and intensity of the characteristic peak in XRD spectra. According to Bragg's law, increasing of d-spacing results in the broadening and shifting of related XRD peak toward lower diffraction angles 2θ. By monitoring the position 2θ, shape and intensity of the characteristic peak for organoclay in nanocomposites structure, it is possible to determine the degree of intercalation/exfoliation. Thus, the formation of an intercalated structure should result in a decrease of 2θ, indicating an increase in d-spacing value. The interlayer d-spacing observed by XRD for PNC has been used to describe the nanoscale dispersion of clay in the polymermatrix[32, 58]. From 2θ values, d-spacing is calculated by Bragg's equation '$n\lambda = 2d \sin\theta$'. XRD patterns of unmodified clay (N100), amino-modified clay (N100A), PP/HDPE pure blend and its nanocomposites reinforced with both unmodified and amino-modified nanokaolinite clays at 2 wt% are given in fig 5.9. The original basal reflection peaks for N100 and N100A are 12.4°and 12.275°, which correspond to intergallery spacing of 7.09 nm and 7.204 nm respectively. Characteristic peak for PP/HDPE/N100 is 11.2540, corresponding to a d-spacing of 7.85 nm and that of PP/HDPE/N100A nanocomposites is 10.881°, which has a d-spacing of 8.12 nm. The increase in d spacing in PP/HDPE/N100A indicates that some PP/HDPE molecular chains are intercalated between the clay galleries, forming an intercalated structure.

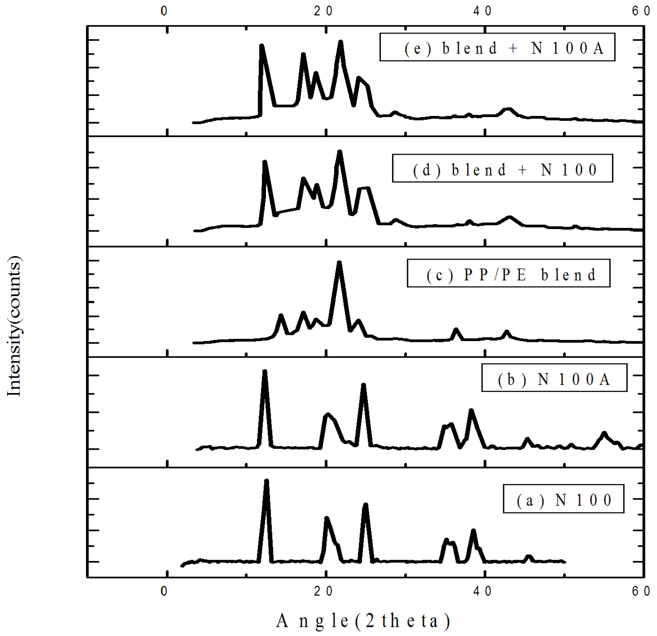


Figure 5.9 XRD pattern of nanoclays and their composites

Table 5.4. Dispersion characteristics of PP/HDPE nanoclay composites

Material	2θ	d-spacing
N100	12.4	7.09nm
N100A	12.275	7.204nm
PP/HDPE blend	Blurred	-
PP/HDPE blend+2wt% N100A	10.881°	8.12nm
PP/HDPE blend+2 wt% N100	11.254°	7.85nm

Scanning electron microscopy (SEM)

Scanning electron microscopy is an effective means for the morphological investigation of composites. Through SEM study, the distribution and compatibility between fillers and matrix can be observed. The change in mechanical properties is brought by morphological change, as documented in Fig. 5.10 - 5.12 showing SEM micrographs. SEM micrograph of pure blend (PP/HDPE) is shown in fig. 5.10. The fractured surface of pure blend is relatively smooth, homogenous with no separation of continuous and dispersed phases, and therefore exhibits good compatibility between the two blended phases. The tensile fractured surface of PP/HDPE/N100A is given as fig. 5.11. It is possible to see smooth surface with better dispersion and homogeneity in that PNC. The SEM morphology of fracture surface of PP/HDPE/N100 unmodified clay nanocomposites is displayed in fig. 5.12. Some amount of improper mixing and reduction in compatibility is seen (fig. 5.12 for the nanocomposites containing unmodified nanoclay (N100), compared with fig 5.11). There is no agglomeration and voids in the composites containing modified nanoclay (fig 5.11). This may be the reason for greater enhancement in mechanical properties for composites with modified nanoclay containing amino silane-modified clay edges. Similar morphological observation is reported in some earlier research papers[23, 35, 58-60].

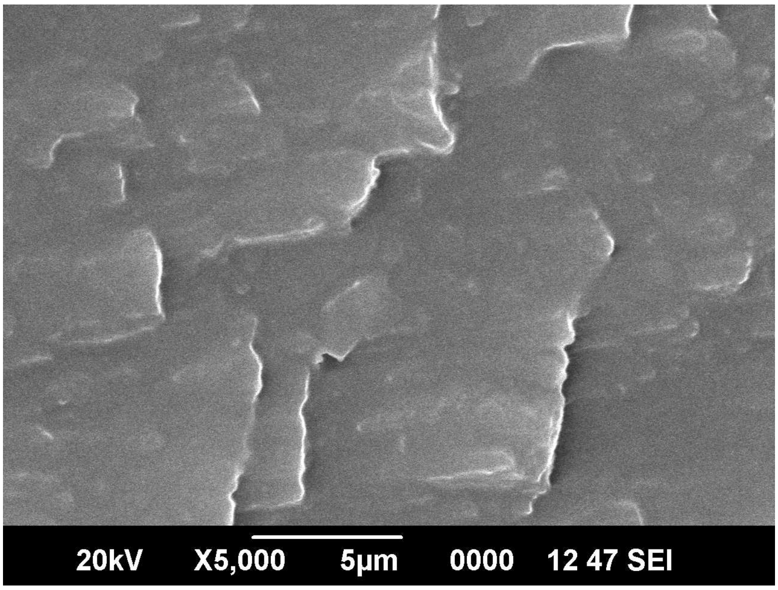


Figure. 5.10 SEM micrograph of pure blend (80PP/20HDPE)

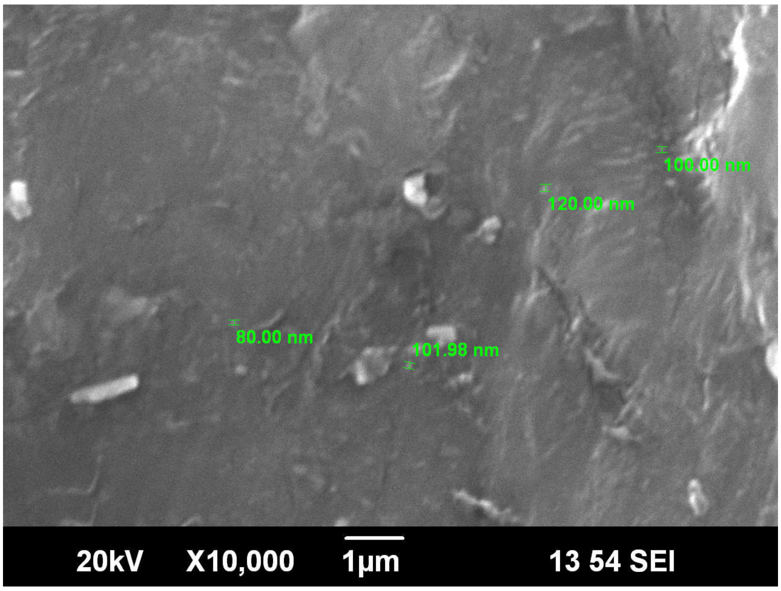


Figure 5.11 SEM micrograph of nanocomposite (80PP/20HDPE/N100A)

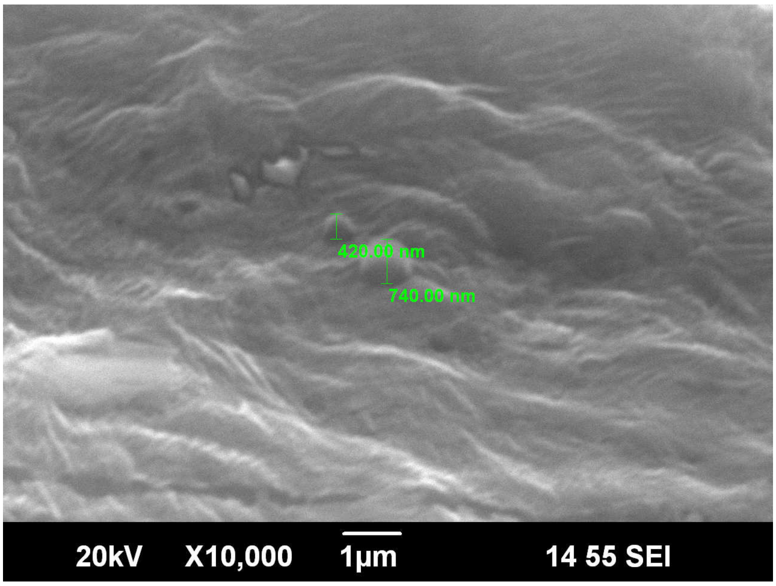


Figure 5.12 SEM micrograph of nanocomposite (80PP/20HDPE/N100)

5.3.2 Effect of nanoclay content:

Inclusion of nanoclay even at very low loading into the polymer matrix will alter the properties of the polymer significantly. Hariprasad and coworkers[61]demonstrated that toughness, stiffness and high storage modulus are coexistent in PP/clay nanocomposites and is strongly influenced by organoclay concentration. Similar observations were reported by numerous researchers from the pioneers – Toyota research group[9-11, 62-64]. In this section to study the effect of clay content, PP/HDPE/N100A and PP/HDPE/N100 composites are prepared with various filler loading as 1, 2 and 3 wt%. The resultant composites are compared with pure blend. The composites and blend for testing were prepared at 160°C melt compounding temperature, 50 rpm mixing shear and 8 minutes of processing time.

Melt flow index (MFI)

MFI is a measure of ease of flow of a melt of a thermoplastic polymer. It is defined as the mass of polymer, in grams, flowing in ten minutes through a capillary of a specific length and diameter by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. It is also a measure of molecular weight, with high melt flow rate corresponding to low molecular weight. The MFI data of PP/HDPE blends with both modified and unmodified nanofiller is represented in fig.5.13.

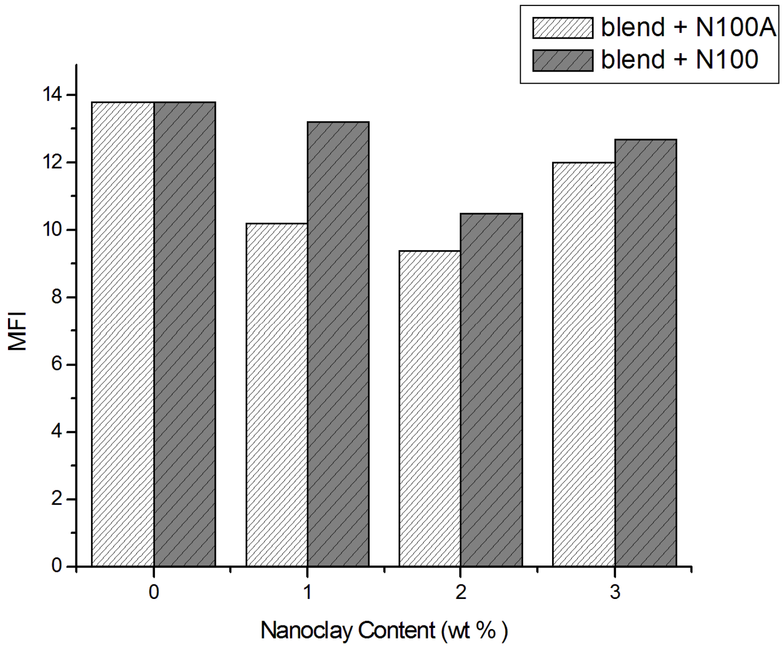


Figure 5.13 MFI of PP/HDPE/kaolinite clay nanocomposites at various filler loading.

It is evident from the figure that the MFI values of PP/HDPE/N100A composites are less than PP/HDPE/N100 composites and of pure blend and also the lowest MFI values are obtained for 2 wt% PP/HDPE/N100A composites. As the interfacial adhesion and dispersion between the polymer matrix and clay layers increase, there offers a resistance to flow which leads to a reduction in MFI value.

Thermal stability

Thermal stability is an important property where the nanocomposites' morphology plays a major role[65]. Studies on the thermal stability show that inorganic fillers which are widely used industrially to improve the mechanical properties of polymers have different effects on their thermal degradation characteristics. The decomposition temperature of PP was increased by adding nanosilica[66], clay[67,68], $CaCO_3$[69]. Degradation characteristics of PP/HDPE/modified nanoclay composites are given in Table.5.5. It is clear that the incorporation of modified nanoclay increases the maximum degradation temperature of PP/HDPE blend from 353°C to 424°C at 2 wt%. At higher nanoclay content, thermal stability is found to decrease which may be due to the poor dispersion of nanoclay particles. The TGA thermogram of PP/HDPE/modified nanoclay composites is shown in fig. 5.14. The PP/HDPE/N100A composites display a remarkable improvement in thermal stability especially at 2 wt% of nanoclay. The degradation characteristics and thermogram of PP/HDPE/unmodified clay nanocomposites are illustrated in Table5.6 and in fig.5.15. Recently, there have been many reports concerned with the improved thermal stability of nanocomposites prepared with various types of organoclays and polymer matrices [70-73]. Zhu *et al.* studied the thermal stability of PS matrix after incorporating different types of nanoclays [74]. Even with as little as 0.1 wt% of clay present in the nanocomposite, the onset temperature was significantly increased**.** The role of clay in the nanocomposite structure is very important. The clay acts as a heat barrier, which enhances the overall thermal stability of the system, as well as assists in the formation of char after thermal decomposition. In the early stages of thermal decomposition, the clay would shift the onset of decomposition to higher temperature. After that, this heat barrier effect would result in a reverse thermal stability. In other words, the stacked silicate layers could hold accumulated heat that could be used as a heat source to accelerate the decomposition process, in conjunction with the heat flow supplied by the outside heat source [75].

Table 5.5 TGA results of PP/HDPE/N100A composites

Sample	T_{onset} (°C)	10% Weight loss(°C)	50% Weight loss (°C)	80% Weight loss (°C)
PP/HDPE +1wt%N100A	410	446.6	487.2	647.9
PP/HDPE +2wt%N100A	424	435.5	476.1	636.9
PP/HDPE +3wt%N100A	404	441.8	482.8	498.9
Pure Blend	353	400	459	482

Table 5.6 TGA results of PP/HDPE/N100 composites

Sample	T_{onset} (°C)	10% Weight loss(°C)	50% Weight loss (°C)	80% Weight loss (°C)
PP/HDPE +1wt%N100	354	419.3	456.5	471
PP/HDPE +2wt%N100	364	432	482	654
PP/HDPE +3wt%N100	312	348.1	421.3	438.5
Pure Blend	353	400	459	482

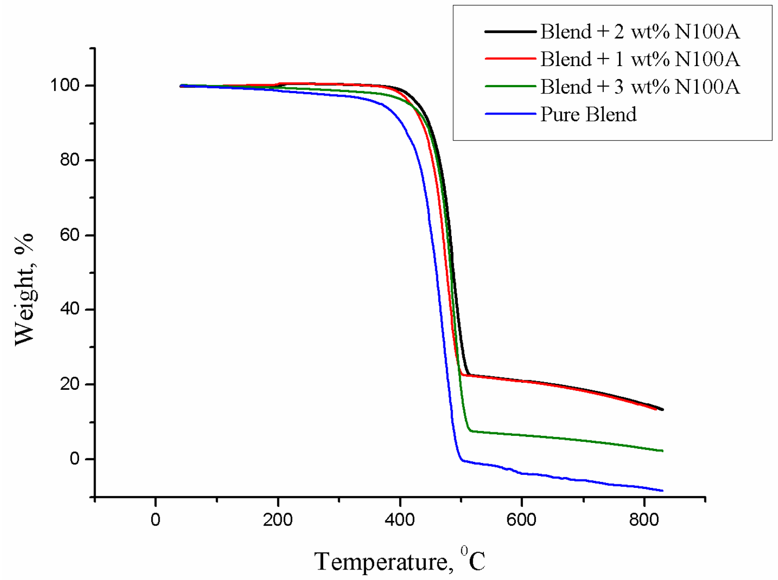


Figure 5.14 TGA thermogram of PP/HDPE/N100A at various filler loadings

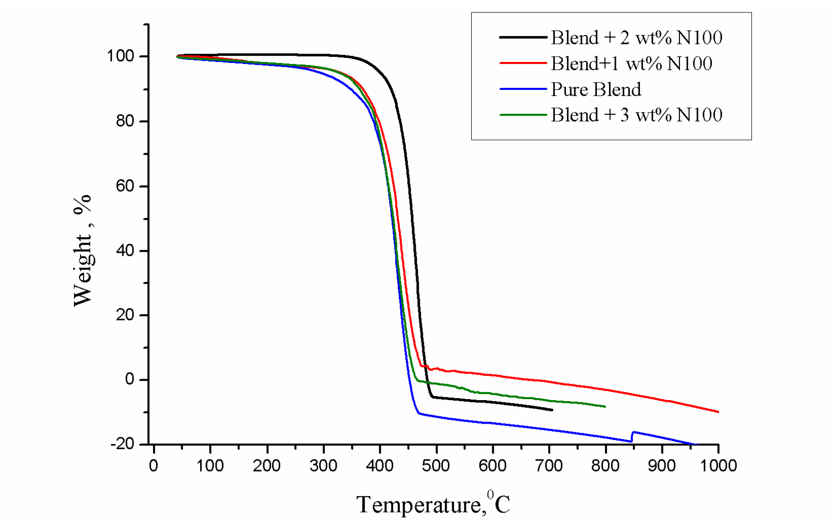


Figure 5.15 TGA thermogram of PP/HDPE/N100 at various filler loadings

Dynamic mechanical analysis (DMA)

Dynamic mechanical properties are important parameters for characterization of processing and use of polymeric materials. Dynamic storage modulus (E$^{'}$) is the most important property to assess the load-bearing capability of a nanocomposites material, which is very close to the flexural modulus[61] and is usually used to study the relaxation in polymers. The ratio of loss modulus (E$^{''}$) to storage modulus (E$^{'}$) is known as mechanical loss factor or mechanical damping ratio (tanδ). Sanjay Nayak[34] and coworkers reported an increase in storage modulus of PP/clay composites. Hasegawa *et al.*[76, 77] reported that the improvement in dynamic mechanical properties above the glass transition temperature (Tg) is more significant than below Tg. According to them the modulus increases by a factor of less than 2 below Tg and it increases by a factor of more than 2 above Tg. This shows that strong matrix-filler interaction takes place above Tg. In this section dynamic mechanical analysis above room temperature (above Tg) of both modified and unmodified nanoclay containing composites at different filler loadings are presented (figs. 5.16 and 5.17). As the surface area of the filler increases, interaction increases, hence the modulus also increases. The addition of higher volume fraction of nanofillers decreases the modulus of composite due to aggregation of nanofiller[78].

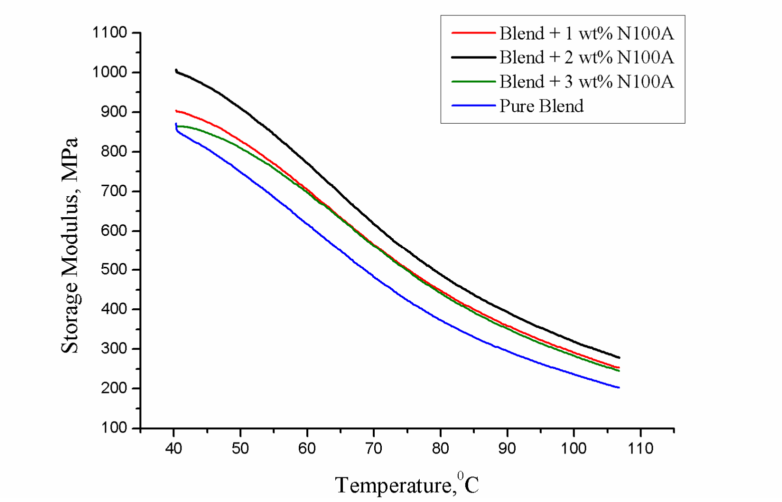


Figure 5.16 Storage modulus vs temperature curve for PP/HDPE/N100A at various filler loadings

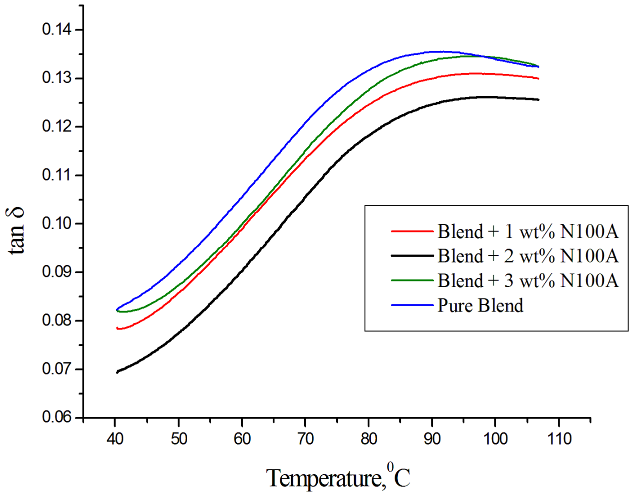


Figure 5.17 Storage modulus vs temperature curve for PP/HDPE/N100 at various filler loadings

Damping ratio (tanδ) curves of both PP/HDPE modified and unmodified nanoclay composites at various filler loadings are drawn as figures 5.18 and 5.19. The damping curve of PNC lies below that of pure blend which shows more reinforcement. Table.5.6 summarizes the storage modulus of PNC at various temperatures.

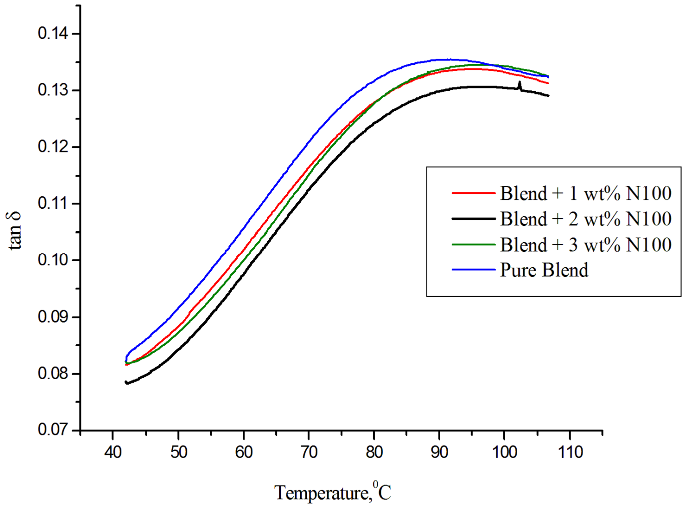


Figure 5.18 tanδ vs temperature curve for PP/HDPE/N100A at various filler loadings

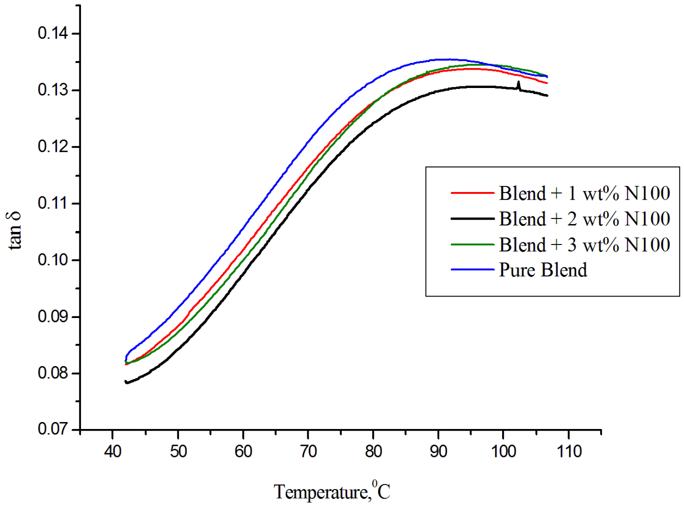


Figure 5.19 tanδ vs temperature curve for PP/HDPE/N100 at various filler loadings

Table 5.7 Storage modulus of PP/HDPE/nanokaolinite composites prepared at different filler content

Sample	Storage Modulus at 40°C (MPa)	Storage Modulus at 60°C (MPa)	Storage Modulus at 80°C (MPa)	Storage Modulus at 100°C (MPa)
PP/HDPE +1wt%N100A	904.9	703.5	447.5	291.4
PP/HDPE +2wt%N100A	1007	770.4	488.5	319.5
PP/HDPE +3wt%N100A	866.8	696.4	441.1	283.2
PP/HDPE +1wt%N100	925.3	725.6	458.6	295.6
PP/HDPE +2wt%N100	930	735.8	468.9	302.1
PP/HDPE +3wt%N100	866.8	694.4	441.1	282.3
Pure Blend	871.4	616.6	373.3	236.2

Differential scanning calorimetry (DSC)

The study of nonisothermal crystallization of polymer composites has great practical significance because industrial processing is usually done on non isothermal conditions. It is reported that surface of filler particles act as nucleation site for semicrystalline polymer, thereby altering the amount or type of crystallinity. Dikobe *et al.* [79] noted that the kinetics of crystallization and structure of HDPE depends on both filler content and polymer-filler interactions. In the presence of nucleating agent the crystallization of PP/HDPE/nanoclay composites occurs at higher temperature and higher rate than pure PP/HDPE blend. DSC cooling scans of PP/HDPE/N100A and PP/HDPE/N100 composites at various filler loadings compared against pure blend is demonstrated in figures 5.20 and 5.21 and heating scans in figures 5.22 and 5.23.

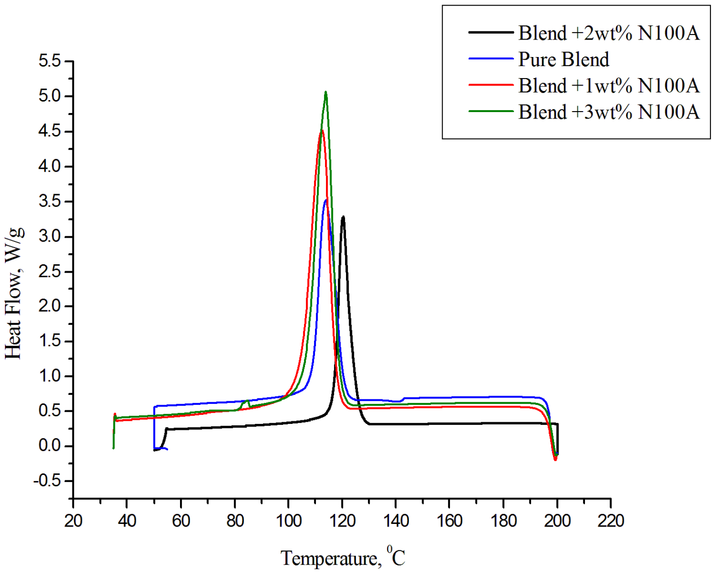


Figure 5.20 DSC cooling scans of PP/HDPE/N100A composites

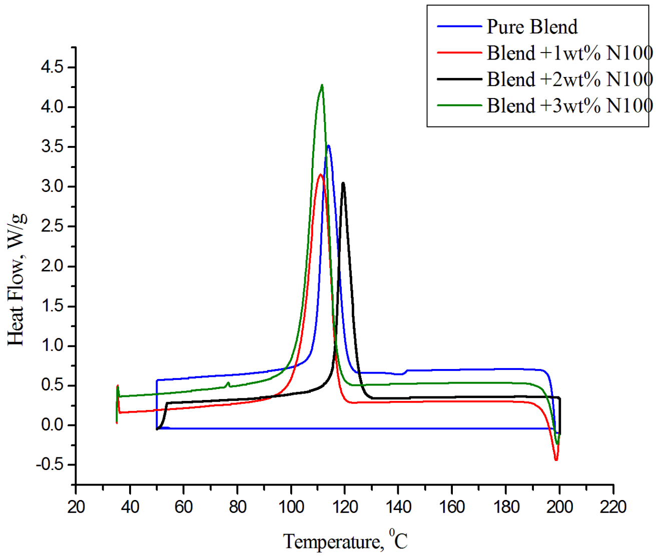


Figure5.21 DSC cooling scans of PP/HDPE/N100 composites

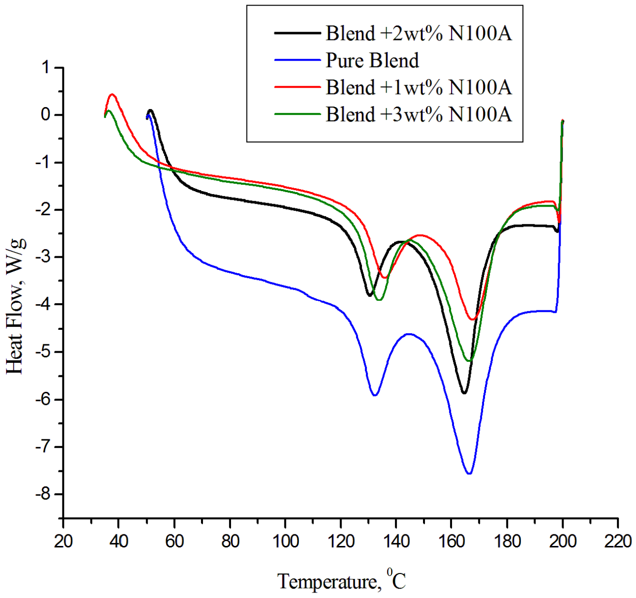


Figure5.22 DSC heating scans of PP/HDPE/N100A composites

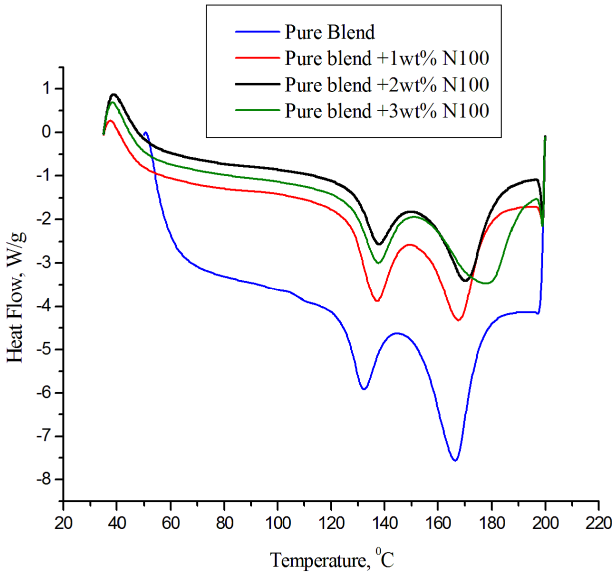


Figure5.23 DSC heating scans of PP/HDPE/N100 composites

The non isothermal crystallization characteristics of PP/HDPE/ nanoclay composites are summarized in Table 5.8. It is reported that a small amount of well dispersed organoclays can act as the effective nucleating agents to accelerate the crystallization of PP matrix and thus promote the mechanical performance through surface nucleate PP crystalline phase [80]. On the other hand there is no much alteration in the melting characteristics of PP/HDPE blend on the addition of nanoclay.

Table 5.8 Effect of nanoclay content on crystallization and melting characteristics of PP/HDPE/ nanoclay composites.

Sample	Tc, °C	Tm1, °C	Tm2, °C	ΔHc (J/g)	ΔHm1 (J/g)	ΔHm2 (J/g)
Pure blend	117.5	131.2	163.5	81.69	17.84	32.56
PP/HDPE/1wt% N100A	117.8	128.4	162.7	88.07	23.04	30.67
PP/HDPE/2wt% N100A	122.61	131.5	162	105.1	21.42	38.24
PP/HDPE/3wt% N100A	116.9	126.3	160.8	92.5	19.51	32.89
PP/HDPE/1wt% N100	115.3	127.4	163.2	86.8	26.75	38.24
PP/HDPE/2 wt% N100	120.22	129.2	160.2	100.61	18.12	30.35
PP/HDPE/3wt% N100	114.8	125.3	167.8	90.22	20.69	31.33

Dynamic rheological analysis (DRA)

The rheology of the polymer nanocomposites has attracted the attention of both academics and industries. The composite rheological behaviour is sensitive to the structure, shape, particle size and surface modification of the dispersed phase. Understanding the rheology is important to optimize the melt-processing behaviour in processes such as extrusion and injection moulding. In addition, it may be used to directly assess the dispersion of nanocomposites in the melt state. The rheological behaviour of PP/layered silicate nanocomposites without polar interaction was studied [81-83]. The compatibilized hybrids showed a large increase in zero shear viscosity, and apparent yield behaviour at low frequency region. The solid-like rheological response originated from large frictional interaction of clay platelets, which are randomly oriented and form a percolated network structure incapable of relaxing completely causes an enhancement in storage modulus and complex viscosity[81]. In order to understand the processability of these materials (i.e., the final stage of any polymeric material), one must understand the detailed rheological behaviour of these materials in the molten state. Understanding the rheological properties of PNC melts is not only important in gaining a fundamental knowledge of the processability but is also helpful in understanding the structure–property relationships in these materials.

Figure 5.24 illustrates the variations of storage modulus with frequency for the nanocomposites containing various levels of aminosilane modified nanokaolinite clay (N100A). As it can be seen, in the frequency range used (0.1 to 100 rad/s) all composites containing nanoclay show a higher modulus than pure blend, a higher modulus is obtainied for higher clay containing composites. But after reaching 2 wt% nanoclay, no further enhancement in modulus is obtained. This suggests that 2 wt% N100A is the ideal precursor to modify PP/HDPE blend by melt compounding. Similar results were obtained for Aalaie *et al.*[84]. They investigated the rheological property of PP/HDPE blend in the presence of organoclay. They observed that for all compositions, the shear viscosity continuously decreased with increasing shear rate at 190°C; that is shear-thinning behaviour occurred, following the power law. Also addition of organoclay increased shear stress and shear viscosity. They repeated the study at 210°C. A similar behaviour was also observed at 210°C. The viscosity decreased with increasing temperature and hence they concluded that the processability is improved.

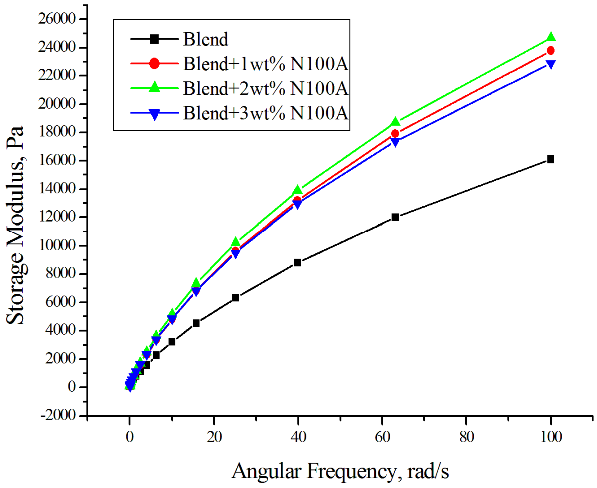


Figure 5.24 Storage modulus vs angular frequency of nanocomposite containing different nanoclay content.

In fig. 5.25 variations of complex viscosity with frequency on a log scale for nanocomposites having different nanoclay content are compared with pure blend. Complex viscosity increases as nanoclay is added indicating reinforcement effect and the composites containing 1, 2 and 3 wt% nanoclay has more or less same viscosity. This indicated that the processibility is not altered by varying the clay content. It is indicated that viscosity continuously decreased with increasing shear rate; i.e., the shear-thinning effect occur for all the systems, following the power law. This behaviour is typical of polymer melts, coming from the disentanglement process and the increase in the average end-to-end distance of polymeric chains caused by shearing. The shear viscosity and shear stress increase with the addition of organoclay, which is attributed to the strong interaction between polymeric matrix and silicate layers.[85,86]

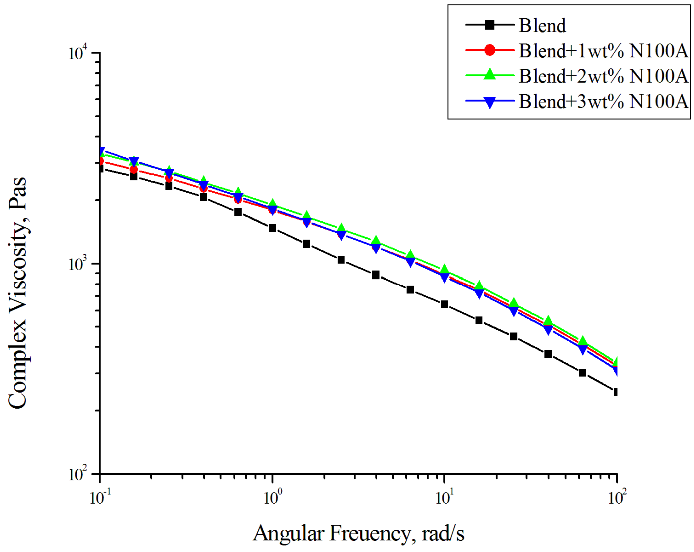


Figure 5.25 **Complex viscosity vs angular frequency of nanocomposite with various nanoclay content**

X-ray diffraction (XRD)

It is reported in the literatures that an increase in the inter gallery spacing, which is related to the intercalation of the polymer through the clay galleries, results in a new diffraction pattern corresponding to the increased spacing of clay galleries [30, 87]. According to these authors, the degree of intercalation in the composite can be determined by changes in the sharpness and intensity of the corresponding reflection peaks. The X-ray diffraction patterns of amino clay (N100A), and PP/HDPE/N100A composites at various filler loadings are documented in fig.5.26. The composite with 2 wt% N100A shows maximum reduction in 2θ (2θ value shifted to 10.881° which corresponds to a d spacing of 8.12 nm) which gives the evidence of intercalated/exfoliated composites. PP/HDPE/N100A composites with 1 and 3 wt% nano clay report 2θ values of 11.89° and 11.9° which correspond to spacing of 7.43nm and 7.4 nm against the d-spacing of 7.2 for amino clay.

These composites also possess some degree of intercalation as the distance between clay sheets has increased.

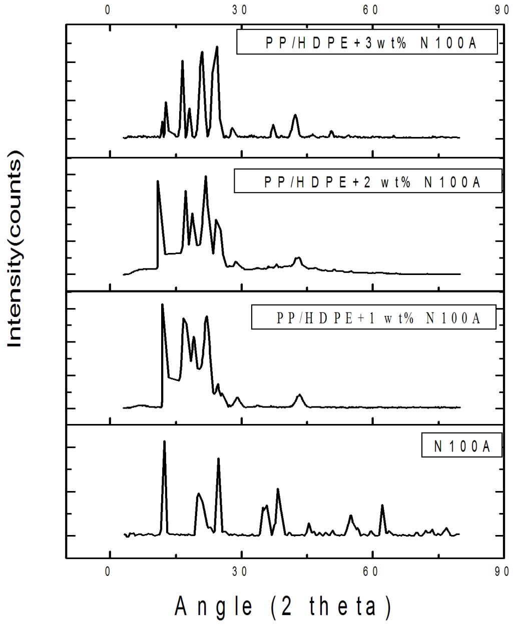


Figure.5.26 XRD pattern of N100A and its composites

Scanning electron microscopy (SEM)

The SEM images of the fracture surface of the polymer nanocomposites are shown in figures 5.27 to 5.29. Comparing the SEM images of composites with different nanoclay content, it is clear that a higher extent of exfoliation has taken place in composites containing 2 wt% nanoclay, that is fig 5.28. Both in fig. 5.27 and in fig.5.29, that is, composites containing 1 wt% and 3 wt% nanoclay, some amount of agglomeration and lack of proper dispersion can be seen. This explains the increase in mechanical behaviour of nanocomposites at a nanoclay loading of 2 wt%. In general the SEM observations are in agreement with XRD pattern and confirm that nanoclay is exfoliated in the polymer matrix.

S G Lei *et al.* [33] pointed out that it is very difficult to estimate the size of clay aggregates using SEM, because the aggregates are non-isometric and randomly dispersed in the matrix. The size of observed aggregates is therefore, strongly dependent on the orientation of the particles. However the interfacial adhesion and dispersion of clay layers with the polymer matrix will lead to the reduced size clay aggregates and smooth polymer surface. SEM micrographs illustrate that as the clay concentration in the nanocomposites increases, larger agglomerates of particles are observed and the average distance between the agglomerates decreases. Also, some large deformed portions are seen, giving the fracture surface a coarse appearance. This might be due to pull-out of large aggregates of clay particles. Agglomerates give rise to lower clay-polymer surface interactions and higher stress concentrations. On the other hand, smaller agglomerate size and exfoliation of the clay result in highly improved mechanical properties[88]. These morphological observations are consistent with tensile results in Chapter 4.

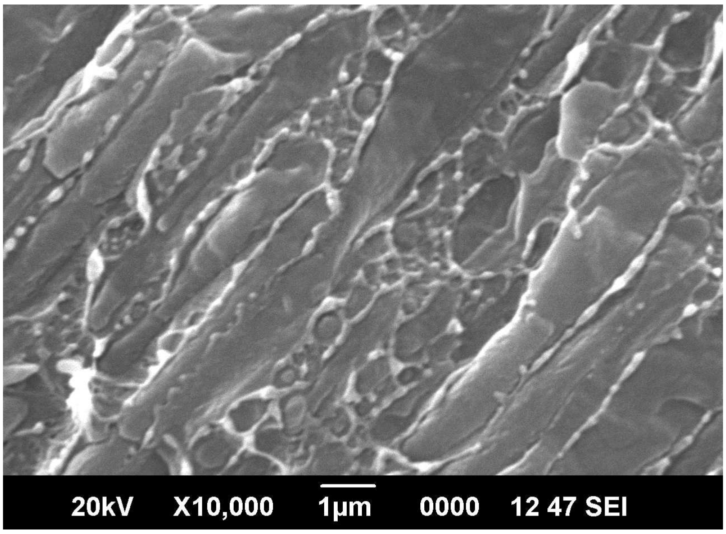


Figure 5.27 SEM micrograph of nanocomposite containing 1wt% nanoclay (80PP/20HDPE/N100A)

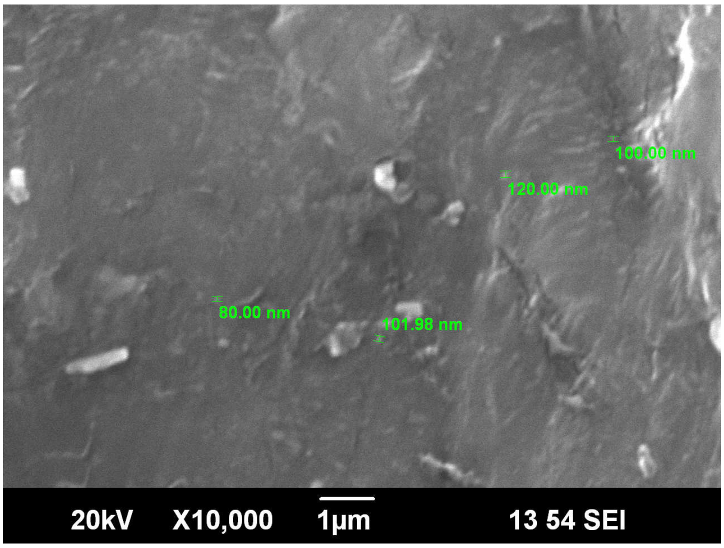


Figure 5.28 SEM micrograph of nanocomposite containing 2wt% nanoclay (80PP/20HDPE/N100A)

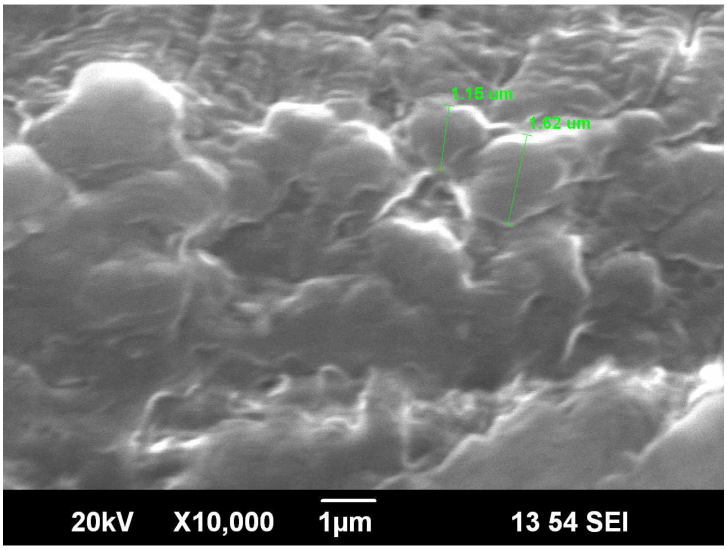


Figure 5.29 SEM micrograph of nanocomposite containing 3wt% nanoclay (80PP/20HDPE/N100A)

5.3.3 Effect of melt mixing temperature

In melt intercalation method for production of nanocomposites, the most important parameters which lead to gain exfoliated or intercalated morphology are surface modification of nanofiller by surfactants and proper processing conditions. Various researchers studied the effect of processing conditions and [88-92] reported that intercalation/exfoliation of clay layers is not possible without proper processing conditions. Gatos and coworkers[93] found that increasing temperature and high shear mixing improve the mechanical performance of polymer nanocomposites. The results of Chapter 4 also point out that melt compounding temperature is the most important factor in determining the properties of nanocomposites. In this section the effect of mixing temperature in the thermal and dynamic mechanical properties of nanocomposites are analyzed. The nanocomposites containing 2wt% modified and unmodified nanoclay are prepared at different melt compounding temperatures of 150°C, 160°C, 170°C, with similar mixing shear of 50 rpm and 8 minutes processing time.

Thermal stability

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated. Thermal stability of the materials can be improved by inorganic nanofillers. Morphology also affects the thermal stability of the composites. The inorganic fillers industrially used to improve the mechanical properties of polymer materials have different effects on the thermal stability of PP/HDPE blend. The decomposition temperature of the blend can be increased by adding nanosilica, [94]$CaCO_3$, [95]nanoclay,[96, 97] carbon nanotubes [98]etc.

In fig. 5.30 and 5.31 the TGA thermograms of PNC processed at different processing temperatures were depicted. It is clear from the figures that the PNC processed at 160°C melt compounding temperature provide better thermal characters than PNC processed at other temperatures. The result is identical for both modified and unmodified clay composites. As temperature increases, viscosity decreases, and thus the stress necessary to break the clay aggregates decreases. At the same time, diffusion is improved, which can help to intercalate and exfoliate the platelets. This may be increase of thermal properties at 160°C processing temperature. In addition, a temperature too high could cause a degradation of the organoclay intercalants, leading to a collapse of the interlayer galleries and decreased intercalation [99]. This may be and the degradation of polymer matrix itself may be reason for the decrease of thermal properties at 170°C processing temperature.

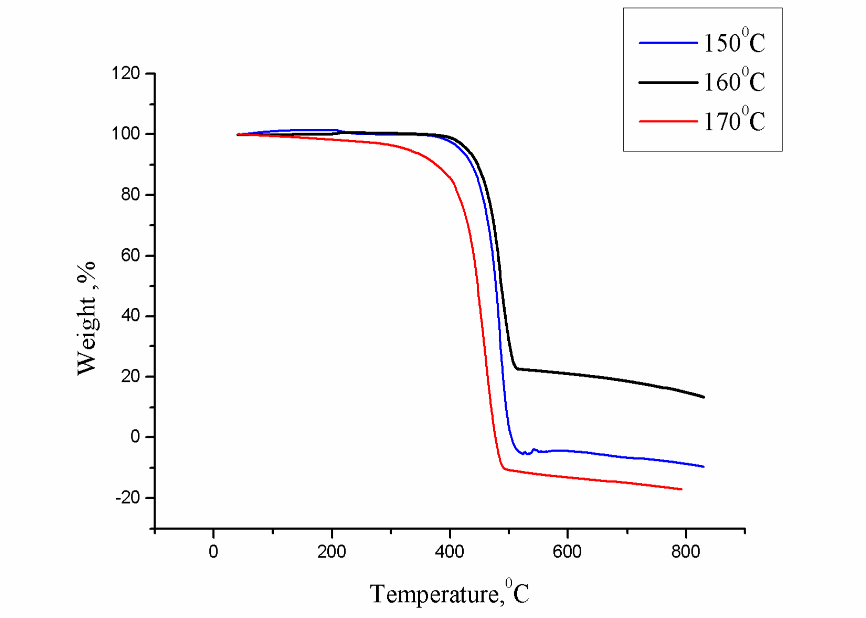


Figure. 5.30 TGA thermogram of PP/HDPE/N100A composites

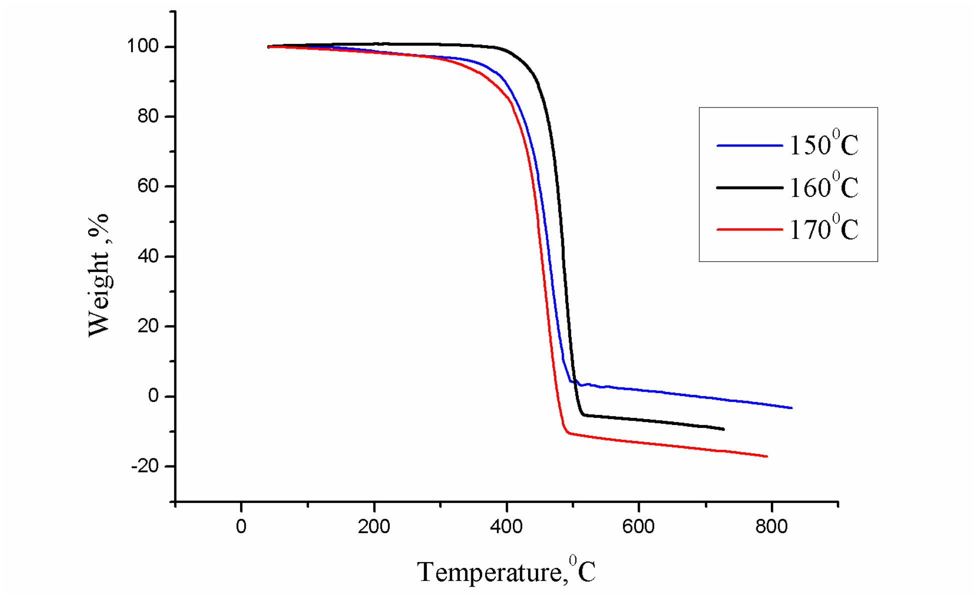


Figure. 5.31 TGA thermogram of PP/HDPE/N100 composites

The results of degradation characteristics of N100 and N100A composites are summarized in tables 5.9 and 5.10. There is an increase of about 40°C for the onset of degradation from 407°C to 440°C when the processing temperature changes from 150°C to 160°C and when the temperature is increased further the thermal stability decreases drastically to about 338°C for modified clay nanocomposites. For PP/HDPE/N100 composites also there is a drastic decrease in the degradation temperature when the processing temperature deviates from the optimum value. The results imply that processing temperature has significant effect on the thermal properties of the nanocomposites produced by melt intercalation technique.

Table 5.9 TGA results of PP/HDPE/N100A composites prepared at various melt mixing temperatures

Samples	$T_{(onset)}$ °C	10% Weight loss(°C)	50% Weight loss (°C)	80% Weight loss (°C)
Composite prepared at 150°C	407	436.66	477.48	490.18
Composite prepared at 160°C	440	446.61	486.66	780
Composite prepared at 170°C	338	376.69	446.82	463.75

Table 5.10 TGA results of PP/HDPE/N100 composites prepared at various melt mixing temperatures

Samples	T_{onset} (°C)	10% Weight loss(°C)	50% Weight loss (°C)	80% Weight loss (°C)
Composite prepared at 150°C	327	396.85	457.43	477.10
Composite prepared at 160°C	433	444.85	482	654
Composite prepared at 170°C	376	376.88	446.81	463.74

Dynamic mechanical analysis (DMA)

The influence of processing temperature on the dynamic mechanical properties of PP/HDPE/ nanoclay composites are investigated as a function of temperature at a constant frequency of 1Hz and the plots so obtained are shown in fig. 5.32 and fig. 5.33. The storage modulii of PP/HDPE/N100A composites prepared at various temperatures indicate the same trend as thermo gravimetric analysis. As the temperature increase initially, the viscosity of the melt decreases leading to better dispersion of clay particles. But Modesti *et al.* [38] reports that a low barrel temperature profile favors dynamic mechanical properties. Also high temperature of 170°C along with applied shear stress causes degradation of polymer matrix which causes a decrease in storage modulus. The properties are summarized in table 5.11

Table 5.11 Storage modulus of PP/HDPE/nanokaolinite composites prepared at various processing temperatures

Sample	E' at 40°C (MPa)	E' at 60°C (MPa)	E' at 80°C (MPa)	E' at 100°C (MPa)
PP/HDPE/N100A at 150°C	900.6	719.4	456.6	297.3
PP/HDPE/N100A at 160°C	1007	770.4	488.5	319.5
PP/HDPE/N100A at 170°C	866.8	696.4	441.1	283.2
PP/HDPE/N100 at 150°C	904.9	701.5	447.5	290.5
PP/HDPE/N100 at 160°C	930	735.8	468.9	302.1
PP/HDPE/N100 at 170°C	944	715	455.8	295

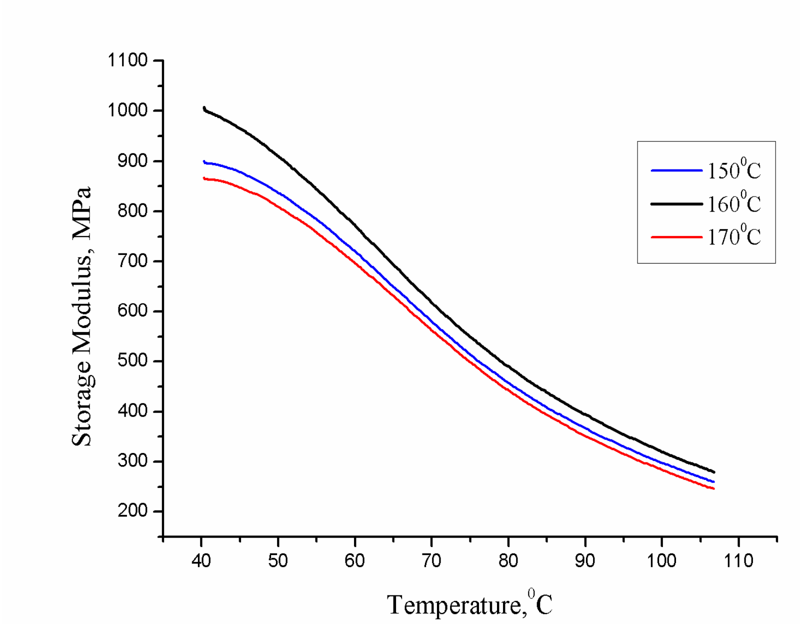


Figure. 5.32 Storage modulus curves of PP/HDPE/N100A composites

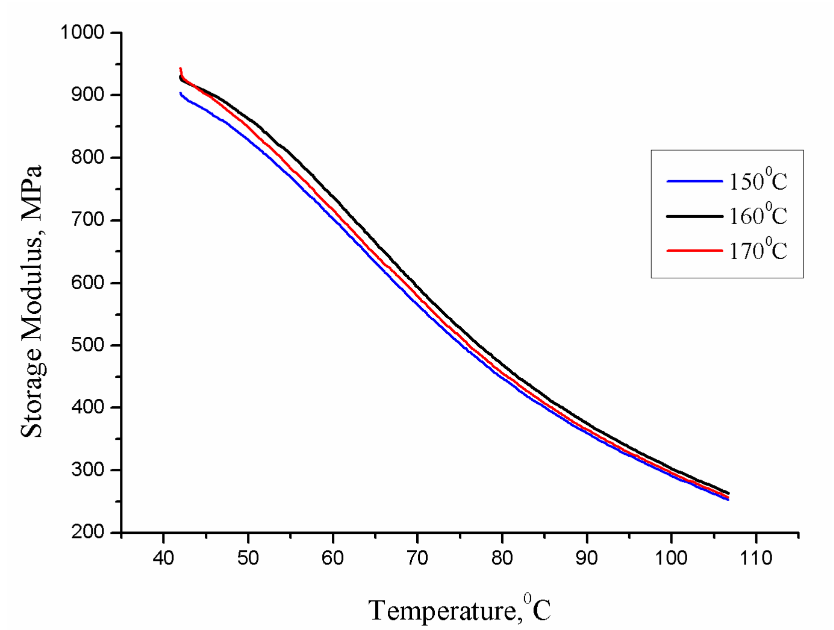


Figure. 5.33 Storage modulus curves of PP/HDPE/N100 composites

The above observations are supported by the improvements recorded in tensile and flexural properties. The storage modulus increases from 900.6 MPa to 1007MPa when processing temperature is increased from 150°C to 160°C and finally decreases to 866.8 Mpa when temperature is further increased. The damping coefficients of PP/HDPE/nanoclay composites processed at various melt compounding temperatures are demonstrated in fig.5.34 and 5.35.

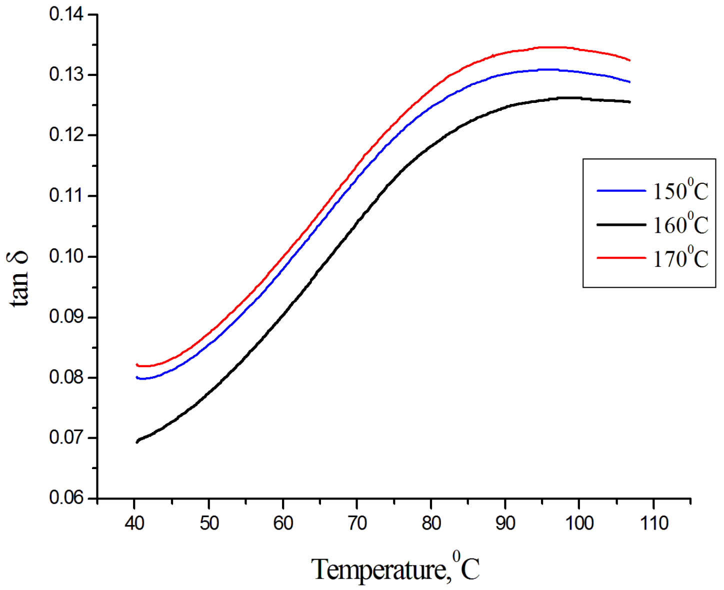


Figure 5.34 Damping ratio (tan δ) curve of PP/HDPE/N100A composites processed at various melt mixing temperatures.

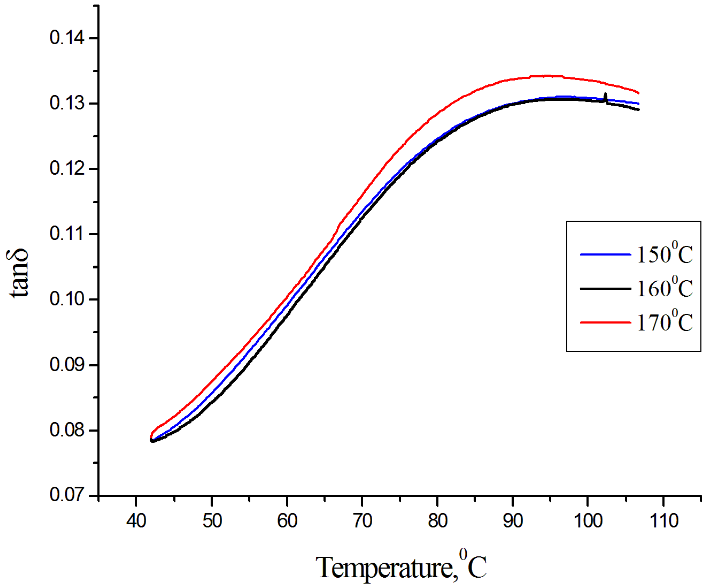


Figure 5.35 Damping ratio (tan δ) curve of PP/HDPE/N100A composites processed at various melt mixing temperatures.

Above figures shows the variation of tanδ [ratio of loss to storage modulus ($E^{''}/E'$) plotted as a function of temperature. The tan δ curves represent the ratio of dissipated energy to stored energy and relates to the glass transition temperature (Tg) of the polymer. Damping ratio (tan δ) is useful in determining the occurrence of molecular mobility transitions such as Tg. It also predicts about the performance of material under varying load conditions and behaviour of the melt during processing under pressure such as injection moulding. The tan δ curve of the composite processed at 160°C melt compounding temperature shows a lower value indicating more reinforcement.

5.4 Conclusions

- The effect of melt processing temperature, nanoclay content and surface modification of nanokaolinite clay on thermal, dynamic mechanical, crystallization and morphological properties of PP/HDPE nanokaolinite clay composites are studied.
- The inclusion of nanofiller significantly improves the thermal, crysatllization and dynamic mechanical properties of the composites.
- The surface modified nanoclay enhances the properties much better than unmodified nanokaolinite clay. Surface modification can act as a molecular bridge between the non polar polymer and polar clay layers. It enhances filler matrix adhesion and effective dispersion of clay galleries. Addition of N100A clay improves degradation temperature by 50°C, storage modulus by 30 MPa, crystallisation temperature by 10°C than pure blend.

- As the clay content varies from 1 to 2 wt% thermal, mechanical and crystallization properties increase and then decreases at 3wt%. The decrease may be due to agglomeration of clay particles reducing the effect of filler from nano level to micro dimensions. The optimum properties are obtained at 2 wt% nanoclay content.
- The effect of processing temperature on the properties of nano composites is illustrated in section C. The processing temperature has significant effect on thermal stability and dynamic mechanical properties. The optimum properties are obtained at 160°C melt processing temperature.
- Dynamic rheological studies show that both storage modulus and complex viscosity increases for composite containing nanoclay than that of pure blend. The maximum enhancement in properties is obtained for composites containing 2wt% amino modified nanoclay.
- XRD results illustrate a higher degree of intercalation with improved d-spacing (of 8.12 nm than 7.2nm of N100A) with composites containing 2 wt% amino modified nanokaolin clay composites.
- Morphological characterization using SEM also substantiates the enhancement in thermal and mechanical properties of 2 wt% N100A composites.
- Modified nanoclay (N100A) can be used to reinforce the PP/HDPE blends and can reduce the cost of polymer products

References

[1] A. Pegoretti, A. Dorigato, A. Penati (2007) "Tensile mechanical response of polyethylene clay nanocomposites". eXPRESS Polymer Letters Vol. 1., No.3:123-131.

[2] Truss R.W., Yeow T.K. (2006) "Effect of exfoliation and dispersion on the yield behaviour of melt compounded polyethylene-montmorillonite nanocomposites". Journal of Applied Polymer Science, 100: 3044-3049.

[3] Xie Y.C., Yu D.M., Kong J., Fan X.D., Qiao W.Q (2006) "Study on morphology, crystallisation behaviours of highly filled maleated polyethylene –layered silicate nanocomposites". Journal of Applied Polymer Science, 100:4004-4011.

[4] Zhong Y., De Kee D (2005) "Morphology and properties of layered silicate-polyethylene nanocomposite blown films". Polymer engineering and Science, 45:469-477.

[5] Shah R.K., Paul D.R (2006) "Organoclay degradation in melt processed polyethylene nanocomposites". Polymer 47:4075-4084.

[6] Pegoretti A., Dorigato A., Penati A (2006) "Production and characterisation of polyurethane-clay nanocomposites in 2nd International Symposium on Nanostructured and Functional Polymer –based Materials and Nanocomposites". Lyon, France.

[7] Liu Xuening, Hunan (2005) "Effect of modified kaolin on the crystallization property of PP/Kaolin nanocomposites". Science in China Ser.B chemistry, Vol 48, No.2:326-333.

[8] B.Swoboda, E. Leroy., *et al.*, (2009) "Organomodified Ultrafine kaolin for mechanical reinforcement and improved flame retardancy of Recycled Polyethylene Teraphthalate". Royal Society of Chemistry: 59-73.

[9] Kawasumi M, Hasegawa N, Kato M, Usuki A, Okada A (1997) "Preparation and mechanical properties of polypropylene-clay hybrids". Macromolecules, 30:6333.

[10] Hasegawa N, Kawasumi M, Kato M, Usuki A, Okada A (1998) “Preparation and mechanical properties of polypropylene-clay hybrids using a maleic anhydride-modified polypropylene oligomer”. J Appl Polym Sci 67:87.

[11] Hasegawa N, Okamoto H, Kato M, Usuki A (2000) “Preparation and mechanical properties of polypropylene-clay hybrids based on modified polypropylene and organophilic clay”. J Appl Polym Sci 78:1918.

[12] Doh JG, Cho I (1998) “Synthesis and properties of polystyrene –organo-ammonium montmorollonite hybrid”. Polym Bull 41:511.

[13] Ma JS, Qi ZN, Hu YL, (2001) “Synthesis and characterisation of polypropylene/ clay nanocomposites”. J Appl Polym Sci 82:3611

[14] Manias E, Touny A, Wu L, Stawkecher K, Lu B, Chung TC (2001) “Polypropylene/montmorillonite nanocomposites. Review of the synthetic routes and material properties”. Chem Mater 13:3516.

[15] Kato M, Usuki A, Okada A (1997) “Synthesis of polypropylene oligomer-clay intercalation compounds”. J Appl Polym Sci 66:1781.

[16] Oya A, Kurokawa Y, Yasuda H (2000) “factors controlling mechanical properties of clay mineral/polypropylene nanocomposites”. J Mater Sci 35:1045.

[17] Peter R, Hansjorg N, Stefan K, Rainer B, Ralf T, Rolf M (2000) “Polypropylene/organoclay nanocomposite formation : influence of compatibiliser functionality and organoclay modification”. Macromol Mater Eng 275:8.

[18] Ton-That M-T, Perrin F, Lacand P, Cole KC, Denault J, Enright G (2001) “Preparation and performance of nanocomposites based on polypropylene and layered nanoclays”. Polymer Nanocomposites Montreal, Canada, November 14-16.

[19] Usuki A, Kato M, Okada A, Kurauchi T (2007) “Synthesis of polypropylene clay hybrid”. J Appl Polym Sci 63:137.

[20] Bahadur P, Sastry NV, (2002) “Principles of polymer science”. Pangbourne: Alpha Science International Ltd.

[21] Shahin Aklaghi, Alireza Sharif, Mohammadreza Kalaee, Alireza Elahi, Mohammadhadi Pirzadeh, Saeedeh Mazinani, Mehdi Ashfari (2012) “Effect of stabilizer on the mechanical, morphological and thermal properties of compatibilized high density polyethylene/ethylene vinyl acetate copolymer/ organoclay nanocomposites”. Materials and Design 33:273-283.

[22] G.S. Venkatesh, A.Deb, Ajay Karmarkar, Shakthi S Chauhan (2012) “Effect of nanoclay content and compatibilizer on viscoelastic properties of montmorillonite/polypropylene nanocomposites”. Materials and Design 37;285-291.

[23] Mosleh Shirazi S, Janghorban K (2012) “Investigation of physical and chemical properties of poly-propylene hybrid nanocomposites”. Mater Des 34:474–478.

[24] Dayama N, Bhabani KS (2012) “Microstructural correlation to micromechanical properties of polyamide- 6/low density polyethylene-grafted-maleic anhydride/nanoclay ternary nanocomposites”. Mater Des 33:510–522.

[25] LV Z, Yang Y, Wu R, Tong Y (2012) “Design and properties of a novel nucleating agent for isotactic polypropylene”. Mater Des 37:73–78.

[26] Zare Y, Garmabi H, Sharif F (2011) “Optimization of mechanical properties of PP/nanoclay/CaCO3 ternary nanocomposite using response surface methodology”. J Appl Polym Sci 122:3188–3200.

[27] Gunning MA, Istrate OM, Geever LM, Lyons JG, Blackie P, Chen B, Higginbotham CL (2012) “The effect of maleic anhydride grafting efficiency on the flexural properties of polyethylene composites”. J Appl Polym Sci 124:4799–4808.

[28] Vijayalakshmi NS, Murthy RAN (1992) “Modification of polyethylene by unsaturated compounds”. J Appl Polym Sci 44:1377–1382.

[29] Dennis HR, Hunter DL, Chang D, Kim S, White JL, Cho JW, Paul DR (2001) “Effect of melt processing condition on the extend of exfoliation in organo-clay based nanocomposites”. Polymer 42:9513–9522.

[30] Vaia RA, Giannelis EP (1997) “Lattice of polymer melt intercalation in organically modified layered silicates”. Macromolecules 30:7990–7999.

[31] Kallel T, Massardier-Nageotte V, Jaziri M, Gerard J-F, Elleuch B (2003) “Compatibilization of PE/PS and PE/PP blends. Effect of processing conditions and formulation”. J Appl Polym Sci 90:2475–2484.

[32] Banalia K, Aicha S (2012) “Properties of polypropylene/polyamide nanocomposites prepared by melt processing with a PP-g-MAH compatibilizer”. Mater Des 34:313–318.

[33] S.G. Lei, S.V. Hoa, M-T Ton-That (2006) “Effect of clay types on the processing and properties of polypropylene nanocomposites". Composites Science and technology 66: 1274-1279.

[34] Sanjay K Nayak, Smita Mohanty, and Sushanta K Samal (2009) “Effect of clay types on the mechanical, dynamic mechanical and morphological properties of polypropylene nanocomposites”. Polymer-Plastics Technology and Engineering 48:976-988.

[35] Asha KK, George TS, Anjana R, Joseph N, George KE Effect of modified kaolin clays on the mechanical properties of polypropylene/polystyrene blends. J Appl Polym Sci doi:10.1002/app. 38043.

[36] Liu SL, Lu XH, Liew FY, Lim SH, Yong MS. “Melt processing and properties of intercalated polypropylene/ organoclay nanocomposites”. STR/04/004/FT.

[37] M.A.Mohd Salleh, J.Abd.Razak, N.A.Ibrahim, A.Fakhru’l Razi, A.R.Suraya (2008), “The influence of melt compounding parameters on the tensile properties of low fillerloading of untreated-MCNTs-polyproplene(pp) nanocomposites”. Journal of Engineering Science and Technology Vol. 3 No.1 97-108.

[38] M. Modesti, A.Lorenzetti, D. Bon, S. Besco (2006) “Thermal behavior of compatibilised polypropylene nanocomposites:Effect of processing conditions”. Polymer Degradation and Stability 91:672-680.

[39] Ray SS, Okamato M (2003) “Polymer/layered silicate nanocomposites: a review from preparation to processing”. Prog Polym Sci 28:1539–1544.

[40] ASTM D 1238-10. “Standard test method for melt flow rates of thermoplastics by extrusion plastometer”, volume 08.01. ICS number code 83.080.20 (thermoplastic material).

[41] Abbas-Abadi MS, Haghighi MN, Yeganeh H (2012)” Effect of the melt flow index and melt flow rate on the thermal degradation kinetics of commercial polyolefins”. J Appl Polym Sci 126:1739–1745.

[42] Qiu Z-C, Zhang J–J, Huang C-L, Niu Y, Yang K–K, Wang Y-Z (2012) “The influence of the surface character of the clays on the properties of poly (p-dioxanone)/ fibrous clay nanocomposites”. J Appl Polym Sci 125:E247–E259.

[43] George TS, Krishnan A, Joseph N, Anjana R, Geroge KE (2012) “Effect of maleic anhydride grafting on nanokaolin clay reinforced polystyrene/high density polyethylene blends”. Polym Compos. doi:10.1002/pc.22276.

[44] Nayak SK, Mohanty S, Sushanta KS (2009) “Effect of clay types on the mechanical, dynamic mechanical and morphological properties of polypropylene nanocomposites”. Polym Plast Tech Eng 48:976–988.

[45] Zhang M, Lin B, Sundararaj U (2012) “Effects of processing sequence on clay dispersion, phase morphology and thermal and rheological behaviours of PA6-HDPE-clay nanocomposites”. J Appl Polym Sci 125:E714–E724.

[46] Abbas-Abadi MS, Haghighi MN, Yeganeh H (2012) “Effect of the melt flow index and melt flow rate on the thermal degradation kinetics of commercial polyolefins”. J Appl Polym Sci 126:1739–1745.

[47] Nigam V, Soni H, Saroop M, Verma GL, Bhattacharya AS, Setua DK (2012) “Thermal, morphological and X-Ray study of polymer-clay nanocomposites”. J Appl Polym Sci 124:3236–3244.

[48] Komalan C, George KE, Kumar PAS, Varughese KT, Thomas S (2007) “Dynamic mechanical analysis of binary and ternary polymer blends based on nyln copolymer/EPDM rubber and EPM grafted maleic anhydride compatibilizer”. Express Polym Lett 10:641–653.

[49] Xiaodong Wang, Riguang Jin and Hanguan Li (1995) “Mechanical, Thermal, Morphological and Rheological Properties of Polypropylene/ Ultrahigh Molecular Weight Polyethylene Blends”. J. Mater Sci. Technol, Vol 11: 46-52.

[50] C. L. Rohn (1995) ‘‘Analytical Polymer Rheology: Structure- Processing-Property Relationships,’’ Hanser Gardner Pub- lisher Inc., Cincinnati.

[51] M. L. Robeson (2007) ‘‘Polymer Blends: Comprehensive Re- view,’’ Hanser Gardner Publisher Inc., Cincinnati.

[52] S. Mayu, A. Tohru, A. Harald, A. L. D. Kilcoyne, R. Fisher, J. C. Sokolov and M. H. Rafailovich (2006) ‘‘Compati- bilizing Bulk Polymer by Using Organoclays,’’ Macro- molecules, Vol. 39, No. 14, pp. 4793-4801. doi:10.1021/ma060125+

[53] L. A. Utracki (2000) ‘‘Polymer Blends,’’ RAPRA Review Reports, Vol. 11, No. 3, 2000, pp. 1-170.

[54] S. Velankar, P. V. Puyvelde, J. Mewis and P. Moldenaers (2004) ‘‘Steady-Shear Rheological Properties of Model Com- patibilized Blends,’’ Journal of Rheology, Vol. 48, No. 725, pp. 725-744. doi:10.1122/1.1765662.

[55] Q. Zheng, M. Zuo, M. Peng, L. Shen and Y. Fan (2007) ‘‘Rheological Study of Microstructures and Properties for Polymeric Materials,’’ Frontiers of Material Science in China, Vol. 1, No. 1, pp. 1-6. doi:10.1007/s11706-007-0001-5.

[56] L. A. Utracki (2002) ‘‘Polymer Blends Handbook,’’ Kluwer Academic Publishers, Dordrecht, 2002.

[57] M. Alavi, M. Esfandeh, J. Morshedian, Y. Jahani (2010) “Study of the rheological properties of polypropylene/talc/nanoclay ternary hybrid nano composites”. e-Polymers no. 028.

[58] Anjana R, George KE, George TS, Krishnan A (2012) “Optimisation of processing conditions of PP/ HDPE/nanokaolinite clay composites by response surface methodology”. Int J Plast Technol 16(2):136–149.

[59] Akhlaghi S, Sharif A, Kalaee M, Elahi A, Pirzadeh M, Mazinani S, Afshari M (2012) “Effect of stabilizer on the mechanical, morphological and thermal properties of compatibilized high density polyethylene/ethylene vinyl acetate copolymer/organoclay nanocomposites”. Mater Des 33:273–283.

[60] Gholamian F, Ghariban-Lavasani S, Garshasbi MM, Ansari M, Bataghv F, Moraveji A, Ranjbar Z The effects of water absorption and surface treatment on mechanical properties of epoxy nanocomposite using response surface methodology. Polym Bull. doi: 10.1007/s00289-013-0938-8.

[61] K. Hariprasad, M. Senthilkumar (2010) “Dynamic Mechanical Properties of PP/MMT/OMMT Nanocomposites”.

[62] S.Y Lee. I.A Kang, G.H Doh, W.J Kim, J.S Kim, H.G Yoon, Q.Wu (2008) “Thermal, mechanical and morphological properties if polypropylene/ clay/wood flour nanocomposites”. eXPRESS Polymer Letters Vol.2,No.2, 78-87.

[63] Ajayan P.M., Schadler L.S., Braun P.V (2006) “Nanocomposite Science and Technology”. Wiley-VCH, Weinheim.

[64] Ktawczak P (2007) “Compounding and processing of polymer nanocomposites: from scientific challenges to industrial stakes”. Express Polymer Letters, 1,188.

[65] Chavarria F, Naim K, White P, Hill A.J, Hunder, D.L, Paul, D.R (2003) ”Morphology and properties of nanocomposites from organoclays with reduced cation exchange capacity”. J. Appl. Polym. Sci. 105(5),2910-2924.

[66] Hui S, Chathopadhyay S, Chaki TK (2010) “Thermal and thermo-oxidative degradation study of a model LDPE/EVA based TPE system: effect of nano silica and electron beam irradiation”. Polym Compos 31(8):1387–1397.

[67] Oya A, Kurokawa Y, Yasuda H (2000) "Factors controlling mechanical properties of clay mineral/ polypropylene nanocomposites". J Mater Sci 35:1045.

[68] Jan Golebiewski, Andrzej Galeski (2007) "Thermal stability of nanoclay polypropylene nanocomposites by simultaneous DSC and TGA". Composite Science and technology 67:3442-3447.

[69] Yasser Zare, Hamid Garmabi, Farhad Sharif (2011) "Optimization of Mechanical Properties of PP/Nanoclay/$CaCO_3$ Ternary Nanocomposite Using Response surface Methodology". J Appl Polym Sci 122:3188-3200.

[70] Girish Galgali, Sachin Agarwal, Ashish Lele (2004) "Effect of clay orientation on the tensile modulus of polypropylene nanoclay composites". Polymer 45:6059-6069.

[71] Walid H Awad, Gunter Beyer, Daphne Benderly, Wouter L Ijdo, Ponusa Songtipya, Maria del Mar Jimenez-Gasco, E Manias, Charles A Wilkie (2009) "Material properties of nanoclay PVC composites". Polymer 50:1857-1867.

[72] Fabio Bertini, Maurizio Zanetti, Guido Audisio, Giovanna Costa, Luciano Falqui (2006) "Characterization and thermal degradation of polypropylene-montmorillonite nanocomposites". Polymer degradation and stability 91:600-605.

[73] Isil Isik-Gulsac, Ulku Yilmazer, Goknur Bayram (2012) "Mechanical and rheological properties, and Morpholgy of polyamide-6/organoclay/ elastomer nanocomposites". Journal of Applied Polymer Science, Vol.125: 4060-4073.

[74] M Kannan (2010) "Preparation and characterization of nanoclay-filled polymer blends". 10.1002/spepro.003051.

[75] Jeffrey Jordan, Karl I Jacob, Rina Tannenbaum, Mohammed A Sharag, Iwona Jasiuk (2005) "Experimental trends in polymer nanocomposites – a review". Materials Science and Engineering A 393:1-11.

[76] Hasegawa, N., Kawasumi, M., Kato, M., Usuki, A. and Okada, A. (1998). Preparation and mechanical Properties of Polypropylene–Clay Hybrids Using a Maleic anhydride-modified polypropylene Oligomer, Journal of Applied Polymer Science, 67(1): 87–92.

[77] Hasegawa, N., Okamato, H., Kato, M. and Usuki, A. (2000). Preparation and Mechanical Properties of Polypropylene–Clay Hybrids Based on Modified polypropylene and organophilic Clay, Journal of Applied Polymer Science, 78: 1918.

[78] Kato, M., Usuki, A. and Okada, A. (1997). Synthesis of Polypropylene oligomer-clay Intercalation Compounds, J. of Applied Polymer Science, 66(9): 1781–1785.

[79] D.G Dikobe, A,S Luyt (2010) "Comparative study of the morphology and properties of PP/LLDPE/wood powder and MAPP/LLDPE/wood powder polymer blend composites". eXPRESS Polymer Letters Vol.4, No.11 729-741.

[80] Lei SG. (2003) "Formulation and mechanical properties of polypropylene nanocomposites". M .Asc thesis, Concordia University, Department of Mechanical and Industrial engineering".

[81] Galgali G, Ramesh C, Lele A (2001) "A rheological study on the kinetics of hybrid formation in polypropylene nanocomposites." Macromolecules. 34: 852.

[82] Solomon M, Almusallam A.S, Seefeldt K.F, Somwangthanaroj A, Varadan P (2001) "Rheology **of** Polypropylene/Clay Hybrid Materials." Macromolecules. 34:1864.

[83] Reichert P, Hoffmann B, Bock T, Thomann R, Ulhaupt R, Friedrich C (2001) "Morphological stability of poly(propylene) nanocomposites." Macromol. Rapid Commun.22:519.

[84] Jamal Aalaie, Fatemeh Dashtaki & Mahmood Hemmati (2011) "Study on the Rheological Behavior of the Polyethylene/Polypropylene Blend Nanocomposites". Journal of Macromolecular Science, Part B, 50:6, 1087-1097.

[85] Lee K.M, Han C.D (2003) “Rheology of organoclay nanocomposites: Effects of polymer ma- trix/organoclay compatibility and the gallery distance of organoclay”. .Macromolecules 36:7165–7178.

[86] Schmidt G, Nakatani A.I, Butler P.D, Karim A, Han C (2000) “Shear orientation of viscoelastic polymer-clay solutions probed by flow birefringence and SANS”. Macromolecules 33:7219–7222.

[87] Jiankun L, Yucai K, Zongneng Q and Xiao, Su y (2001) “Study on Interaction and Exfoliation Behaviour of Organoclays in Epoxy Resin”. J Polym Sci part B:Polym Phys., 39: 115-120.

[88] Cigdem Basara, Ulku Yilmazer*and Goknur Bayram. (2005) Synthesis and characterization of epoxy based nanocomposites. Journal of Applied Polymer ScienceVolume 98, Issue 3, pages 1081–1086.

[89] Homminga D, Goderis B, Hoffman H, Reynaers H, Groeninckx G (2005), “Influence of shear flow on the preparation of polymer layered silicate nanocomposites”. Polymer 46: 9941-9957.

[90] Borse K.N, Kamal M.R (2006) “Melt processing effects on the structure and mechanical properties of PA-6/clay nanocomposites”. Polymer Engineering and Science,46:1094-1108.

[91] Zhu L, Xanthos M, (2004) “Effects of process conditions and mixing protocols on structure of extruded polypropylene nanocomposites”. Journal of Applied Polymer science,93:1891-1899.

[92] Wu Y-P, Ma Y, Wang Y-Q, Zhong L-Q (2004) “Effect of Characteristics of rubber, mixing and vulcanisation on the structure and properties of rubber/clay nanocomposites by melt blending”. Macromolecular Materials and Engineering, 28:890-894.

[93] Gatos K.G, Thomman R, Karger-Kocsis J (2004) “Characteristics of ethylene propylene diene monomer rubber/organoclay nanocomposites resulting from different processing conditions and formulations”. Polymer International,53:1191-1197.

[94] Hussain, F.; Hojjati, M.; Okamoto, M. & Gorga, R.E. (2006) "Review article: Polymer-matrix nanocomposites, processing, manufacturing, and Application". An Overview Journal of Composite Materials, Vol. 40, No. 17, 1511-1565.

[95] Jiang, L.; Lam, Y.C.; Tam, K.C.; Chua, T.H.; Sim, G.W. & Ang, L.S. (2005) "Strengthening acrylonitrile-butadiene-styrene (ABS) with nano-sized and micron-sized calcium carbonate". Polymer, Vol. 46, 243-252.

[96] Giannelis, E.P. (1998). Polymer-layered silicate nanocomposites: synthesis, properties and applications". Appl. Organomet. Chem., Vol. 12, 675–680.

[97] Hedayati, A. & Arefazar, A. (2009). Multi-scale analysis of polypropylene based organoclay containing composites, part 1: Morphology. Polymer Testing, Vol.28, 128-138.

[98] Groosiord. N.; Loos, J.; Laake, L.; Maugey, M.; Zakri, C.; Koning, C.E. & Hart, A.J (2008) "High-conductivity polymer nanocomposites obtained by tailoring the characteristics of carbon nanotube fillers".Adv. Func. Mater., Vol. 18, 3226-3234.

[99] Muzny CD., Butler BD., Hanley H. J. M., Tsvetkov F. & Peiffer DG. (1996). "Clay platelet dispersion in a polymer matrix". Materials Letters, 28, 379-384.

…….

Chapter 6

MECHANICAL PROPERTIES OF PP/HDPE/ NANOKAOLINITE CLAY/E-GLASS FIBRE HYBRID COMPOSITES

Contents

6.1 Introduction

In the last few decades, inorganic clay minerals, such as montmorillonite, have been widely used as reinforcement materials for polymers due to their nanoscale size and intercalation/exfoliation properties [1-3]. Nanoclays are less expensive than other nanomaterials, partly because they are produced in existing, full-scale production facilities and because the basic materials come from readily available natural sources[4]. Clay and layered silicate fillers have been most widely investigated for this reason, and now there is a wide body of knowledge on their use in polymer composites[5-7].

It is well known that the combination of polymer and clays, at the nanoscale, can result in remarkably improved mechanical and functional properties with respect to pure polymers or conventional composites (either micro- or macrocomposites)[8]. Such nanocomposites exhibit improved physical properties, compared to those of the unfilled polymer matrix, as lows: mechanical strength, barrier properties, thermal resistance and dimensional stability. These improvements are seen even at low filler concentration (1-5 wt %)[9-12]. The improvement in properties has motivated the academic and industrial communities to develop nanocomposites, looking particularly at the composition and the preparation method[13].

Although clay has many attractive properties, its applications are limited largely because the clay dispersion cannot be easily achieved [14]. The factors that determine intercalation/exfoliation include the type of polymer, layered silicate and organic modifier, the preparation technique and processing conditions[15-16]. It has also been reported that clay aspect ratio and orientation play an important role in determining the properties of polymer nanocomposites[17].

Surface modifications of clay minerals have received attention because it allows the creation of new materials and new applications. Organoclays are the most dominant commercial nanomaterial to prepare polymer nanocomposites, accounting for nearly 70 % of the volume used[4]. The preparation of polymer/clay nanocomposites with good dispersion of clay layers within the polymer matrix is not possible by physical mixing of polymer and clay particles[18]. Being only 1 nm thick, the smaller the reinforcing elements are, the larger is their internal surface and hence their tendency to agglomerate due to the high face to face stacking of layers. It is not easy to disperse nanolayers in most polymers due to their tendency to agglomerate rather than to disperse homogeneously in a matrix and their intrinsic hydrophilicity which make them incompatible with hydrophobic polymers[14, 18, 19]. Only a few hydrophilic polymers, such as PEO and PVA, can be miscible with clay nanolayers[15].

According to Pluta,[13] improvement of nanocomposites properties should be dependent not only on the organoclay concentration but also on the degree of its dispersion. Degree of dispersion is very important because failure can be induced by agglomerates. In general, many of the properties associated with PNC are a function of the extent of exfoliation of the individual clay sheets. This is controlled by the processing conditions as well as by matching the interaction of organomodified clay to the polymer matrix. The latter is well documented[11, 13, 20-23]. However, which processing factor imparts the better level of dispersion is still under discussion[24-29].

It is well known that mixing is a key step in almost every polymer processing operation, affecting material properties, processability and cost.[30] PLA nanocomposites formed by melt blending have been described previously.[13, 31-33] However, these studies have not reported how the conditions were chosen. Some studies have looked at different processing conditions in PLA[22, 34] and other polymer, such as polyamides [25, 29, 35-36], but they failed to show that which conditions are optimum. Very few studies optimised processing conditions for polymer nanocomposites [27, 37]. Process conditions must be optimised to achieve a high degree of exfoliation and dispersion. Developing a better understanding of the mixing process and its effect on dispersion is critical to optimising morphology.

DoE is a powerful technique for studying a process, to understand the impact of variables on the process, and thereby provide an insight into continuous quality improvement possibilities. DOE has been used to improve process yield, capability, performance and to reduce process variability[38]. DoE is widely used in research and development to solve optimisation problems [39-43]. However, application of DOE techniques by the engineering fraternity is limited, and they are often applied incorrectly [44] due to lack of skills in manufacturing and lack of statistical knowledge.

Fibreglass, (also called as glass fibre), is a material consisting of numerous extremely fine fibres of glass. Fibreglass is commonly used as an insulating material. It is also used as a reinforcing agent for many polymer products; to form a very strong and light weight fibre-reinforced plastic (FRP). Fibreglass has roughly comparable properties to other fibres such as nylon and carbon fibre. Although it is not as strong nor as rigid as carbon fibre, it is very much cheaper and significantly less brittle. Glass fibre is formed when thin strands of silica-based or other formulation glass are extruded into many fibres with small diameters suitable for textile processing. The types of fibreglass most commonly used are mainly E-glass (alumino-borosilicate glass with less than 1 wt% alkali oxides, mainly used for glass-reinforced plastics), A-glass (alkali-lime glass with little or no boron oxide), C-glass (alkali-lime glass with high boron oxide content, used for example for glass staple fibres), D-glass (borosilicate glass with high dielectric constant), R-glass (alumino silicate glass without MgO and CaO with high mechanical requirements), and S-glass (alumino silicate glass without CaO but with high MgO content with high tensile strength)

Because of their favourable properties (e.g. high specific tensile and compressive strength, controllable electrical conductivity, low coefficient of thermal expansion, good fatigue resistance and suitability for the production of complex shape materials), fibre-reinforced composites are very widely used. According to literature, they have become the alternatives of conventional structural materials such as, steel, wood or metals in many applications. Typical areas of composite applications are car industry, aircraft fabrication, wind power plant, boats, ships, etc. During human history, composites made occasionally large breakthroughs in construction and other materials. Nowadays, the situation has been the same with modern fibre-reinforced composites for which mass production of polymers provide stable background[45-46].

For industrial application, the E- and S-type glass fibres are the most commonly used because they have the most favourable cost-mechanical properties relationships[47]. Thermoset composites have been applied in the last 1940s in aircraft industry for the first time. Those materials were laminated polyester composites, and the first application was the cover of radar antennas because there was a need for such non-metallic materials that allowed radio waves through free from distortions. The manufactured parts were found to have better weight/volume ratio than the ones made from metallic materials. Since then, thermoset composites have been applied as construction materials.

Short glass fibre filled systems with loading levels ranging from 15 to 50% are employed for several engineering applications. It is reported that addition of these fillers has drawbacks such as increased moulded part weight, brittleness, opacity and processing difficulty. At higher fibre loadings the long term durability of the polymer is decreased. To overcome these drawbacks, a hybrid composite with improved properties and low filler concentration is highly desirable. In this regard, nanofillers will be a better choice. These composites combine the rigidity of the fibre with the toughness of nanoparticles. Although hybrid fibre reinforced polymer composites are gaining importance, the challenge is to produce low cost hybrids with superior properties. The selection of the components that make up the hybrid composite is determined by the purpose of hybridization, requirements imposed on the material or the construction being desired. Development of clay/glass fibre/polymer composites is one of the latest evolutionary steps in polymer technology. This have attracted great attention due to potentially large improvements in mechanical and physical properties that can be achieved by incorporating small amounts of clays (1-3wt%) into glass fibre/polymer composites. The simultaneous use of both clay and fibre fillers, so called hybridization leads in many cases to synergistic effects, improving properties such as impact strength, wear resistance, stiffness, fracture toughness and dynamic response[48-49]. Thermal, mechanical and morphological properties of PP/nanoclay/glass fibre reinforced composites have been studied by Mohd Ishak and co-workers[45]. Norkhairunnisa *et al.*.[46] also conducted similar studies on other polymers.

Box-Behnken - a DoE technique was used in this study to find the optimum processing conditions, optimum nanoclay content and glass fibre content for preparing the hybrid composites. The following section describes the procedures for this study.

6.2 Methodology

In this study four variables are selected: processing temperature, mixing time, nanoclay content and glass fibre content. These variables are chosen because they are considered to have the most significant effects on processing of nanocomposites[13, 27, 34, 50]. Three levels of temperature, time, nanoclay content and fibre content were selected as high, centre point and low (shown in Table 6.1). The melt compounding temperature was varied from 150°C to 170°C, time of mixing from 4 to 12 minutes. The nanoclay content varied in this study was 1, 2 and 3 wt% of total mixture and fibre content varied was from 10 to 30 wt% of total mixture.

Table 6.1 Variables in Box– Behnken design

Variables	Levels used, actual (coded)		
	Low(-1)	**Medium(0)**	**High(1)**
Mixing Temperature(°C)	150	160	170
Mixing Time(min)	4	8	12
Nano clay content(%)	1	2	3
Glass fibre content	10	20	30

PP/HDPE/nanokaolinite clay/glass fibre hybrid composites are prepared by melt compounding in a Torque Rheometer (Thermo Haake Rheocord) with roller type rotors. This is an eco friendly method where no solvents are required [51]. The 80/20 by wt PP/HDPE mixture containing required amount of nanoclay was initially introduced into the mixer and after mixing was carried out for about 1 to 2 minutes (when the mixing torque was stabilized) glass fibre is added and mixing is continued for the rest of the time. The mixing shear rate was kept constant at 50 rpm which is the optimum value obtained based on the studies of Chapter 4. Experimental design table was formulated using a three level-four factor Box-Behnken method of RSM. 27 combinations of variables were selected as given by design table and melt mixing is carried out in all these combinations. The nanoclay was dried in an oven at 70°C for 1 hour before mixing. After mixing the melt is hot pressed in a hydraulic press into thin sheets and cut into small pieces. Dumb bell and rectangular shaped specimens were prepared by injection moulding in a semi automatic plunger type injection moulding machine.

Tensile properties of the samples are determined using a Universal Testing Machine (Schimadzu AGX-I) at a cross head speed of 50mm/min as per ASTM-D-638[52]. The samples used for testing are dumb bell shaped specimens with an overall length of 115mm, a width in the gauge section of 8mm and thickness of 3.2±0.4mm. Flexural properties are measured by three point loading system on the same UTM, as per ASTM-D-790[53] at a cross head speed of 5 mm/min. Izod impact test on un-notched rectangular bar samples are carried out following ASTM D 256[54] test method on a pendulum type RESIL IMPACT JUNIOR (CEAST). Flexural and impact specimens are rectangular bars of dimensions 40×12×3.2 mm (width × length × thickness). A minimum of five samples are tested in each hybrid composites and the average results are recorded. The organization of this section can be summarized as follows:

- In the first section (section 6.3.1) mechanical properties of PP/HDPE/modified nanoclay/glass fibre composite is analysed using Box-Behnken method and the response equations are developed for tensile strength, tensile modulus, % elongation at break(break strain), flexural strength, flexural modulus and impact strength. The mechanical properties were optimized for the variables- nanoclay content, fibre content and temperature and time of melt mixing. Response surface and contour plots were drawn and main and interaction effects analysed.

- In the second section (section 6.3.2) model equations are developed for PP/HDPE/unmodified nanoclay/glass fibre composites and the mechanical properties are analysed with contour, response surface, main effects and interaction effects plots. Response optimization is carried out.
- In the final section (section 6.3.3) statistical analysis of developed model was carried out using regression analysis, p and ANOVA tests for both modified and unmodified PP/HDPE/nanoclay/glass fibre hybrid composites. Further statistical check was carried out by calculating and analysing statistical parameters such as : coefficient of correlation (R), average absolute relative error (AARE), average root-mean-square error (RMSE), normalized mean-biased error (NMBE) and scatter index (SI).

6.3 Results and discussion

The variables of interest- melt compounding temperature, time of mixing, nanoclay content and glass fibre content are varied in three levels based on the design table suggested by Box-Behnken method of DoE. The 27 combinations of variables, are selected and mixing was carried out in all combinations with both modified and unmodified nanoclay. The experimental results obtained are tabulated. Model equations are developed based on the regression analysis conducted on these sets of data. Response surface and contour plots are drawn to visualise how each response varied in the selected design space. Main effects and interaction effects plots are drawn to illustrate the effect of each variable on the responses.

6.3.1 Mechanical properties of PP/HDPE/modified kaolinite clay/E glass fibre hybrid composites

The variables and levels in the Box Behnken design with their coded values are given in Table 6.1. The melt compounding temperature is varied from 150°C to 170°C, and time of mixing from 4 to 12 minutes. The nanoclay content varied in this study is 1, 2 and 3 wt% of total mixture, fibre content varied is 10 to 30 wt%. The composites are prepared with 80/20 PP/HDPE blend containing varying composition of modified nanoclay (N100A) and E-glass fibre as fillers. The experimental design table illustrating the combination of variables and the respective responses are shown in Table 6.2

Tensile strength, tensile modulus, flexural strength and flexural modulus and impact strength have trends of increasing initially with the temperature, time, nanoclay and glass fibre content, reaching a maximum and then decreasing whereas break strain shows a reverse trend. The results reveal that all the variables have an effect on the properties of nanocomposite and the optimum properties are obtained at the middle levels except for impact strength. Addition of glass fibre is found to increase impact strength very well and larger values of impact strength are obtained at 30 wt% glass fibre content. Liu *et al.*.[16] has shown that inclusion of nanoclay alters the crystallinity of the matrix and leads to a decrease in impact strength. But, glass fibre on the other hand is excellent impact modifier and simultaneous addition of modified nanoclay and glass fibre synergistically modifies all the mechanical properties. Hence the resultant hybrid composite can be considered as a superior product having strength, toughness and stiffness comparable to other materials used for sophisticated engineering applications.

Table. 6.2 Box-Behnken Experimental Design table with responses.

Sl No	Temp °C	Time min	Clay wt%	Fibre wt%	TS	TM	BS	IS	FS	FM
1	150	8	2	30	39.19	1016.34	6.46	40.55	52.54	1523.22
2	150	12	2	20	43.02	1091.49	6.25	38.76	56.31	1672.33
3	160	8	1	10	42.17	1235.66	5.1	36.45	55.76	1622.56
4	160	8	2	20	47.7	1454.86	4.55	42.68	65.08	2249.44
5	160	4	2	10	38.7	1059	7.38	35.95	50.22	1012.32
6	160	8	3	10	44.56	1135.5	6.35	36.22	53.98	1453.88
7	150	8	2	10	37.39	1023.22	7.55	34.36	49.33	1256.33
8	160	4	2	30	41.5	1003.55	5.83	39.77	54.66	1845.33
9	150	4	2	20	32.6	723.5	8.3	33.24	45.66	982.32
10	160	8	1	30	44.6	1403.6	5.75	44.34	59.21	1966.34
11	160	8	2	20	47.93	1452.66	4.65	43.12	65.32	2255.55
12	160	4	1	20	41.7	1045.32	6.86	38.99	54.08	1455.45
13	150	8	1	20	39.4	1053.96	6.55	36.89	49.14	1013.22
14	160	4	3	20	41.6	1078.52	6.27	37.55	54.67	1423.55
15	160	12	2	30	42.0	1012.02	6.84	43.72	54.32	1566.78
16	160	12	2	10	42.92	1034	6.3	39.53	54.88	1656.89
17	170	8	2	30	40.8	1220.14	6.56	37.67	50.12	1245.33
18	160	12	1	20	44.16	1420.14	4.88	38.54	59.34	1745.66
19	170	8	3	20	40.92	1185.32	6.14	37.56	51.33	1244.34
20	170	8	1	20	42.96	1289.14	5.45	37.23	54.55	1455.44
21	160	8	2	20	47.35	1460.34	4.24	42.45	65.12	2256.43
22	160	12	3	20	43.01	1351.38	5.78	38.77	59.34	1845.66
23	170	4	2	20	43.2	1311.48	5.85	36.52	56.33	1920.12
24	170	12	2	20	37.49	1236.76	7.02	37.66	50.32	1123.45
25	160	8	3	30	42.06	1257.25	5.98	45.66	53.55	1322.45
26	170	8	2	10	40.79	1063	6.29	34.32	52.25	1398.44
27	150	8	3	20	39.4	1114.71	6.12	36.13	53.18	1456.34

There is an increase of 49.01% in tensile strength, 66.9% increase in flexural strength and 31.8% increase in impact strength. Also tensile and flexural modulus increase by 52.49% and 85.4% respectively, but the break strain decreases by 31%. The mechanical properties increase at 2 wt% nanoclay content as there may be good dispersion and proper interfacial adhesion at this loading rate between nanoclay, polymer matrix and glass fibre. At higher loading rate the nanoclay form agglomerates and the effect is reduced by adding microfiller. This also hinders the proper dispersion and interfacial adhesion of glass fibre with polymer matrix. Moftakharian and coworkers[55] studied the effect of nanoclay and glass fibre on polystyrene, and reported that although inclusion of nanoclay is detrimental to impact properties, melt addition of both nanoclay and glass fibre synergistically modifies both impact and flexural strength of polystyrene. Incorporation of organoclay has increased the interfacial adhesion between the fibre and the matrix. This helps in efficient transfer of stress from matrix to fibre during crack opening. So, if the fibres have a high modulus and strength and if they do not slide or pull out during crack propagation, the glass fibre can tolerate high stress and both matrix and fibre will fracture together. A composite with a strong interface is able to bear load even after several fibres are broken as the load can be transferred to the intact portions of broken as well as unbroken fibres. This may be the reason for enhanced impact, tensile and flexural properties on the addition of organoclay and glass fibre in to PP/HDPE blend

The experimental data were analysed by the response surface regression procedure using the following second order polynomial equation:

$$y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i<j=1}^{3} \beta_{ij} x_i x_j \text{ ....} (1)$$

where y is the response, xi and xj are the uncoded independent variables and β_0, βi, βii and βij are intercept, linear, quadratic and interaction constant coefficients respectively. Each coefficient estimates the change in the mean response per unit increase in 'X' when all other predictors are held constant. The equations for all responses are listed in Table 6.3, where X_1, X_2, X_3 and X_4 are mixing temperature, mixing time, nanoclay loading and fibre content in coded variables.

Table 6.3 Response equations for mechanical properties of PP/HDPE/ modified nanoclay/glass fibre hybrid composites.

Response	**R^2 %**	**Adjusted R^2 %**	**Model Equations(in coded form)**
Tensile Strength	99.5	98.8	$47.66+1.26X_1+1.1X_2-0.29X_3+0.3X_4-5.3X_1^2-3.43X_2^2-1.59X_3^2-2.83X_4^2-4.02X_1X_2-0.5X_1X_3-0.44X_1X_4-0.26X_2X_3-0.92X_2X_4-1.2X_3X_4$
Flexural Strength	95.8	90.9	$65.17+0.73X_1+1.57X_2-0.5X_3+0.6X_4-8.5X_1^2-4.8X_2^2-3.9X_3^2-6.0X_4^2-4.2X_1X_2-1.8X_1X_3-1.3X_1X_4-0.15X_2X_3-1.25X_2X_4-0.97X_3X_4$
Tensile Modulus	82.9	73	$1455.95+106.89X_1+77.03X_2-27.1X_3+30.21X_4-202.05X_1^2-197.29X_2^2-46.87X_3^2-185.28X_4^2-110.68X_1X_2-41.14X_1X_3+41.01X_1X_4-25.49X_2X_3+8.37X_2X_4 11.55X_3X_4$
Flexural Modulus	89.2	86.5	$2253.81+40.28X_1+80.97X_2-42.7X_3+89.09X_4-557.54X_1^2-312.66X_2^2-343.28X_3^2-360.16X_4^2-371.7X_1X_2-163.55X_1X_3-105X_1X_4+32.97X_2X_3-230.78X_2X_4-118.8X_3X_4$
% Strain at Break	93.9	86.8	$4.48+0.086X_1+1.23X_2-0.05X_3+2.9X_4-4.45X_1^2-2.2X_2^2-1.52X_3^2-0.99X_4^2-1.1X_1X_2+0.27X_1X_3-0.71X_1X_4+0.42X_2X_3+0.09X_2X_4+0.39X_3X_4$
Impact Strength	89.3	76.9	$42.75-0.33X_1-0.29X_2+0.17X_3-0.13X_4+1.25X_1^2+1.13X_2^2+0.34X_3^2+0.98X_4^2+0.8X_1X_2+0.28X_1X_3+0.34X_1X_4+0.37X_2X_3+0.52X_2X_4-0.3X_3X_4$

Each coefficient estimates the change in the mean response per unit increase in x when all other predictors are held constant. MINITAB software package was used for regression analysis. The factors with positive coefficients have a positive effect on the property and vice versa. The R^2 values for all responses are obtained in the range of 73–99%. Although, R^2 closer to 100 means that the model is more valid but range achieved for R^2 in this study is an indication of a very good fitting of the experimental data by the response surface method in the models.

The contour plots are useful for creation of desirable response. They represent the contribution of two factors simultaneously, while the other two factors are kept at their average levels. Figure 6.1(a) displays the contour plots of tensile strength. As there are four factors, six figures are obtained, each with a different combination of two factors. The circular nature of contour plots implies that there is a maximum region encircled at the centre. The maximum values of tensile strength are obtained for 160°C compounding temperature, 8 minutes processing time, 2 wt% clay content and 20wt% gf content. And the contrast of colour scheme versus the value of tensile strength in the side table suggests that tensile strength is increased to a value greater than 47.5 MPa in the central dark region. The contour plots of tensile modulus are illustrated in figure 6.1(b). The processing temperature where the tensile modulus is maximum is 160°C, but the maximum modulus enhancement is obtained in the nanoclay content range-1.5 to 2.5 wt%, processing times of 7.5 to 10.5 minutes and fibre content of 15 to 25 by wt%. Even though a sharp value for optimum cannot be distinguished from the contour plots, the circular nature indicates that there is absence of any saddle points and there is maximum encirclement at the central region. The contour plots of flexural properties are identical to that of tensile strength showing the same optimum region of encirclement.

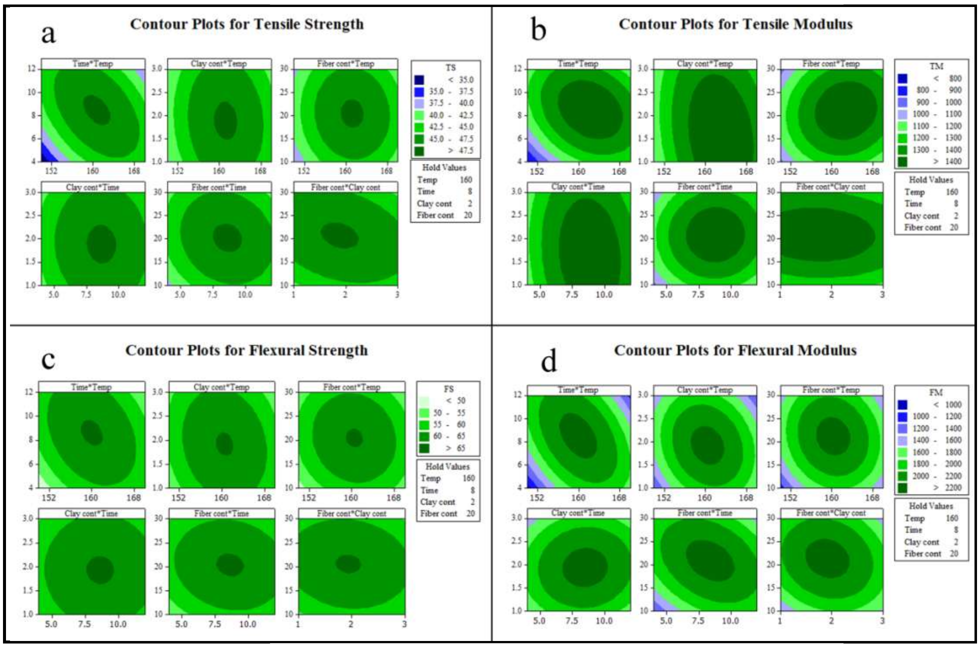


Figure 6.1 (a) Contour plots for tensile strength (b) Contour plots for tensile modulus (c) Contour plots for flexural strength (d) Contour plots for flexural modulus

The contour plots of break strain and impact strength are drawn as figures 6.2 (a) and (b). The maximum elongation at break decreases at optimum values of processing condition and filler content. The literatures report in a confusing way about this property. Some researchers, claim that the easy slippage of polymer chains in the presence of free surfactant of nanoclay in exfoliated or intercalated morphology, increases elongation at break [56]. While other researchers report that inclusion of nanoclay alters crystallinity and interfacial adhesion of polymer matrix and filler making the composite more stiff and results in a decreased elongation at break [57-60]. The impact strength increases as processing temperature, time and nanoclay content increase, reaches an optimum value and then decrease. But in the case of fibre content, the impact strength continues to increase even after 30 wt% gf. But as the usage of high amount of filler is detrimental to most other composite properties, gf content is limited to 30 wt% in this study. Impact strength enhancement is the most interesting result and the increase the applicability level of the hybrid composite so produced. The increase in impact strength may be attributed to the fact that presence of fibre content reduces the crack propagation and increase toughness by efficient stress transfer.

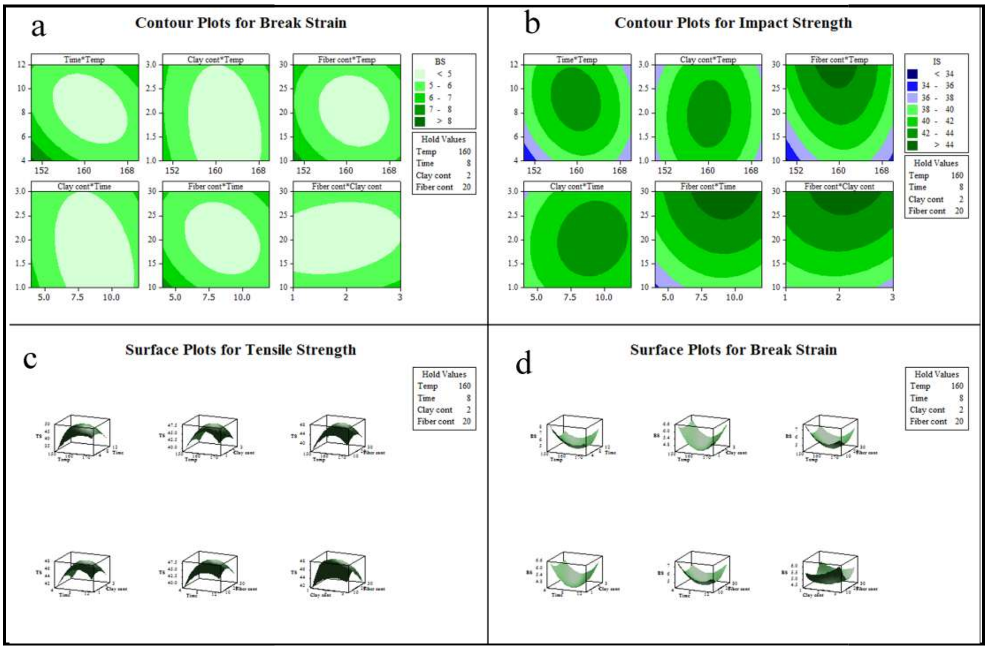


Figure 6.2 (a) Contour plots for break strain (b) Contour plots for impact strength (c) Response surface plots for tensile strength (d) Response surface plots for break strain

Main effect plots illustrate the average values of response at various levels of other factors. These plots indicate the influence of each parameter on the responses. During melt processing, nanoclay particles are broken in to individual layers with polymer matrix molecules. This effectively produces much higher ability to load carrying. The enhancement of mechanical properties even at low content of nanoclay is considerable [61]. The main effect plots of the PP/HDPE/N100A/gf hybrid composites are reported in figures 6.3 and 6.4 (a) and (b). Tensile modulus (fig. 6.3 (a)) represent a drastic increase as processing temperature is increased from 150°C to 160°C. Further increase in temperature has not much effect in the tensile modulus of composite.

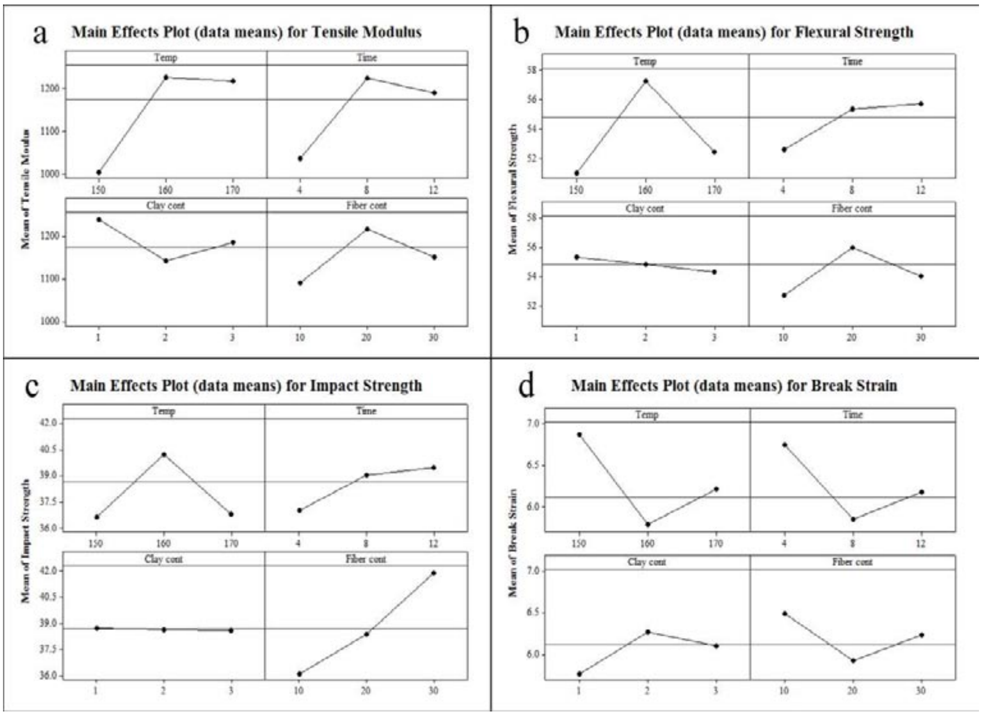


Figure 6.3 **(a) Main effects plot for tensile modulus (b) Main effects plot for flexural strength (c) Main effects plot for impact strength(d) Main effects plot for break strain**

As the processing time and filler content is increased, the modulus increases initially and then decreases. Zhu and Xanthos [62] reported that coupling of long residence time and high shear rate might result in poor exfoliation of nanofiller. In the case of flexural strength the properties first increase as the variables are increased and then decrease. The main effect plot of impact strength is illustrated in fig. 6.3 (c). It is seen in the plot that nanoclay has not much effect on the impact strength and that fibre content is the most determining factor as far as impact strength is considered. In the case of break strain, the properties decrease at the middle level and then increases.

The main effects plots of tensile strength and flexural modulus are illustrated in fig 6.4 (a) and fig 6.4 (b). Both the properties are found to increase on increasing the variables, reaches a maximum at the middle settings and then decreases.

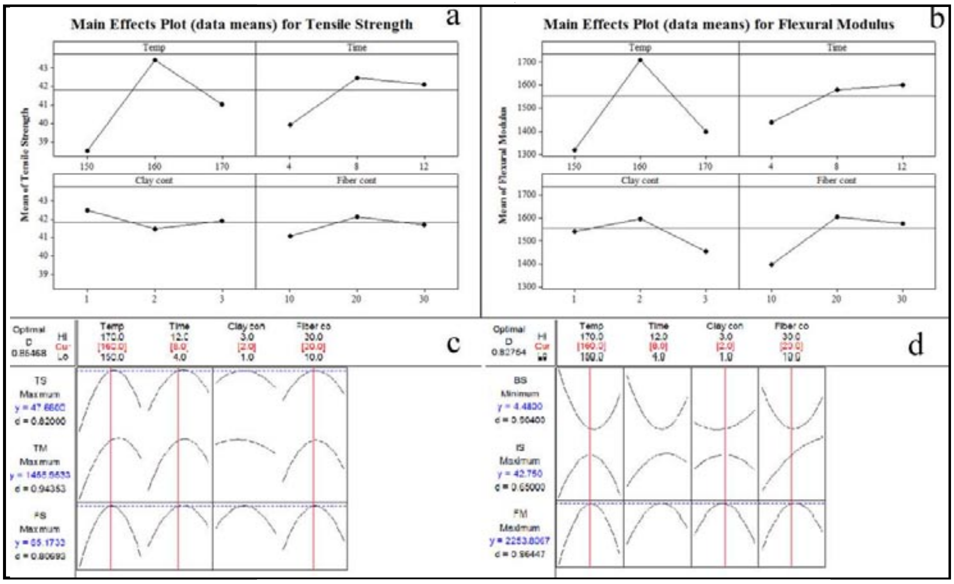


Figure 6.4 **(a) Main effect plots for tensile strength (b) Main effects plots for flexural modulus (c)&(d) Response optimization plots of mechanical properties PP/HDPE/N100A/E-glass fibre composites**

The optimization plots of the mechanical properties are given as figure 6.4 (c) and (d). The optimization plots are drawn through the top summit point of the response surface plots. The optimum values obtained for the variables where mechanical properties got enhanced are as follows: melt compounding parameters of 160°C and 8 min processing time, 2 wt% nanoclay content and 20 wt% glass fibre content. The optimized values obtained from figure for each mechanical property are shown in Table 6.4

Table.6.4 Results of optimization plots

Sl No	Property	Optimum Value
1	Tensile Strength	47.66 MPa
2	Tensile Modulus	1455.95 MPa
3	Flexural Strength	65.17 MPa
4	Flexural Modulus	2253.8 MPa
5	Impact Strength	42.74KJ/mm^2
6	Break Strain	4.48

6.3.2 Mechanical properties of PP/HDPE/unmodified kaolinite clay/ E- glass fibre hybrid composites

In this section the mechanical properties of hybrid composites that contain unmodified kaolinite clay (N100) and E-glass fibre is analysed in detail. The variables and levels in the Box Behnken design with their coded values are given in Table 6.1. The melt compounding temperature is varied from 150°C to 170°C, and time of mixing from 4 to 12 minutes. The nanoclay content varied in this study are 1, 2 and 3 wt% of total mixture, while fibre content varied in the range of 10 to 30 wt%. The composites are prepared with 80/20 PP/HDPE blend containing varying composition of unmodified nanoclay (N100) and E-glass fibre as fillers. The nanoclay is preheated in an oven before mixing to avoid moisture content. The experimental design table illustrating the combination of variables and the respective responses are shown in Table 6.6.

Table 6.5 Box–Behnken experimental design table with experimental response values of mechanical properties

Sl No	Time °C	Temp min	Clay wt%	Fibre wt%	TS	TM	BS	IS	FS	FM
1	8	160	3	30	39.8	1312.34	4.8	29.7	40.3	1292.01
2	12	160	2	10	39.6	1265.57	5.9	27.2	42.2	1432.13
3	8	170	2	30	40.5	1324.27	5.34	30.6	42.8	1401.78
4	12	160	1	20	38.5	1263.34	5.8	32.9	40.6	1317.23
5	8	160	2	20	43.5	1565.87	3.6	26.8	45.4	1945.99
6	8	150	3	20	38.9	1477.85	4.3	30.1	41.1	1347.12
7	8	160	2	20	43.1	1545.78	3.9	26.8	45.9	1923.04
8	8	170	1	20	39.7	1546.86	3.8	23.9	41.2	1394.76
9	4	160	2	10	40.8	1254.03	6.3	36.3	42.8	1485.15
10	8	160	2	20	43.6	1532.12	3.3	26.9	45.2	1914.24
11	12	150	2	20	38.2	1312.34	5.5	32.4	41.4	1341.63
12	12	170	2	20	40.9	1446.18	3.98	26.2	43.2	1591.85
13	12	160	3	20	40.4	1552.2	4.3	27.3	42.5	1685.05
14	8	150	2	30	37.8	1199.43	5.2	28.3	40.3	1265.8
15	8	160	1	10	39.4	1252.15	5.9	31	41.4	1284.45
16	12	160	2	30	40.3	1291.57	5.6	31.9	42	1462.28
17	8	160	3	10	40.8	1300.31	6.3	33.9	42.3	1454.87
18	8	170	2	10	40.8	1316.64	4.8	25.2	42.485	1423.94
19	4	160	1	20	39.5	1466.46	5.1	29.6	41.37	1497.42
20	8	160	1	30	40.05	1252.11	6.2	30.8	40.859	1344.37
21	4	160	2	30	39.1	1240.02	5.5	29.33	40.493	1338.05
22	4	170	2	20	39.6	1496.34	4.6	30.4	41.809	1419.7
23	8	150	2	10	40.1	1195.08	6.9	38.1	43.128	1346.59
24	4	150	2	20	39.6	1291.44	5.2	35.2	41.742	1456.58
25	8	170	3	20	40.5	1359.65	4.9	29.8	42.388	1468.84
26	8	150	1	20	38.3	1182.26	6.5	27.2	42.31	1303.14
27	4	160	3	20	39.4	1293.19	5.4	30.6	40.31	1347.67

There is considerable increase in mechanical properties on the addition of nanoclay and glass fibre in PP/HDPE blend. The tensile strength increases to 43.4 MPa (35.86%), the flexural strength increases from 39.61 MPa to 45.97 MPa (16.54%) but the impact strength decreases to 26.77 KJ/mm^2 from 32.38KJ/mm^2 (17.3%). The impact behaviour of composites is an important parameter that has to be studied as cracks due to sudden loads are very common in service conditions. The impact strength of a composite depends on its toughness, nature of interface region, geometry of the composite and test conditions. The toughness of the composite is governed by the nature of interfacial bonding. If the interface is weak, the crack will be propagated along the fibre matrix interface causing debonding. As a result, new surfaces will be formed which leads to significant increase in the energy absorbing capacity of the polymer composites. In the case of unmodified nanoclay composites, there is not much interfacial adhesion between the fibre and clay surfaces and the synergistic effect of adding both fillers in the polymer matrix is not obtained. This may be the reason for the decrease of impact strength. But in the case of hybrid composites containing modified nanoclay (N100A), the clay increases the interfacial adhesion between the polymer matrix and glass fibre and acts as binding agent between the filler and matrix thereby increasing impact as well as tensile and flexural properties. Similar results are obtained for other researchers also.[12, 63-68].

The experimental data are analysed by the response surface regression procedure using the following second order polynomial equation given by equation 1

The equations for all responses are listed in Table 6.7, where X_1, X_2, X_3 and X_4 are mixing time, mixing temperature, nanoclay loading and fibre content in coded variables.

Table 6.7. Response equations for mechanical properties of PP/HDPE/ unmodified nanoclay/E-glass fibre hybrid composites.

Response	R^2 %	Adjusted R^2%	Model Equations(in coded form)
Tensile Strength	98.0	95.7	$43.39+0.75X_1-0.007X_2+0.36X_3-0.34X_4-2.01X_1^2-1.1X_2^2-1.97X_3^2-1.51X_4^2+0.69X_1X_2-0.0003X_1X_3+0.48X_1X_4+0.49X_2X_3+0.57X_2X_4-0.42X_3X_4$
Flexural Strength	98.1	95.9	$45.55+0.32X_1+0.27X_2+0.18X_3-0.64X_4-1.52X_1^2-1.92X_2^2-2.39X_3^2-1.84X_4^2+0.42X_1X_2+0.59X_1X_3+0.78X_1X_4+0.75X_2X_3+0.53X_2X_4-0.35X_3X_4$
Tensile Modulus	99.1	98.1	$1547.92+69.29X_1+7.48X_2+27.73X_3+3X_4-84.24X_1^2-81.19X_2^2-70.44X_3^2-201.34X_4^2-17.76X_1X_2-120.7X_1X_3+0.82X_1X_4+115.53X_2X_3+10X_2X_4+3.02X_3X_4$
Flexural Modulus	99.5	99	$1927.76+53.33X_1+23.8X_2+37.85X_3-26.9X_4-272.93X_1^2-196.3X_2^2-276.03X_3^2-301.72X_4^2+71.77X_1X_2+7.53X_1X_3+14.66X_1X_4+129.39X_2X_3+44.31X_2X_4-55.69X_3X_4$
% Strain at Break	95.4	90.0	$3.631-0.51X_1-0.09X_2-0.27X_3-0.28X_4+0.49X_1^2+0.7X_2^2+0.79X_3^2+1.4X_4^2-0.24X_1X_2+0.86X_1X_3+0.5X_1X_4-0.451X_2X_3+0.14X_2X_4-0.4X_3X_4$
Impact Strength	83.2	73.5	$26.64-2.1X_1-1.15X_2+0.49X_3-0.9X_4+1X_1^2+2.5X_2^2+0.96X_3^2+2.89X_4^2-0.35X_1X_2+0.7X_1X_3+3.8X_1X_4-1.67X_2X_3+2.9X_2X_4-0.98X_3X_4$

R-square (coefficient of determination) value is the percentage of response variable variation that is explained by its relationship with one or more predictor variables. The R^2 values for all responses are obtained in the range of 0.73 to 1(Table.6.7). When R^2 is closer to one it means that the model is more valid and the range achieved for R^2 in this study is an indication of very good fitting of experimental data by the response surface methodology. Significantly high R^2 suggests that the final model can satisfactorily account for the variations in the process response.

Response surface plots and contour plots are based on the model equations obtained in the regression analysis and are displayed in fig. 6.5 and fig 6.6. The three-dimensional response surface plots, obtained as a function of two factors maintaining all other factors constant, are helpful in understanding both the main effects and the interaction effects of these two factors. The corresponding contour plots, represented by the projection of the response surfaces in the x–y plane, provide a straightforward determination of the effects of the independent variables on the dependent variable [68]. The response surface plots in figure 6.6 are part of a parabolic cylinder, exhibiting a minimum and maximum ridge, respectively, in the investigated domain. The two dimensional contour plots are a series of curves that identify different combinations of variables for which the response is constant. The circular shapes of contour plots indicate that a maximum lies in the selected range of operation and the selected range of process parameters and filler loading were appropriate. Contour plots illustrate the change in properties when two or more variables vary together and allow predictions to be made for combinations not actually evaluated. The response surface plot is a three dimensional graph that represents the functional relationship between the response and two variables, while the other variables are held at constant levels. The plot is used to visualise how a response reacts to changes in variables. The response surface plots of the mechanical properties indicate that the response passes through a maximum and then decreases for tensile strength and vice versa for impact strength. The trend followed by other properties is similar to that of tensile strength.

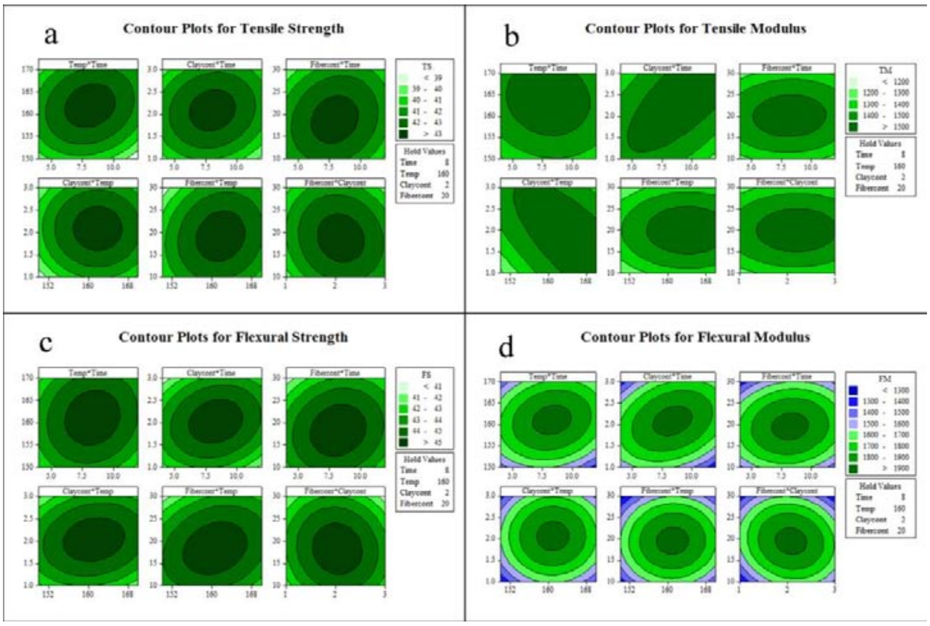


Figure 6.5 (a) Contour plots for tensile strength (b) Contour plots for tensile modulus (c) Contour plots for flexural strength (d) Contour plots for flexural modulus PP/HDPE/N100/E-glass fibre hybrid composites

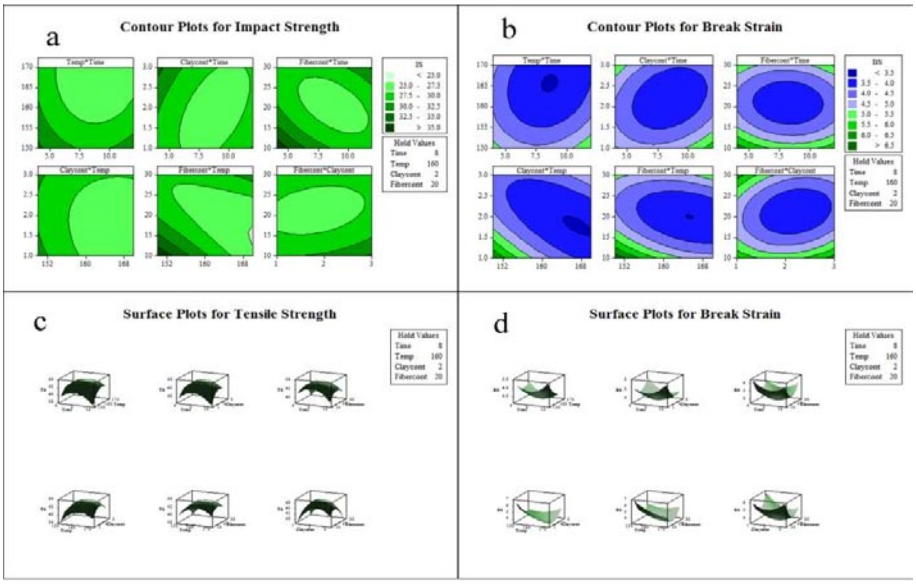


Figure 6.6 (a) Contour plots for impact strength (b) Contour plots for break strain (c) Surface plots for tensile strength (d) Surface plots for break strain of PP/HDPE/N100/E-glass fibre hybrid composites

A “main effect” is the effect of one of the independent variables on the dependent variable, ignoring the effects of all other independent variables. A statistical interaction occurs when the effect of one independent variable on the dependent variable changes depending on the level of another independent variable. The main effects plots of PP/HDPE/N100/gf hybrid composites are illustrated in figure 6.7 and 6.8 (a) and 6.8(b).

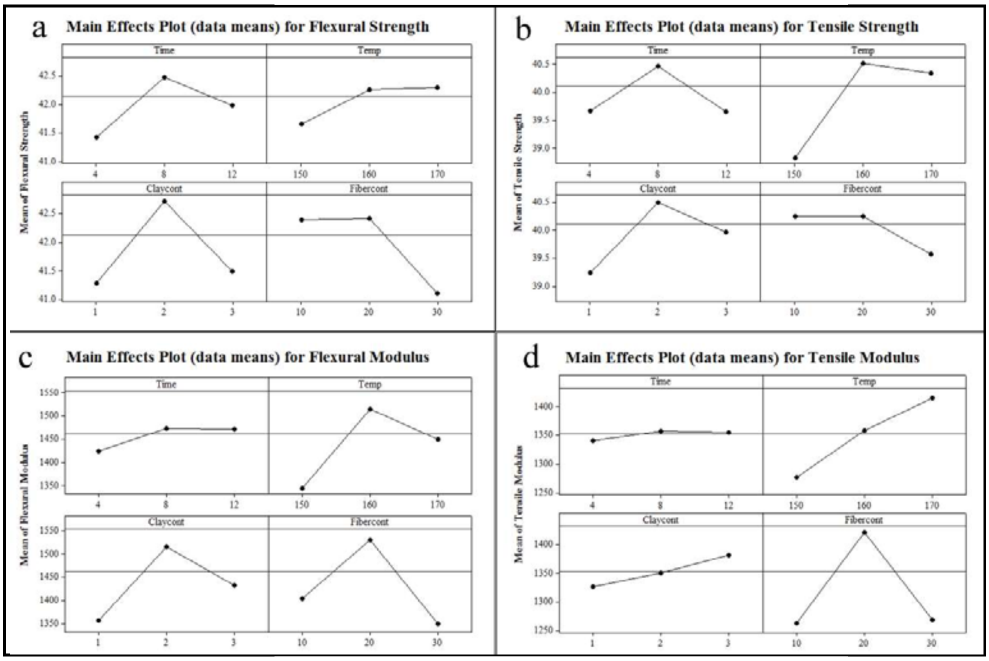


Figure 6.7 (a) Main effects plot for flexural strength (b) Main effects plot for tensile strength (c) Main effects plot for flexural modulus (d) Main effects plot for tensile modulus of PP/HDPE/N100/gf hybrid composites

As it is seen in figure 6.7 that flexural strength depends on all the four factors. As the processing time, temperature and clay content are increased flexural strength increases, reaches a maximum value and then decreases. As the variables increase from low to middle value, there may be better dispersion and binding between the matrix and fillers. At very low processing time and temperature there may be agglomeration of fibres and nanoclay and this may be the result of low values of flexural strength. As the factors are increased from middle level to high level, there may be failure of interfacial adhesion due to matrix degradation. As the fibre content increases to 30 wt%, the flexural strength decreases. This may be because as the filler content is increased the properties of hybrid composite change entirely to that of a micro composite. The other mechanical properties also follow the similar trend of flexural strength. Similar observations are reported by other researchers also in hybrid composites of other materials [46, 69-71].

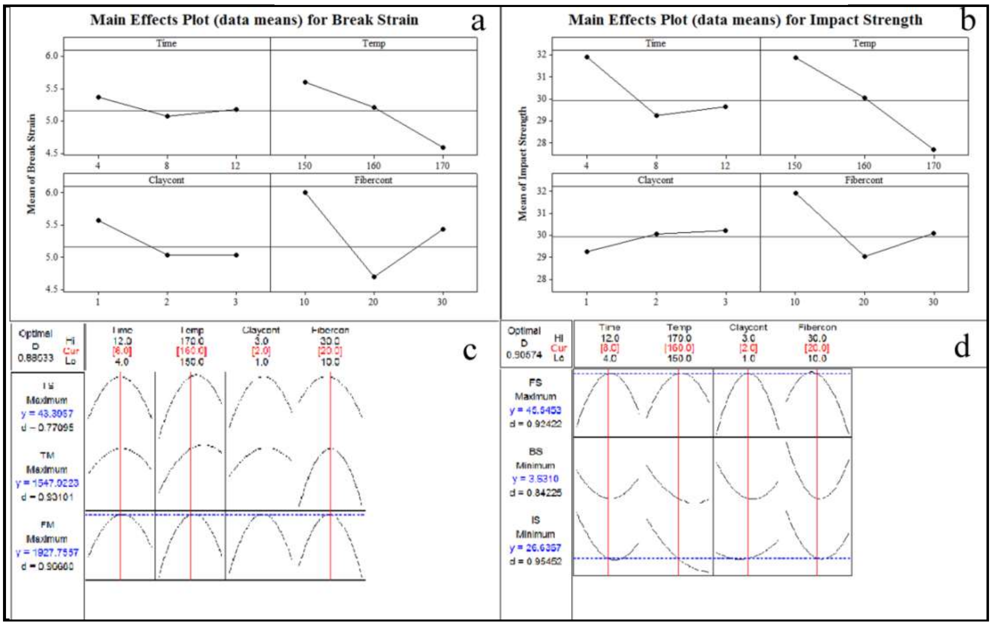


Figure 6.8 (a) Main effects plot for break strain (b) Main effects plot for impact strength (c) & (d) Response optimization plots of mechanical properties

The main effects plots of break strain and impact strength are illustrated in fig. 6.8 (a) and fig 6.8 (b). The impact strength and break strain displays a reverse trend shown by other mechanical properties. As the unmodified clay cannot act as a bridge between polymer matrix and glass fibres, it cannot impart synergistic effect, and this may be the reason for reduced impact strength for PP/HDPE/unmodified clay/glass fibre hybrid composites. The response optimization for all the responses are carried out using MINITAB software and the graphs are represented as figures 6.8 (c) and (d). The optimum values obtained for the responses are summarized in table 6.8.

Table 6.8 Results of optimization plots

Sl No	Property	Optimum Value
1	Tensile Strength	43.3 MPa
2	Tensile Modulus	1547.05 MPa
3	Flexural Strength	45.53 MPa
4	Flexural Modulus	1927.75 MPa
5	Impact Strength	26.63 KJ/mm^2
6	Break Strain	3.53

6.3.3 Statistical Analysis

6.3.3.1 Statistical analysis of PP/HDPE/N100A/E-glass fibre hybrid composites

The first step in the analysis involves finding the significant parameters. The analysis in this study is done using uncoded units. Use of uncoded units helps to eliminate any spurious statistical results due to different measurement scales of the factors and makes them easier to interpret [7]. The parametric test (p-test) is carried out for all the mechanical properties and the significant results are tabulated in Tables 6.9. 95% confidence level is chosen for setting up the DoE experimental design which suggested an ‘α’ value of 0.05. Probability of occurrence (p-value) that quantifies the significance of terms in the polynomial model should ideally be less than the chosen α-level, such as 0.05, for the term to be significant. The significance level of each term is indicated. The values of significance level indicates that the factors-temperature,

Table 6.9. p value and significance level of each process variable affecting the mechanical properties

Term	Tensile Strength		Tensile Modulus		Flexural Strength		Flexural Modulus		Impact Strength		Break Strain	
	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %
Constant	0	100	0	>100	0	>100	0	>100	0	>100	0	>100
Time	0.94	>6	0.005	>99.5	0.115	>88.5	0.449	>55.1	0.851	>14.9	0.006	>99.4
Temp	0	>100	0.031	>96.9	0.003	>99.7	0.142	>85.8	0.016	>98.4	0.013	>98.7
Clay cont	0.001	>99.9	0.406	>59.4	0.263	>73.7	0.423	>57.7	0.92	>8	0.105	>89.5
Fibre cont	0.002	>99.8	0.356	>64.4	0.146	>85.4	0.109	>89.1	0	>100	0.21	>79
Temp*Temp	0	>100	0.001	>99.9	0	>100	0	>100	0	>100	0	>100
Time*Time	0	>100	0.001	>99.9	0	>100	0.002	>99.8	0.007	>99.3	0	>100
Clay cont*Clay cont	0	>100	0.341	>65.9	0	>100	0.001	>99.9	0.043	>95.7	0.04	>96
Fibre cont*Fibre cont	0	>100	0.002	>99.8	0	>100	0.001	>99.9	0.164	>83.6	0	>100
Temp*Time	0.001	>99.9	0.065	>93.5	0	>100	0.001	>99.9	0.182	>81.8	0	>100
Temp*Clay cont	0.007	>99.3	0.465	>53.5	0.031	>96.9	0.092	>90.8	0.73	.27	0.123	>87.7
Temp*Fibre cont	0.002	>99.8	0.467	>53.3	0.097	>90.3	0.262	>73.8	0.376	>62.4	0.067	>93.3
Time*Clay cont	0.999	>0.1	0.649	>35.1	0.846	>15.4	0.718	>28.2	0.599	>40.1	0.048	>95.2
Time*Fibre cont	0.007	>99.3	0.881	>11.9	0.118	>88.2	0.024	>97.6	0.907	>9.3	0.009	>99.1
Clay cont*Fibre cont	0.015	>98.5	0.836	>16.4	0.215	>78.5	0.208	>79.2	0.625	>37.5	0.157	>84.3

clay content and fibre content are the most important factors in deciding the properties of nanocomposite and also that interaction effects are less compared to other properties.

The statistical analysis of the experimental and model results is further carried out by ANOVA test. For significance check, F value given in ANOVA table is used. Probability of F value greater than calculated F value due to noise is indicated by p value. If p value is less than 0.05, significance of corresponding term is established. For lack of fit, p value must be greater the 0.05. An insignificant lack of fit is desirable as it indicates anything left out of model is not significant and the developed model fits. Based on analysis of variance (ANOVA) test full quadratic model was found to be suitable for tensile strength, flexural strength, flexural modulus and break strain with regression p-value less than 0.05 and lack of fit more then 0.05. The ANOVA table for tensile modulus is shown in Table.6.10.

Table 6.10 Analysis of Variance for tensile modulus

Source	**DF**	**Seq SS**	**Adj SS**	**Adj MS**	**F**	**P**
Regression	14	692447	692447	49460.5	4.16	0.009
Linear	4	228067	307150	76787.4	6.45	0.005
Square	4	398473	398473	99618.3	8.37	0.002
Interaction	6	65907	65907	10984.5	0.92	0.512
Residual Error	12	142752	142752	11896		
Lack-of-Fit	10	142720	142720	14272	912.41	0.001
Pure Error	2	31	31	15.6		
Total	26	835199				

Here the p values of regression, linear and square terms are less than 0.05 and this indicates that these terms are significant in the model. For lack of fit the p value is 0.001, which is less than 0.05 and this indicates the model does not fit well with experimental data. The p value for interaction term is 0.512 which implies that there are no interaction effects present between melt compounding parameters in the preparation of PNC.

The ANOVA table for impact strength is shown in Table.6.11. Here the p values of regression, linear and square terms are less than 0.05 and this indicates that these terms are significant in the model. For lack of fit the p value is 0.04, which is somewhat less than 0.05, indicates that model is inadequate for properly estimating the values of impact strength and this may be due to the decrease in the value of impact strength as the nanoclay is added to the polymer matrix. The p value for interaction term is 0.733 which is more than the chosen degree of confidence level and this implies that the interaction effects are not significant in the preparation of polymer-clay nanocomposites by melt compounding technology.

Table 6.12 Analysis of Variance for impact strength

Source	**DF**	**Seq SS**	**Adj SS**	**Adj MS**	**F**	**P**
Regression	14	239.8	239.8	17.13	7.18	0.001
Linear	4	120.1	114.1	28.5	11.96	0
Square	4	111.2	111.2	27.8	11.66	0
Interaction	6	8.4	8.4	1.4	0.59	0.7
Residual Error	12	28.6	28.6	2.4		
Lack-of-Fit	10	28.4	28.4	2.8	24.49	0.04
Pure Error	2	0.2	0.2	0.12		
Total	26	268.4				

A final statistical analysis of the capability of the developed model to predict the properties of the PNC is carried out by evaluating the statistical parameters like correlation coefficient (R), average absolute relative error

(AARE), average root-mean-square error (RMSE), normalized mean-biased error (NMBE) and scatter index (SI) whose equations are as described in Chapter 4 (equations 7 to 11). The results of statistical analysis is tabulated in table 6.13

Table 6.13 Statistical coefficients of PP/HDPE/N100A/E-glass fibre hybrid composites

Property	R	AARE	NMBE	RMSE	SI
TS	0.99	0.46	-0.023	0.24	0.006
FS	0.98	1.45	0.007	0.99	0.02
IS	0.94	2.11	-1.4E-13	1.02	0.03
TM	0.91	5.18	0.0003	72.7	0.062
FM	0.94	6.68	-0.0002	118.9	0.077
BS	0.97	3.05	0.06	0.22	0.04

The correlation coefficient is a commonly used statistic and provides information on the strength of the linear relationship between experimental and predicted values. The closeness of R toward unity indicates better fitting of the model toward experimental data. The AARE and RMSE are computed through a term-by-term comparison of the relative error and therefore are unbiased statistics for measuring the predictability of a model. These values are high for tensile modulus and flexural modulus. The NMBE provides information on the mean bias in predictions from a model. A positive NMBE indicates over prediction, whereas a negative NMBE indicates under prediction from a model. It can be seen from the table that NMBE values are so small for all mechanical properties and sufficiently able to predict the corresponding responses with better levels of accuracy [72]. The scatter index provides deviation from a linear behaviour and a small value indicates better performance of the model. Low values of SI indicate that the model fits with the experimental data without much scattering. From the statistical evaluation, it is clear that the model fits with the experimental data very well for all mechanical properties except tensile modulus and flexural modulii.

6.3.3.2 Statistical analysis of PP/HDPE/N100/E-glass fibre hybrid composites

Multivariate optimization of polymeric systems can be carried out using the following procedure

1) Choose a statistical design to investigate the experimental region of interest.
2) Perform the experiments in random chronological order.
3) Perform p test and analysis of variance (ANOVA) on the regression results so that the most appropriate model with no evidence of lack of fit can be used to represent the data.

Here in this section, regression analysis, ANOVA test and statistical parameters evaluation are conducted for PP/HDPE/unmodified clay nanocomposites.

The results of p tests of all mechanical properties are demonstrated in Table 6.14. The significance level of each term is indicated. The value of significance level indicates that the factors melt compounding temperature, fibre content and the interaction effects are the most important in determining the properties of nanocomposites.

Table.6.14 p value and significance level of each process variable affecting the mechanical properties

Term	Tensile Strength		Tensile Modulus		Flexural Strength		Flexural Modulus		Impact Strength		Break Strain	
	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %	p value	Significance level %
Constant	0	>100	0	>100	0	>100	0	>100	0	>100	0	>100
Time	0	>100	0.005	>99.5	0.115	>88.5	0.449	>55.1	0.851	>14.9	0.006	>99.4
Temp	0	>100	0.031	>96.9	0.003	>99.7	0.142	>85.8	0.016	>98.4	0.013	>98.7
Clay cont	0.015	>98.5	0.406	>59.4	0.263	>73.7	0.423	>57.7	0.92	>8	0.105	>89.5
Fibre cont	0.012	>98.8	0.356	>64.4	0.146	>85.4	0.109	>89.1	0	>100	0.21	>79
Temp*Temp	0	>100	0.001	>99.9	0	>100	0	>100	0	>100	0	>100
Time*Time	0	>100	0.001	>99.9	0	>100	0.002	>99.8	0.007	>99.3	0	>100
Clay cont*Clay cont	0	>100	0.341	>65.9	0	>100	0.001	>99.9	0.043	>95.7	0.04	>96
Fibre cont*Fibre cont	0	>100	0.002	>99.8	0	>100	0.001	>99.9	0.164	>83.6	0	>100
Temp*Time	0	>100	0.065	>93.5	0	>100	0.001	>99.9	0.182	>81.8	0	>100
Temp*Clay cont	0.016	>98.4	0.465	>53.5	0.031	>96.9	0.092	>90.8	0.73	>27	0.123	>87.7
Temp*Fibre cont	0.031	>96.9	0.467	>53.3	0.097	>90.3	0.262	>73.8	0.376	>62.4	0.067	>93.3
Time*Clay cont	0.173	>82.7	0.649	>35.1	0.846	>15.4	0.718	>28.2	0.599	>40.1	0.048	>95.2
Time*Fibre cont	0	>100	0.881	>11.9	0.118	>88.2	0.024	>97.6	0.907	>9.3	0.009	>99.1
Clay cont*Fibre cont	0	>100	0.836	>16.4	0.215	>78.5	0.208	>79.2	0.625	>37.5	0.157	>84.3

Significance level of temperature is greater than the other factors i.e., time and clay content. Also interaction terms are less significant which indicates the presence of less interaction effects. Unlike the other mechanical properties the significant level of clay content is very low indicating that addition of unmodified nanoclay is not very good for modifying impact properties of PP/HDPE/nanokaolinite clay composites.

Further statistical analysis of the model developed for the mechanical properties of PP/HDPE/N100 nanocomposites is done by ANOVA tests. The ANOVA table for tensile modulus is shown in Table.6.15. Here the p values of regression, linear, square and interaction terms are less than 0.05 and this indicates that these terms are significant in the model. For lack of fit the p value is 0.59, which is more than 0.05 and this indicates very good fit of the model with experimental data.

Table 6.15 Analysis of Variance for tensile modulus

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	401662	401662	28690.2	97.55	0
Linear	4	67603	96691	24172.8	82.19	0
Square	4	220692	220692	55173	187.59	0
Interaction	6	113367	113367	18894.5	64.24	0
Residual Error	12	3529	3529	294.1		
Lack-of-Fit	10	2953	2953	295.3	1.02	0.59
PureError	2	576	576	288.2		
Total	26	405192				

The ANOVA table for impact strength is shown in Table.6.16. Here the p values of regression, linear and square terms are less than 0.05 and this indicates that these terms are significant in the model. For lack of fit the p value is 0.034, which is somewhat less than 0.05 and indicates that model is inadequate for properly estimating the values of impact strength and this may be due to the decrease in the value of impact strength as the nanoclay is added to the polymer matrix.

Table 6.16 Analysis of Variance for impact strength

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	251.4	251.4	17.96	4.23	0.008
Linear	4	81.6	90.42	22.6	5.33	0.011
Square	4	60.5	60.54	15.13	3.57	0.039
Interaction	6	109.2	109.2	18.2	4.29	0.015
ResidualError	12	50.92	50.92	4.24		
Lack-of-Fit	10	50.57	50.57	5.057	29.18	0.034
PureError	2	0.347	0.35	0.17		
Total	26	302.32				

Table 6.17 Standard statistical evaluation during validation of the model performance

Property	R	AARE	NMBE	RMSE	SI
TS	0.99	0.373	-0.009	0.199	0.0049
FS	0.99	0.39	0.02	0.204	0.0048
IS	0.91	3.49	-0.01	1.37	0.046
TM	0.99	0.65	0.002	11.4	0.0084
FM	0.99	0.66	0.00076	12.66	0.0087
BS	0.99	0.97	2.87E-13	0.093	0.018

In the reported values, RMSE is high for tensile modulus and flexural modulus which suggests that the developed model is not very adequate in predicting the modulus. All the other properties were well predicted by the model within the range of operation.

Synergistic effect of glass fibre and organoclay: The results of mechanical properties of PP/HDPE/N100A/glass fibre composites show that there is increase of 49.01% in tensile Strength , 66.9% increase in flexural strength and 31.8% increase in impact strength, also tensile and flexural modulus increases by 52.49% and 85.4% respectively, but only the break strain decreases by 31%.

6.4 Conclusions

- Hybrid composites are prepared using PP, HDPE, nanokaolinite clay and E-glass fibre.
- The mechanical properties of PP/HDPE blend like tensile and flexural strength and modulus can be significantly increased by the inclusion of nanokaolinite clay and glass fibre. The synergistic effect of nanoclay and glass fibre improves the mechanical properties even at low fibre loadings. This increases the overall performance of the composite without much change in density and specific weight.
- Box Behnken method of RSM can be effectively applied for combined optimization of melt mixing parameters, nanoclay content and glass fibre content.
- Organoclay can act as a molecular bridge between the non polar polymer matrix. Modified nanoclay and E glass fibre on incorporation into the polymer matrix increases the tensile strength by 49.01% and there is 66.9% increase in flexural strength, also tensile and flexural modulus increases by 52.49% and 85.4%

respectively. Even though incorporation of nanokaolinite clay decreases the impact strength of PP/HDPE blend, the synergistic effect on combined incorporation of nanoclay and glass fibre increases the impact strength of PP/HDPE blend by 31.8%

- Response equations are developed for all the mechanical properties. Contour and surface plots illustrates the behaviour of the mechanical properties as the variables change from low to high level of experimental range.
- The main effects plots show that melt compounding temperature, nanoclay content and glass fibre content have significant effect in determining the properties of PP/HDPE nanokaolinite clay composites.
- The R^2 value obtained in the range of 0.8-1 and the results of verification experiments indicates that the model fits well with the experimental data within the entire range of experiments.
- The optimum mechanical properties are obtained with melt compounding parameters of 160°C temperature, 8 min of mixing time, and 2 wt% of nanokaolinite clay and 20 wt% glass fibre content by response optimization technique
- The validation of model equations are done using confirmatory experiments and the results prove that the model can navigate the design space very well.
- The statistical analysis of the model developed for the mechanical properties of PP/HDPE/E-glass fibre/ nanokaolinite clay composites

with and without surface modification was carried out using regression analysis, ANOVA test and by evaluating statistical parameters.

- While examining the results of regression analysis the following conclusions can be drawn out-
  a) The p values and significance levels obtained deduce that the melt compounding temperature, nanoclay content and fibre content are the most determining factors in the formulation of PNC by melt compounding technique, while the effect of compounding time and shear rate are less so that they can be screened out from further analysis if necessary.
  b) The p values obtained for interaction terms are high and this suggests that there is not much interaction effect between melt compounding parameters and nanoclay content in the preparation of PNC.
  c) The R^2 statistics deduce that the developed model fits reasonably well with the experimental data.
  d) The results of the ANOVA test conducted for PP/HDPE/ nanoclay/glass fibre composites can be summarized as follows.
  e) The p values obtained for the terms like regression, linear and square indicated that these terms are significant in the model. The p value obtained for interaction terms is less than 0.5 for the ANOVA results of most of the mechanical properties and this suggests that interaction effects are there for such properties.

f) The F value which corresponds for the fit of the model should be greater than the tabulated F value for the selected level of confidence. The results show that this condition is satisfied and the model fit with the experimental data.

g) Finally the p value for lack of fit should be more than α value for the selected level of confidence, i.e., 0.5 for the model to be significant. This condition is satisfied for all properties except tensile and flexural modulii.

- A further statistical evaluation is conducted by evaluating the statistical coefficients as correlation coefficient (R), average absolute relative error (AARE), average root-mean-square error (RMSE), normalized mean-biased error (NMBE) and scatter index (SI). These coefficients are calculated using experimental values and predicted properties by the developed model. The evaluation proved that the developed model fits suitably well with the experimental data and can navigate smoothly in the entire design space except for tensile modulus.
- Statistical evaluation suggests that Box-Behnken experimental design can be used to optimize complex processes like preparation of hybrid composites whose response is affected by a large number of variables, effectively with minimum number of experiments.

References

[1] Tseng C. R., Wu J. Y., Lee H. Y. & Chang F. C. (2001). “Preparation and crystallization behaviour of syndiotactic polystyrene-clay nanocomposites”. Polymer, 42**:** 10063-10070.

[2] Vaia R. A., Ishii H. & Giannelis E. P. (1993). “Synthesis and properties of two-dimensional nanostructures by direct intercalation of polymer melts in layered silicates”. Chemistry of Materials, 5**:** 1694-1696.

[3] Okamoto M., Morita S. & Kotaka T. (2001) b. “Dispersed structure and ionic conductivity of smectic clay/polymer nanocomposites”. Polymer, 42**:** 2685-2688.

[4] Markarian J. (2005). “Automotive and packaging offer growth opportunities for nanocomposites”. Plastics, Additives and Compounding 7**:** 18-21.

[5] Lan T., Kaviratna P. D. & Pinnavaia T. J. (1995). “Mechanism of Clay Tactoid Exfoliation in Epoxy-Clay Nanocomposites”. Chemistry of Materials, 7**:**2144-2150.

[6] Ogawa M. & Kuroda, K. (1997). “Preparation of inorganic–organic nanocomposites through intercalation of organoammonium ions into layered silicates”. Bulletin of the chemical society of Japan, 70**:** 2593-2618.

[7] Theng B. K. G. (1974). The chemistry of clay-organic reactions / B.K.G. Theng, New York:, Wiley.

[8] Okamoto M. (2004). “Polymer/clay nanocomposites”. Encyclopedia of Nanoscience and Nanotechnology, 8**:** 791-843.

[9] Sinha Ray S., Yamada K., Okamoto M. & Ueda K. (2003)c. “New polylactide-layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology”. Polymer, 44**:** 857-866.

[10] Ahmadi S. J., Huang Y. D. & Li, W. (2004). “Review synthetic routes, properties and future applications of polymer-layered silicate nanocomposites”. Journal of Materials Science, 39**:**1919 - 1925.

[11] Krishnamachari P., Zhang J., Lou J., Yan J. & Uitenham L. (2009)a. “Biodegradable Poly(Lactic Acid)/Clay Nanocomposites by Melt Intercalation: A Study of Morphological, Thermal, and Mechanical Properties”. International Journal of Polymer Analysis and Characterization, 14**:** 336-350.

[12] Alexandre M. & Dubois P. (2000). “Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials”. Materials Science and Engineering, 28**:** 1-63.

[13] Pluta M. (2006). “Melt compounding of polylactide/organoclay: Structure and properties of nanocomposites”. Journal of Polymer Science Part B-Polymer Physics, 44**:** 3392-3405.

[14] Muzny C. D., Butler B. D., Hanley H. J. M., Tsvetkov F. & Peiffer D. G. (1996). “Clay platelet dispersion in a polymer matrix”. Materials Letters, 28**:**379-384.

[15] Pavlidou S. & Papaspyrides C. D. (2008). “A review on polymer–layered silicate nanocomposites”. Progress in Polymer Science 33**:** 1119-1198.

[16] Liu J., Boo W. J., Clearfield A. & Sue H. J. (2006). “Intercalation and Exfoliation: A Review on Morphology of Polymer Nanocomposites Reinforced by Inorganic Layer Structures”. Materials and Manufacturing Processes, 21**:** 143-151.

[17] Weon J. I. & Sue H. J. (2005). “Effects of clay orientation and aspect ratio on mechanical behavior of nylon-6 nanocomposite”. Polymer, 46**:** 6325-6334.

[18] Olad A. (2011). Polymer/Clay Nanocomposites. In: (ED.), B. R. (ed.) Advances in Diverse Industrial Applications of Nanocomposites. In Tech.

[19] Fischer H. (2003). “Polymer nanocomposites: from fundamental research to specific applications”. Materials Science and Engineering: C, 23**:**763-772.

[20] Krishnamoorti R., Vaia R. A. & Giannelis E. P. (1996). ‘Structure and Dynamics of Polymer-Layered Silicate Nanocomposites”. Chemistry of Materials, 8**:**1728-1734.

[21] Blumstein A. (1965). “Polymerization of adsorbed monolayers. I. Preparation of the clay–polymer complex”. Journal of Polymer Science Part A: General Papers, 3**:** 2653-2664.

[22] Denault J., Ton-That M.-T. & Bloch J. (2006). “Poly(lactic acid) Nanocomposites: Fabrication Microstructure and Performance”. Design, Applications of Composites Proceedings of the Sixth Joint Canada-Japan Workshop on Composites**,** 11-19.

[23] Paul M.-A., Alexandre M., Degée P., Henrist C., Rulmont A. & Dubois P. (2003)b. “New nanocomposite materials based on plasticized poly(l-lactide) and organo-modified montmorillonites: thermal and morphological study”. Polymer, 44**:** 443-450.

[24] Pogodina N. V., Cerclé C., Avérous L., Thomann R., Bouquey M. & Muller R. (2008). “Processing and characterization of biodegradable polymer nanocomposites: detection of dispersion state”. Rheologica Acta, 47**:** 543-553.

[25] Dennis H. R., Hunter D. L., Chang D., Kim S., White J. L., Cho J. W. & Paul D. R. (2001)b. “Effect of melt processing conditions on the extent of exfoliation in organoclay-based nanocomposites”. Polymer, 42**:** 9513-9522.

[26] Modesti M., Lorenzetti A., Bon D. & Besco S. (2005). “Effect of processing conditions on morphology and mechanical properties of compatibilized polypropylene nanocomposites”. Polymer, 46**:** 10237-10245.

[27] Jollands M. & Gupta R. K. (2010). “Effect of mixing conditions on mechanical properties of polylactide/montmorillonite clay nanocomposites”. Journal of Applied Polymer Science, 118**:** 1489-1493.

[28] Davis C. H., Mathias L. J., Gilman, J. W., Schiraldi D. A., Shields J. R., Trulove P., Sutto T. E. & Delong H. C. (2002). “Effects of melt-processing conditions on the quality of poly(ethylene terephthalate) montmorillonite clay nanocomposites”. Journal of Polymer Science Part B: Polymer Physics, 40**:** 2661-2666.

[29] Zhao J., Liu S., Yu S., Chen G. & Juay Y. (2008). “Effects of process conditions on properties of polymer nanocomposites”. SIMTech technical reports.

[30] Manas-Zloczower I. & Cheng H. (1996). “Analysis of mixing efficiency in polymer processing equipment”. Macromolecular symposia, 112**:** 77-84.

[31] Pluta M., Galeski A., Alexandre M., Paul M. A. & Dubois P. (2002). “Polylactide/montmorillonite nanocomposites and microcomposites prepared by melt blending: Structure and some physical properties”. Journal of Applied Polymer Science, 86**:** 1497-1506.

[32] Sinha Ray S., Yamada K., Okamoto M., Fujimoto Y., Ogami A. & Ueda K. (2003)a. “New polylactide/layered silicate nanocomposites. 5. Designing of materials with desired properties”. Polymer, 44**:**6633-6646.

[33] Di Y., Iannace S., Maio E. D. & Nicolais L. (2005). “Poly(lactic acid)/organoclay nanocomposites: Thermal, rheological properties and foam processing”. Journal of Polymer Science Part B: Polymer Physics, 43**:** 689-698.

[34] Hasook A., Muramatsu H., Tanoue S., Iemoto Y. & Unryu T. (2008). “Preparation of nanocomposites by melt compounding polylactic acid/polyamide 12/organoclay at different screw rotating speeds using a twin screw extruder”. Polymer Composites, 29**:** 1-8.

[35] Chavarria F., Shah R. K., Hunter D. L. & Paul D. R. (2007). “Effect of melt processing conditions on the morphology and properties of nylon 6 nanocomposites”. Polymer Engineering & Science, 47**:** 1847-1864.

[36] Dennis H. R., Hunter D. L., Chang D., Kim S., White J. L. & Cho J. W. (2001)a. “Nanocomposites: The importance of processing”. Plastics Engineering, 57**:** 56-57.

[37] Bourbigot S., Fontaine G., Bellayer S. & Delobel R. (2008). “Processing and nanodispersion: A quantitative approach for polylactide nanocomposite”. Polymer Testing, 27**:** 2-10.

[38] Antony J. & Capon N. (1998). “Teaching Experimental Design Techniques to Industrial Engineers”. International Journal of Engineering Education, 14**:** 335-343.

[39] Dong C. H., Xie X. Q., Wang X. L., Zhan Y. & Yao Y. J. (2009). “Application of Box-Behnken design in optimisation for polysaccharides extraction from cultured mycelium of Cordyceps sinensis”. Food and Bioproducts Processing, 87**:** 139-144.

[40] Ibrahim N., Jollands M. & Parthasarathy R. (2010). “Optimisation of process conditions of PLA/organoclay nanocomposite by using statistical analysis”. Chemeca 2010: The 40th Australasian Chemical Engineering Conference, paper #550 (10 pages). ISBN: 978-085-825-9713.

[41] Bae S. & Shoda M. (2005). “Statistical optimization of culture conditions for bacterial cellulose production using Box-Behnken design”. Biotechnology and Bioengineering, 90**:** 20-28.

[42] Ferreira S. L. C., Bruns R. E., Ferreira H. S., Matos G. D., David J. M., Brandã£o G. C., Da Silva E. G. P., Portugal L. A., Dos Reis P. S., Souza A. S. & Dos Santos W. N. L. (2007). “Box-Behnken design: An alternative for the optimization of analytical methods”. Analytica Chimica Acta, 597**:** 179-186.

[43] Garrote R. L., Coutaz V. R., Luna J. A., Silva E. R. & Bertone R. A. (1993). “Optimizing Processing Conditions for Chemical Peeling of Potatoes using Response Surface Methodology”. Journal of Food Science, 58**:** 821-826.

[44] Antony J. & Kaye M. (1995). ‘Experimental quality’. Journal of Manufacturing Engineer (UK) 74**:**178-181.

[45] Mohd Ishak Z.A., Ariffin A. & Senawi R. (2001). “Effects of hygrothermal aging and a silane coupling agent on the tensile properties of injection molded short glass fibre reinforced poly (butylene terephthalate) composites”. Eur. Polym. J. 37(8): 1635-1647.

[46] Norkhairunnisa M., Azhar A.B. & Shyang C.W. (2007).” Effects of organo montmorillonite on the mechanical and morphological properties of epoxy/glass fibre composites”. Polym. Int. 56(4): 512-517.

[47] Chandradass J., Ramesh Kumar M. & Velmurugan R. (2008). Effect of clay dispersion on mechanical, thermal and vibration properties of glass fiber-reinforced vinyl ester composites. J. Reinf. Plast. Compos. 27(15): 1585-1601.

[48] Rozman H.D, Tay G.S, Kumar R.N, Abusamah A, Ismail H and Ishal Z.A (2001) “Polypropylene oil palm empty fruit bunch-glass fiber hybrid composites:A preliminary study on the flexural an tensile properties”. Journal of European polymer 37:1283-1291.

[49] Thwe M and Liao K (2002) “Effects of environmental ageing on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites”. Journal of composite 33:43-52.

[50] Modesti M., Lorenzetti A., Bon D. & Besco S. (2006). “Thermal behaviour of compatibilised polypropylene nanocomposite: Effect of processing conditions”. Polymer Degradation and Stability, 91**:** 672-680.

[51] Asha KK, George TS, Anjana R, Joseph N, George KE Effect of modified kaolin clays on the mechanical properties of polypropylene/polystyrene blends. J Appl Polym Sci doi:10.1002/app. 38043.

[52] ASTM D638-94b (1995) “Tensile properties of plastics”. Annual book of American Society for Testing and Materials (ASTM) standards.

[53] ASTM D790-92 (1995) “Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials”. Annual book of American Society for Testing and Materials (ASTM) standards.

[54] ASTM D 256-10 (1995) “Standard test method for determining Izod pendulum impact resistance of plastics”. Annual book of American Society for Testing and Materials (ASTM) standards.

[55] Javad Moftakharian Esfahani, Masou Esfandeh, Ali Reza Sabet (2011) “High velocity impact behaviour of glass-fiber reinforced polyester fille with nanoclay”. Journal of Applied Polymer Science, Vol 125: pp 583-591.

[56] I Ghasemi, M Karrabi, M Mohammadi, H Azizi (2010) “Evaluating the effect of processing conditions and organoclay content on the properties of styrene=butadiene rubber/organoclay nanocomposites by response surface methodology”. eXPRESS Polymer Letters Vol. 4, No.2:62-70.

[57] S.G Lei, S.V. Hoa, M-T. Ton that (2006) “Effect of clay types on the processing and properties of polypropylene nanocomposites”. Composites Science and Technology 66:1274-1279.

[58] Sanjay K Nayak, Smita Mohanty, Sushanta K Samal (2009) “Effect of clay types on the mechanical, dynamic mechanical and morphological properties of polypropylene nanocomposites”. Polymer-Plastics Technology and Engineering 48:976-988.

[59] Yu Dong, Debes Bhattacharyya (2008) “Effects of clay type, clay/ compatibiliser content and matrix viscosity on the mechanical properties of polypropylene/organoclay nanocomposites”.composites, Part A 39:1177-1191.

[60] Ling Chen, Shing-Chung Wong, Sreekumar Pisharath (2003) “Fracture Properties of nanoclay filled polypropylene”. Journal of Applied Polymer Science, Vol 88:3298-3305.

[61] Yasser Zare, Hamid Garmabi, Farhad Sharif (2011) “Optimization of mechanical properties of PP/nanoclay/$CaCO_3$ ternary nanocomposite using response surface methodology”. Journal of Applied Polymer Science. Vol122:3188-3200.

[62] Zhu L, Xanthos M (2004) “Effects of process conditions and mixing protocols on structure of extruded polypropylene nanocomposites”. Journal of Applied Polymer Science, 93:1891-1899.

[63] Kornmann, X., Linderberg, H. and Bergund, L.A. (2001). Synthesis of Epoxy–Clay Nanocomposites: Influence of the Nature of the Clay on Structure, Polymer, 42: 1303–1310.

[64] Kawasumi, M., Hasegawan, M., Usuki, A. and Okada, A. (1997). Preparation and Mechanical Properties of Polypropylene–Clay Hybrids, Macromolecules, 30: 6333–6338.

[65] Roy, S., Hussain, F., Lu, H. and Narasimhan, K. (2005). Characterization and Modeling of Strength Enhancement Mechanism in Polymer Clay Nanocomposites, In: AIAA Conference Proceedings, Texas.

[66] Thostenson, E., Li, C. and Chou, T. (2005). Review Nanocomposites in Context, Journal of Composites Science & Technology, 65: 491–516.

[67] Schmidt, D., Shah, D. and Giannelis, E.P. (2002). New Advances in Polymer/Layered Silicate Nanocomposites, Current Opinion in Solid State and Materials Science, 6(3): 205–212.

[68] Wu, Y. T., Zhou, Z., Fan, Q. Q., Chen, L., & Zhu, M. F. (2009). Facile in-situ fabrication of novel organic nanoparticle hydrogels with excellent mechanical properties. Journal of Materials Chemistry, Vol.19, No.39, pp. 7340-7346

[69] Fu, S.Y. & Lauke, B. 1998. Characterization of tensile behaviour of hybrid short glass fibre/calcite particle/ABS composites. Compos. Part A. 29(5-6): 575-583.

[70] Haque, A., Shamsuzzoha, M., Hussain, F. & Dean, D. 2003. S2-glass/epoxy polymer nanocomposites: manufacturing, structures, thermal and mechanical properties. J. Compos. Mater. 37(20): 1821-1837.

[71] Asi, O. 2009. Mechanical properties of glass-fiber reinforced epoxy composites filled with Al2O3 particles. J. Reinf. Plast. Compos. 28(23): 2861-2867.

[72] Deniz B, Ismail HB (2007) “Modeling and optimization I: usability of response surface methodology”. J Food Eng 78:836

.....

Chapter 7

CHARACTERIZATION OF PP/HDPE/NANOKAOLINITE CLAY/E-GLASS FIBRE HYBRID COMPOSITES

Contents

7.1 Introduction

Nanotechnology will enable the development of novel materials providing the basis for the design and development of new properties and structures which will result in increased performance (e.g., nano-energetics and new types of catalysts), reduced cost of maintenance (e.g., wear reduction, self-healing and self-repair), enhanced functionality (eg. adaptive materials) and new types of electronic/opto-electronic/magnetic material properties. The reinforcement of polymers using fillers, whether inorganic or organic, is common in the production of modern plastics. Polymeric nanocomposites (PNC) represent a radical alternative to the conventional filled polymers or polymer blends. In contrast to conventional systems, where the reinforcement is of the order of microns, PNC are exemplified by discrete constituents of the order of a few nanometers (<100 nm) in at least one dimension. The small size of the fillers leads to an exceptionally large interfacial area in the composites. The interface controls the degree of interaction between the filler and the polymer and thus determines the properties. As in conventional composites, the interfacial region is the region beginning at the point in the fibre at which the properties differ from those of the bulk filler and ending at the point in the matrix at which the properties become equal to those of the bulk matrix[1]. It can be a region of altered chemistry, altered polymer chain mobility, altered degree of cure, and altered crystallinity. Interface size has been reported to be as small as 2 nm and as large as about 50 nm. Even if the interfacial region is only a few nanometer, soon the entire polymer matrix has a different behaviour than the bulk. If the interfacial region is more extended, then the polymer matrix behaviour can be altered at much smaller loadings. To implement the novel properties of nanocomposites, processing methods that lead to controlled particle size distribution, dispersion, and interfacial interactions are critical. Nanocomposites can, in principle, be formed from clays and organoclays in a number of ways including in situ polymerization, solution polymerization, and latex polymerization methods. However, the greatest interest has involved melt processing[2] because this is generally considered more economical, more flexible for formulation, and involves compounding and fabrication facilities commonly used in commercial practice. For most purposes, complete exfoliation of the clay platelets, i.e., separation of platelets from one another and dispersed individually in the polymer matrix, is the desired goal of the formation process. However, this ideal morphology is frequently not achieved and varying degrees of dispersion are more common. Melt compounding parameters like mixing temperature, time and shear rate of mixing are very important in this regard. Ghasemi and co-workers[3], Homminga *et al.*[4], Borse and kamal [5], Zhu and Xanthos[6], Modesti[7] *et al*. and Mohammed Salleh[8] have conducted studies in this effect. Out of all these melt compounding parameters, mixing temperature is the most important factor in determining the mechanical properties of nano as well as hybrid composites. Vaia and Giannelis[9] also depicted the importance of melt compounding temperature based on thermodynamic principles. In this section, the effect of mixing temperature on thermal and dynamic mechanical properties of PP/HDPE/N100A/E-glass fibre composites was analysed.

PP and HDPE are two excellent thermoplastic polymers, characterized by their outstanding cost-to-performance ratio. The commercial significance of PP has resulted in an ever increasing drive to enhance its properties further, in particular through reinforcement with various particulates, fibres and layered inorganic fillers [10-12]. HDPE also finds increasing demand in the field of packaging, defence applications etc. The effectiveness of inorganic fillers in improving the physical and mechanical properties of PP/HDPE blend strongly depends on the filler aspect ratio, size, shape, surface characteristics, interfacial adhesion and degree of filler dispersion[13]. It has repeatedly been shown that an inorganic filler such as glass fibre increases the tensile modulus of such composites, yet causes the decrease of the strength and toughness. This could be due to the stress concentration, poor fibre-matrix adhesion and confinement of the matrix molecular mobility around the rigid filler phase. Glass fibre reinforced composites have become attractive structural materials not only in weight sensitive aerospace industry but also in marine, armor, automobile, railways, civil engineering structures, sport goods, and so forth. This is attributed to high specific strength and specific stiffness of the glass fibre reinforced composites.

A relatively new development in the field of polymer composites is the introduction of clay nanoparticles (1 – 100 nm), in which small quantities of high-modulus nanoclay have been shown to give significant improvements in mechanical, barrier and thermal properties [7, 14]. Although numerous researchers have investigated individually, polymer/glass fibre-microcomposites and polymer/nanoclay composite systems, only a few investigations have been reported on polymer/gf/nanoclay hybrid composites.

The range of properties where nanoclays are expected to yield improvements over neat polymers is very wide. The advantages due to the use of nanocomposites are generally manifested in terms of improvements of the quasi-static tensile mechanical properties[15-18] and of the fracture resistance,[19-22] in an increase of the dimensional stability[23] and of the barrier properties,[24] in a better thermal degradation resistance.[25,26] Nevertheless, the mechanical properties obtained so far with polymer nanocomposites are much lower than those typically required to apply as engineering structural materials, such as advanced composites reinforced with high-performance continuous fibres[27]. In recent years, a rising interest has emerged for the development of ternary composites in which both traditional continuous high-strength micro-fibres and nanofillers are concurrently added to a thermosetting[28-31] or a thermoplastic polymer matrix[32-33].

Hybrid composites are materials made by combining two or more different types of fillers in a common matrix. Though in principle, several fillers can be incorporated into the hybrid system, a combination of only two types of filler would be most beneficial. By hybridization it is possible to achieve a balance between performance properties and cost of composites, which would not be attained otherwise[34-35]. In other words by a careful selection of reinforcements and processing techniques, it is possible to engineer the material to better suit the various practical requirements with economic benefits.

Mohan and Kanny [36] in their work, combined PP nanocomposites matrix with chopped gf using a single screw extruder in one–stage compounding. A small amount (5% fibre weight fraction) of nanoscale dispersed layered silicate was shown to enhance the degree of crystallinity and tensile properties as well as rheological and wear properties of the composites. In addition, Chandradass *et al.* [37] used 3 wt% nano fillers in a glass fibre reinforced vinyl ester matrix and studied the mechanical, dynamic mechanical and vibration properties. In both cases, the investigated properties were found to improve relative to the neat matrix and glass fibre composites. Norasmira *et al.* [38] prepared PP/clay nanocomposite systems for use as a matrix material for glass fibres composites using a twin screw extruder in a two–stage compounding. The findings were as follows:

- The aggregates and the number of platelets in the composites increase with the percentage of clay within the PP matrix.
- The thermal stability of PP/gf/nanoclay is seen to have increased by approximately 56°C than the conventional PP/gf composite.
- Tensile strength and tensile modulus of PP/gf composites decreased and increased, respectively, with an increase in fibre loading. The addition of clay nanoparticles improved these properties.
- Flexural strength and flexural modulus increased with an increase in fibre loading. The addition of clay nanoparticles further improved these properties.

Fibre-Reinforced Plastic (FRP) is a composite material made of a polymer matrix reinforced with fibres. The fibre used is glass, carbon, aramid, kevlar, paper, wood, asbestos, etc. Polymers used are thermoplastics, epoxy, vinyl ester, polyester, and phenol formaldehyde resin. FRPs commonly used in the aircraft, aerospace, automotive, marine, sports goods, home appliances and construction industries. Glass fibre reinforced polymers are having high specific strength, high specific stiffness, light weight and, corrosion resistance. They help in improved surface quality and aerodynamics, reduction in components by combining parts and forms into simpler moulded shapes, pedals can be moulded as single units combining both pedals and mechanical linkages simplifying the production and operation of the design. Since glass fibre possess inorganic nature and resin possess organic nature, in between adhesion between these two fillers will be less. In order to improve adhesion between those two, both modified and unmodified clays are mixed with PP/HDPE blend during melt compounding before the addition of glass fibre. The surface modified organoclays can act as a bridge between inorganic glass fibre and organic polymer matrix, leading to the formation of a stronger fibre-matrix interface, thereby causing an increase of the interfacial shear strength to about 30%. Concurrently, the evaluation of the fibre/matrix contact angle revealed an improved wettability between fibre and polymer matrix when organo-modified clays are added [39]. In this section the effect of surface modification of nanoclay on the thermal, crystallization, dynamic mechanical and morphological properties of PP/HDPE/nanoclay/ glass fibre composites is studied.

7.2 Methodology

Polypropylene (PP), high density polyethylene (HDPE) and nanokaolinite clays – both modified (N100A) and unmodified (N100) and E-glass fibre are the materials used for the preparation of polymer/ nanoclay/ glass fibre hybrid composites. The clay was pre dried before mixing by keeping in a vacuum oven at 70°C for 1 hour. The glass fibres were cut into pieces of approximately 6mm length (short glass fibre) before melt compounding.

The hybrid composites were prepared by melt mixing of PP/HDPE in the ratio 80/20 by weight with nanoclay and glass fibre in an internal mixer, Thermo Haake rheocord for 8 min and 50 rpm rotor speed. For evaluating the effect of glass fibre content the composite were prepared varying fibre content from 10 to 30% by wt. To study the effect of surface modification of kaolinite clay, hybrid composites were prepared with both modified and unmodified nanoclays at 2 wt% nanoclay content and compared with short fibre composite of PP/HDPE/glass fibre. To study the effect of melt compounding temperature, the mixing was carried out at three different temperatures- 150°C, 160°C and 170°C. The variation of torque with time of mixing was monitored. The torque was stabilized to a constant value in this mixing time. The resultant compound was hot pressed into thin sheets and cut into pieces. Rectangular specimens for dynamic mechanical testing were prepared by injection moulding in a semiautomatic injection moulding machine.

Melt flow index (MFI) was determined using CEAST Modular Line Melt Flow Indexer according to ASTM D 1238[40]. Thermal stability of PP/HDPE/glass fibre composites, unmodified and modified clay hybrid composites was analyzed. Thermal analysis was done in a TA-Q 600 series instrument in nitrogen atmosphere for samples of 5–7 mg size and temperature range of 400–1,020 °C at 20°C/min. The dynamic mechanical properties were determined using a dynamic mechanical analyzer [DMA; Model 800 supplied by TA Instrument]. The test sample is a rectangular strip of dimension 40 x 12 x 3.2 mm. The dual-cantilever mode of deformation was used under the test temperature range from 40 to 110°C with a heating rate of 30°C/min at a constant frequency of 10 Hz. The crystallization behaviour was analysed using DSCQ100 (TA Instruments). The morphology of the tensile fractured cross section was examined using a scanning electron microscope JEOL-JSM-6390 with an accelerator voltage of 20 kV in a vacuum atmosphere. The samples were subjected to gold sputtering prior to electron microscopy to give necessary conductivity. The samples were analyzed in a Bruker AXS D8 Advance X-Ray Powder Diffractometer (Cu Ka radiation) to find the basal spacing of nanocomposites. The samples were scanned in the range of 3° –80° at incremental step of scanning 0.02° at a wavelength of 1.5406 A°. The rheology study was carried out in Anton Paar Rheometer (MCR 102) at a temperature of 210°C, in plate type geometry (PP50). Frequency sweep tests were carried out on pure blend, nanocomposites and hybrid composites to investigate the time dependent shear behaviour of the composites. In frequency sweep tests, the materials were subjected to varying angular frequencies of 100 rad/s to 0.1 rad/s, at a constant strain of 5%. The data analysis was carried out using Rheoplus software. Amplitude sweep tests were carried out at constant angular frequency of 10 rad/sec, for the sole purpose of determining limit of (linear viscoelastic) LVE range for selected samples.

7.3 Results and discussion

In this section final characterization of hybrid composites were carried out by verifying the thermal, dynamic mechanical, crystallization and morphological properties. The major parameters considered were the effects of surface modification of nanoclay, nanoclay content and melt compounding temperature.

7.3.1 Effect of surface modification of nanoclay

The properties of short fibre reinforced polymer blends depends on the fibre matrix adhesion and compatibilization. Nanoclays are added in this regard to improve the fibre matrix adhesion and efficient stress transfer. In order to evaluate the effect of the clay addition on the fibre-matrix interfacial adhesion, single fibre micro debonding tests were performed by Dorigato *et al*. and found that organoclays increased interfacial adhesion between fibre and matrix. Surface modified clays can thus act as a bridge between inorganic glass fibre and organic polymer matrix and thus increase composite properties. In this section hybrid composites were prepared with 80/20 wt% PP/HDPE blend, 2 wt% nanoclay (both modified and unmodified) and 20 wt% E-glass fibre. PP/HDPE/20wt% gf short fibre reinforced composites were also prepared for comparison. The melt compounding was done at identical mixing conditions of 160° C, 50 rpm and 8 minutes.

Melt flow index

The MFI values of PP/HDPE/gf composites with and without nanoclay at different fibre loadings are represented in fig. 7.1. These values appear to be decreasing with increase in filler loading particularly for amino-modified clay at 20 wt% of the fibre content. This result reveals that the penetration of the polymer chains into the interlayer space of the organoclay is greater for hybrid composites compared to nanocomposites. Consequently, the interaction between the polymer chains, kaolinite sheets and fibre surface should be stronger in hybrid composites. As glass fibre content is more than optimum MFI increases as the flow behaviour changes. The findings of Y. Xu and S. Van Hoa [41] support the above results.

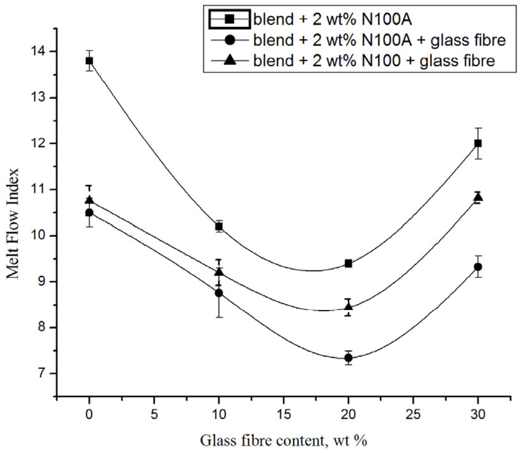


Figure 7.1 Effect of surface modification of nanoclay on MFI of PP/HDPE/nanoclay/E-glass fibre hybrid composites.

Thermal stability

Thermal stability of polymer/clay nanocomposites with short glass fibre has been analyzed and compared with that of pure polymer under non-oxidative (inert gases) conditions. In general, it has been reported that the polymer/clay nanocomposites are thermally more stable than pure polymers [42-45]. The effect of clay layers has been more explained as superior insulation and mass transport barrier against the volatile compounds generated during the decomposition of polymer under thermal conditions [46]. Also, it has been reported that clays assist in the formation of layered carbonaceous char during degradation of polymer/clay nanocomposite [47]. Clay minerals are inorganic materials and are almost stable in the temperature ranges that organic polymers are degraded into volatile compounds. Therefore in TGA experiments the clay content of nanocomposites is remains as residue after the heating program [48].

TGA thermograms of PP/HDPE/gf composite along with both modified and unmodified hybrid composites are illustrated as figure 7.2. It is clear that both modified and unmodified hybrid composites exhibit better thermal stability than PP/HDPE/glass fibre composites. The results of thermal degradation studies are summarized in table 7.1

Table 7.1 TGA results of hybrid composites with both modified and unmodified nanoclay

Samples	T_{onset} (°C)	10% Weight loss(°C)	50% Weight loss (°C)	80% Weight loss (°C)
PP/HDPE/20gf+2 wt% N100	386	446.4	460.3	502.6
PP/HDPE/20gf+2 wt% N100A	425	465.4	488.3	672.3
PP/HDPE/20gf	376	388.6	436.8	455.7

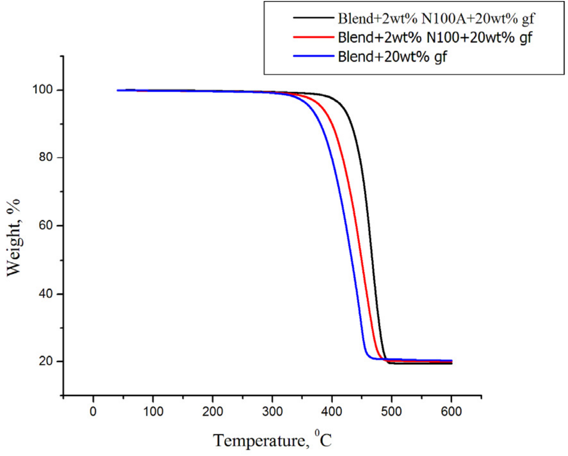


Figure 7.2 Effect of surface modification of nanoclay on thermal stability of PP/HDPE /nanoclay/E-glass fibre hybrid composites.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analyzer is used to study the relaxation in polymers. The performance of the composite under varying load condition is obtained using DMA studies. A sinusoidal varying load of frequency 1Hz is applied and temperature is increased continuously. The storage modulus of the composite was calculated under these conditions. The influence of surface modification of nanoclay to the properties of PP/HDPE/nanoclay/ glass fibre hybrid composites are studied and plotted as figures 7.3(storage modulus curve) and 7.4(tan δ curve). The highest storage modulus value was obtained for hybrid composite containing modified nanoclay (2014 MPa). This value is 24% higher than that of PP/HDPE/glass fibre reinforced composite and 114% higher than that of PP/HDPE blend.

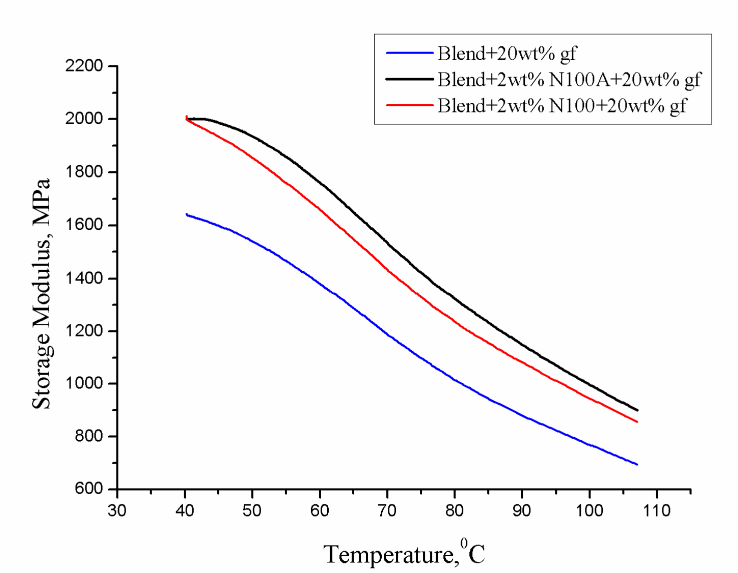


Figure 7.3 Effect of surface modification of nanoclay on storage modulus of PP/HDPE /nanoclay/E-glass fibre hybrid composites.

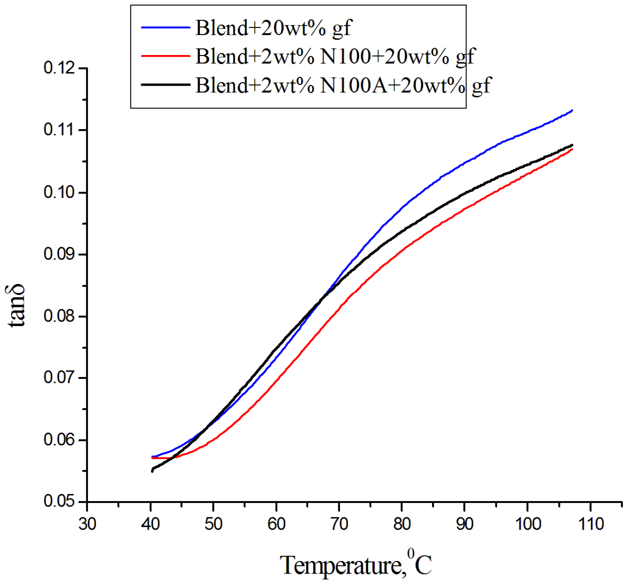


Figure 7.4 Effect of surface modification of nanoclay on damping ratio of PP/HDPE /nanoclay/E-glass fibre hybrid composites.

Kornmann *et al.* [49] reported that tensile modulus and fracture toughness were increased with increasing the clay loading. However, brittleness would limit the applications of nanocomposites. The addition of clay and glass fibre into neat polymer is expected to develop high performance composites with high strength and toughness.

Table 7.2 Storage modulus of PP/HDPE/nanokaolin composites prepared at different surface modification of nanoclay

Sample	Storage Modulus at 40°C (MPa)	Storage Modulus at 60°C (MPa)	Storage Modulus at 80°C (MPa)	Storage Modulus at 100°C (MPa)
PP/HDPE +20wt% gf	1644	1381	1015.5	768.4
PP/HDPE +2wt%N100+20wt% gf	2003	1762	1322.5	996.2
PP/HDPE +2wt%N100A+20wt% gf	2014	1661	1236	945

The storage modulus of hybrid composite at different temperatures with modified and unmodified nanoclay is illustrated in Table 7.2. The above observations are supported by the improvements recorded in tensile modulus and strength. This improvement is due to the increase in polarity of the matrix which enhances the dipole and hydrogen bonding interactions thus improving dispersion, degree of intercalation and interfacial fibre-matrix adhesion.

Differential scanning calorimetry (DSC)

The study of degree of crystallinity assumes particular significance because higher crystallinity, in general, increases modulus and yield stress but reduces toughness. The change in percentage crystallinity, and structural characteristics induced by clay are important in understanding the deformation behaviour. To be relevant to industrial processing, it is desirable to study the crystallization of nanocomposites under non isothermal conditions. Molecular interactions between the polymer and the surface of the nucleating agent must be operative to increase the rate of crystallization and temperature at which the maximum rate occurs upon cooling from the molten state [50]. These polymer-surface interactions reduce the interfacial free energy barrier for spontaneous nucleation. When the nucleation induction period is shorter and the number of primary nucleation sites increases, the overall rate of crystallization increases [51]. The DSC heating and cooling scans of the hybrid composites of PP/HDPE are shown in figures 7.5 and 7.6. As seen in the figure, the temperature of crystallization is increased on the addition of nanoclay and glass fibre and this indicates that the presence of nanoclay and glass fibre synergistically enhances the crystallization temperature and strength of hybrid composites. The melting temperature on the other hand is not much influenced on the addition of the fillers in the polymer blend.

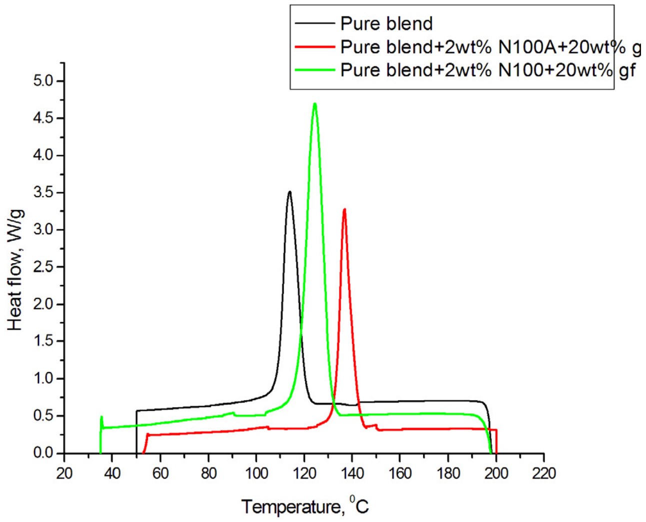


Figure 7.5 DSC cooling scan curves of pure PP/HDPE, and its hybrid composites

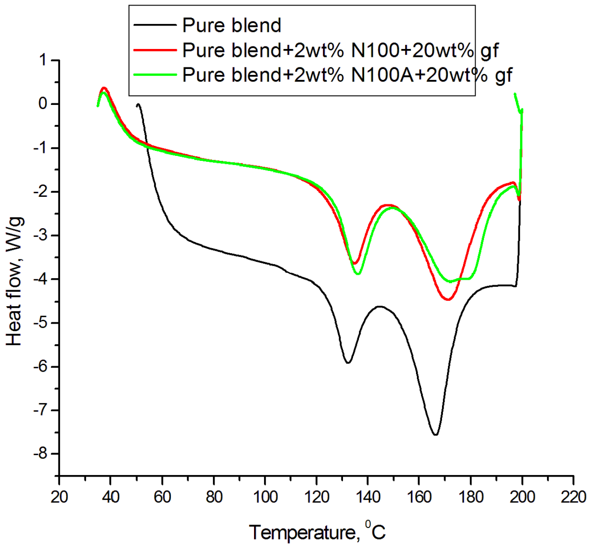


Figure 7.6 DSC heating scan curves of pure PP/HDPE, and its hybrid composites

Dynamic rheological analysis (DRA)

The response of a pure elastic solid to applied stress is expressed by Hooke's law, which states that the strain is proportional to the applied stress.

Similarly, pure Newtonian fluids have been shown to follow a simple relation, which states that the rate of strain is proportional to the stress applied on the fluid. Polymers in general, exhibit an intermediate behaviour and are termed as viscoelastic. The rheological properties of the polymers are strongly dependent on temperature, shear rate and time scale of deformation. The simplest type of viscoelastic behaviour is linear viscoelasticity. This type of behaviour, is observed when both the deformation and deformation rate are sufficiently small, such that the molecules are disturbed from their equilibrium configuration and entanglement state to a negligible extent. Though this kind of deformation is normally not encountered in polymer processing, linear viscoelasticity is normally used for characterizing the molecules, for resin quality control [52]. Since the rheological properties are closely related to the molecular structure, rheological measurements are an important tool for building up an understanding of the molecular structure of the polymers. Rheological measurements on blends, however, are usually done in the linear viscoelastic domain, such as small amplitude oscillatory shear experiments to obtain useful information on blends. Further, rheological models have been developed using linear viscoelastic data to relate microscopic and macroscopic quantities. These models are assessed based on the assumption that for small strain the morphology of the blends would not change and thus properties such as storage modulus and loss modulus would give us an idea about the blend characteristics [53].

The influence of surface modification of nanoclay on the storage modulus is illustrated in figure 7.7 and complex viscosity of hybrid composite is illustrated in table 7.3.The hybrid composites produced with unmodified nano-platelets have a lower modulus and a lower viscosity than those based on organically modified platelets. This is due to the larger amount of multi-platelet stacks in the N100 based nanocomposite, which were also observed in TEM. This situation may also occur during the formation of hybrid composites. In N100A based nanocomposites the melt yield stress increases rapidly at 2 wt% nanoclay, suggesting a strong structure of interacting particles and a synergistic effect. The TEM images represented in Chapter 3 also support these observations.

Table 7.3 Complex viscosity data of short fibre composites and hybrid composites

Sl No	Sample	Complex Viscosity, Pa.s			
		at 100 (rad/s)	at 10 (rad/s)	at 1(rad/s)	at 0.1 (rad/s)
1	Blend+ 20wt% gf	385	1090	2210	3920
2	Blend+ 20wt% gf+ 2wt% N100	483	1510	3310	5970
3	Blend+ 20wt% gf+ 2wt% N100A	492	1460	2890	4470

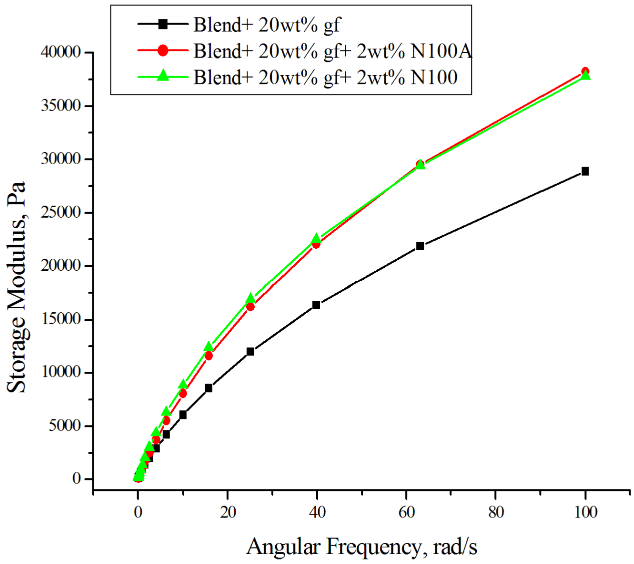


Figure 7.7 Effect of surface modification of nanoclay on storage modulus of PP/HDPE/nanoclay/E-glass fibre hybrid composites

The variation of storage modulus with frequency for the hybrid composites containing 20wt% of glass fibre and various levels of unmodified nanoclay are shown in figure 7.7. The inclusion of glass fibre increases the storage modulus of pure blend as illustrated in the figure 7.8. The composite containing both glass fibre and nanoclay (hybrid composite) show a higher storage modulus than both nanocomposite and microcomposite in the entire frequency range (0.1 rad/s to 100 rad/s). At higher frequencies this difference becomes evident. In composites containing a hybrid of nanoclay and glass fibre, with increasing nanoclay content, storage modulus first increases, reaches an optimum value and then decreases. This expresses that nanoclay has a major share in increasing storage modulus, E' and also that a synergistic effect between nanoclay and glass fibre exists at a certain ratio of filler loading.

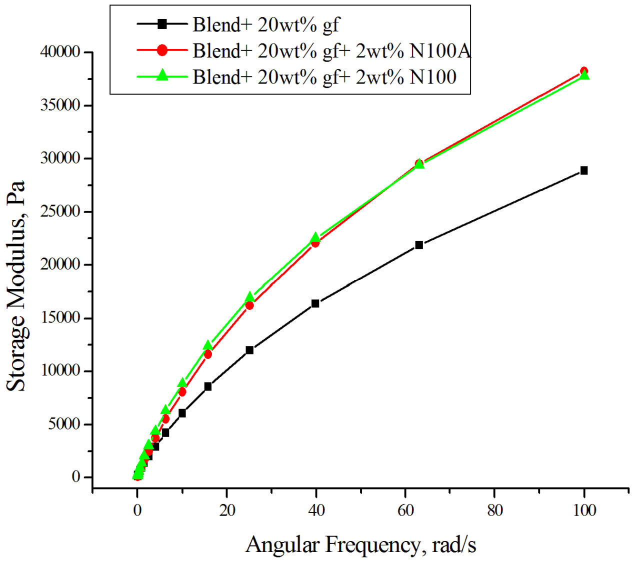


Figure 7.8 Effect of clay loading on storage modulus of PP/HDPE/N100/E-glass fibre hybrid composites

In figure 7.9, the variations of complex viscosity η, with frequency on a log scale for the hybrid composites are compared with that of a micro composite. As it can be seen, for all composites, η decreases with increasing frequency. Also, hybrid composites have higher η than micro composite. It has been well established that long chain-branched molecules are more compact and less liable to entanglements resulting in lower viscosity and melt elasticity. Both micro and hybrid composites display non-Newtonian behaviour in almost the whole range of shear rate.

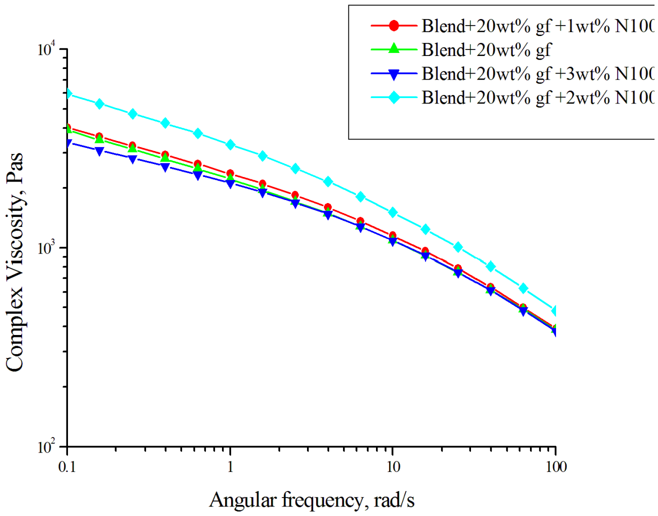


Figure. 7.9 Effect of clay loading on complex viscosity of PP/HDPE/N100/E-glass fibre hybrid composites

The viscosity continuously decreases with increasing shear rate; i.e., the shear-thinning effect occurred for all the systems, following the power law. This behaviour is typical of polymer melts, coming from the disentanglement process and the increase in the average end-to-end distance of polymeric chains caused by shearing. The storage modulus and complex viscosity increase with the addition of nanoclay and glass fibre, which is attributed to the strong interaction between polymeric matrix and silicate layers. The low viscosity at high shear rate may also be associated with the slippage of polymer chains over the nanoclay platelets.

A similar trend as that of hybrid composites containing unmodified clay is exhibited by hybrid composites containing surface modified nanoclay. (figures 7.10 and 7.11). The storage modulus of the nanocomposites is higher than that of the microcomposites. This is probably caused by the surface area of the nanoparticles, which is much larger than that of the micro-particles. This could slow down the movement of the polymer chains in the melt. Hence, the complex viscosity also increases with the incorporation of nanofillers. The high apparent yield stress at these high concentrations is an indication of such a strong structure in the melt in the presence of organically modified nanoclay. When forced to flow, the nanocomposites occur as strongly shear thinning, because of the breaking up of the structure. This higher modulus is accompanied by a stronger increase in melt viscosity. The particle shape and aspect ratio have a strong influence on both the modulus in the solid state and the complex viscosity. The modulus increase is higher for platelets than for fibres for the same volume fraction, because the platelets reinforce in two directions instead of one. The viscosity increases less for platelets than for fibres which makes the hybrid composites more suitable for processing complex structures[54-56].

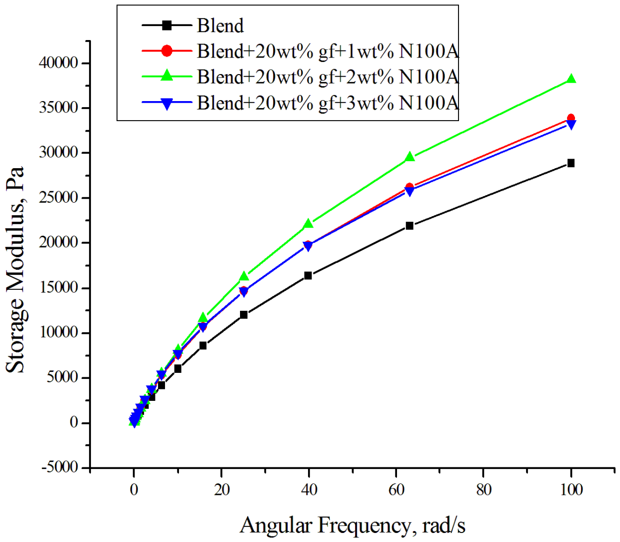


Figure.7.10 Effect of clay loading on storage modulus of PP/HDPE/N100A/E-glass fibre hybrid composites

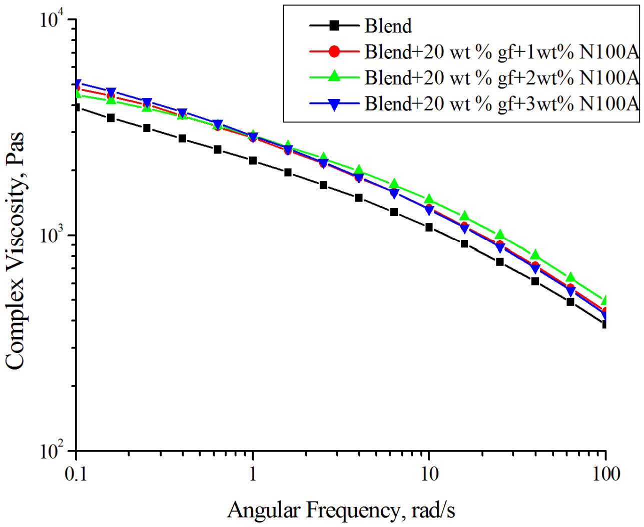


Figure 7.11 Effect of clay loading on complex viscosity of PP/HDPE/N100A/E-glass fibre hybrid composites

The measurements of rheological properties are important to understand the processability of nanocomposites, as well as indicating the strength of polymer-layered silicate interactions and the structure-property relationship in nanocomposites. This is because the rheological behaviour is strongly influenced by nanoscale structure and interfacial characteristics [57]. Under certain conditions, the rheological behaviour of the nanocomposites can vary, controlled by the dispersion degree (at constant loading), organoclay content, or the procedure of preparation. This indicates that optimisation of the fabrication conditions of the nanocomposites is essential [58]. Significance of linear viscoelastic range (LVR) is very high in determining the range of processibility of a material. Linear viscoelastic range is the range of melt operating temperature and processing condition where the material exhibits a Newtonian behaviour in stress versus strain. The plateau region, where storage modulus is independent of strain amplitude is the LVR. In this region the internal structure of the polymer is not affected by shear forces, so storage modulus (E'), loss modulus (E") and complex viscosity (η^*) are independent of imposed strain. The configuration of the macromolecules is unperturbed by the flow history [59]. It means that the microstructure of the material is not affected by shear alignment during the experiment. G′ has been used here because it is the rheological function most sensitive to changes in the mesoscopic structure of the nanocomposite [60, 61].

Dynamic strain sweep measurements to determine the LVR were performed at 175° C and a frequency of 1 rad/sec. The figures showed that the LVR is sensitive to the presence of the organoclay (figure 7.12 and figure 7.13). But in the presence of E-glass fibre, the linear viscoelastic range is greatly decreased (figure 7.14). This may be due to the presence of microfiller. Similar findings were also reported by other research groups [58, 62].

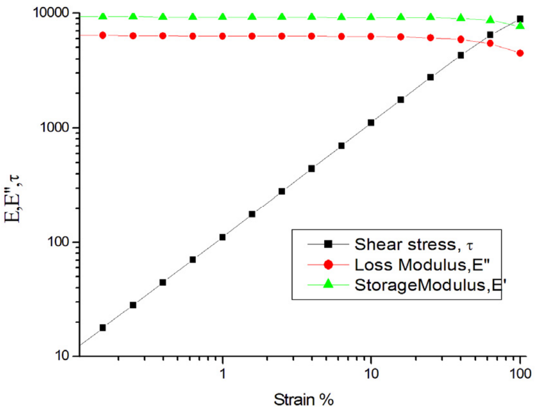


Figure 7.12 Linear viscoelastic range of PP/HDPE blend

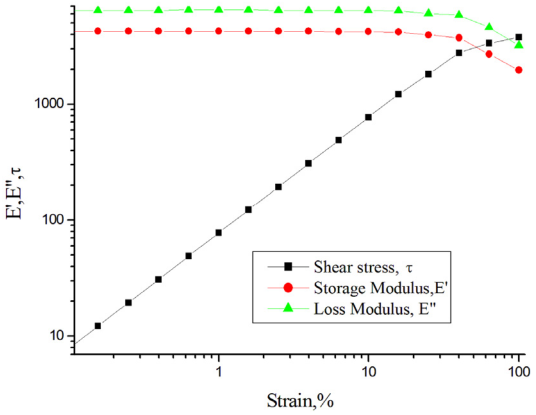


Figure 7.13 Linear viscoelastic range of PP/HDPE/N100A nanocomposite

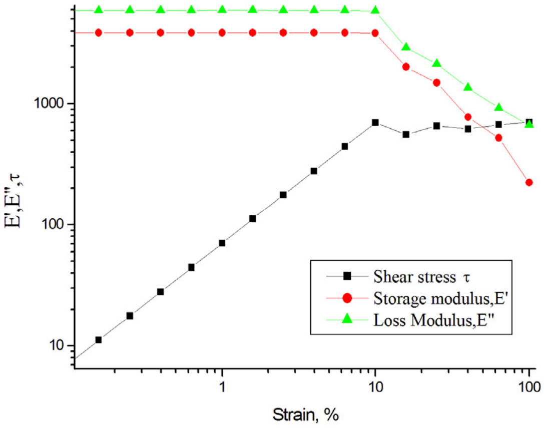


Figure 7.14 Linear viscoelastic range of PP/HDPE/2 wt% N100A/20 wt% E-glass fibre hybrid composites

X-ray diffraction (XRD)

The intensity and special characteristics of X-ray diffractograms is generally taken as a measure of classifying the microstructure as either intercalated or exfoliated. X-ray signals are highly qualitative in nature and strongly influenced by the sample orientation of platelets, as well as by defects present in the crystal structure of kaolinite clays. Thus, a classification of nanocomposite microstructure based on the intensity may prove to be faulty, but it is quite possible for there to be significant amount of exfoliation present if there is a shift in 2θ and increase in d spacing values [63].

Figure 7.15 depicts XRD patterns of unmodified clay (N100), amino modified clay (N100A), PP/HDPE/nanoclay/glass fibre hybrid composites reinforced with both unmodified and amino-modified nanokaolinite clays at 2 wt%. The original basal reflection peaks for N100 and N100A are 12.4° and 12.275°, which correspond to intergallery spacing of 7.09 and 7.204 nm respectively. Characteristic peak for PP/HDPE/N100/gf hybrid composites is 10.729° corresponding to a d-spacing of 8.239 nm and that of PP/HDPE/ N100A/gf hybrid composites is 10.658° and has a d-spacing of 8.29 nm. The increase in d spacing in PP/HDPE/N100A/gf hybrid composites indicates that some PP/HDPE molecular chains are intercalated between the clay galleries, forming an intercalated structure.

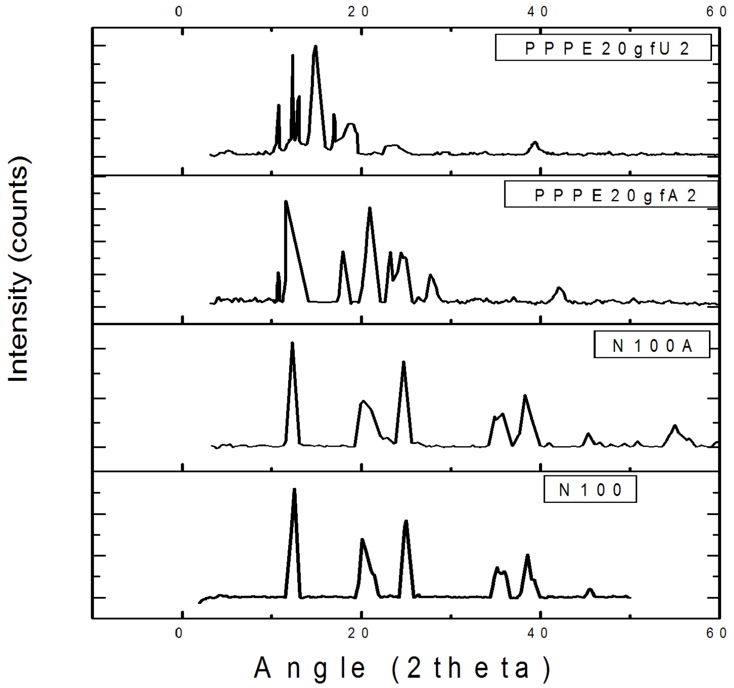


Figure 7.15 XRD patterns of nanoclay (N100 and N100A) and their hybrid composites

Scanning electron microscopy (SEM)

Scanning electron microscopy is an effective means for the morphological investigation of composites. The scanning electron micrographs (SEM) of hybrid composites of PP/HDPE blend modified with nanoclay and glass fibre is depicted in figures from 7.16 to 7.19. The SEM image clearly reveals that there is less fibre matrix adhesion in PP/HDPE/N100/gf composites as indicated by many holes of fibre pull out. But in figure 7.18, broken fibre ends are seen and fibres are well embedded in the matrix. The enhanced interfacial fibre matrix adhesion has contributed to the significant increase in synergism and mechanical and thermal properties. Also, clay particles are effectively dispersed in hybrid composites containing modified nanoclay particles[64]. Studies of the fracture surface SEM images of PP/nanoclay/glass fibre reinforced composites reported similar results.

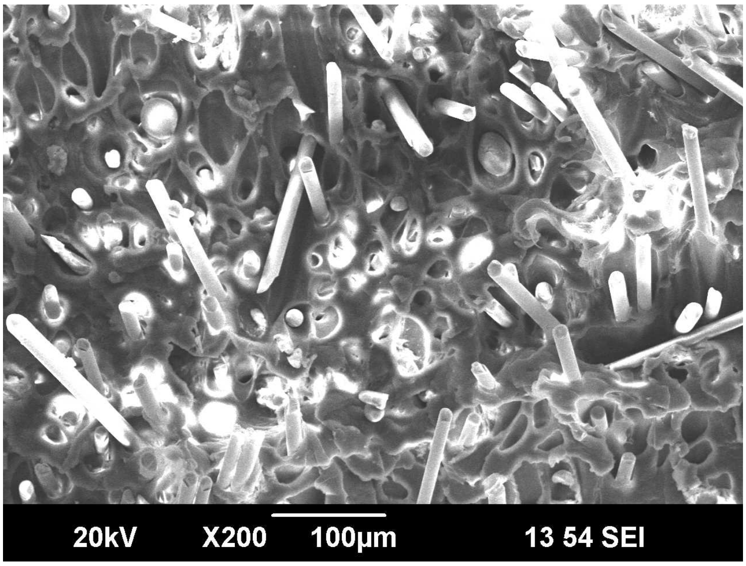


Figure 7.16 SEM image of PP/HDPE/N100/gf composites

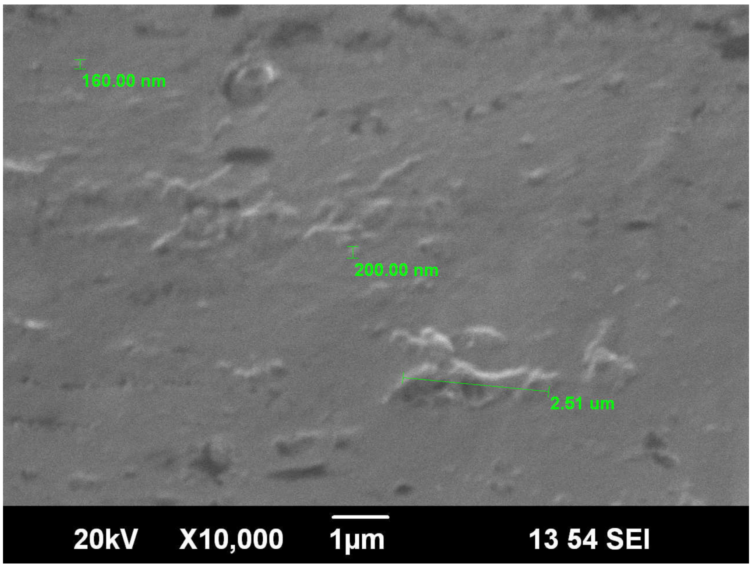


Figure 7.17 SEM image of PP/HDPE/N100/gf composites at higher magnification

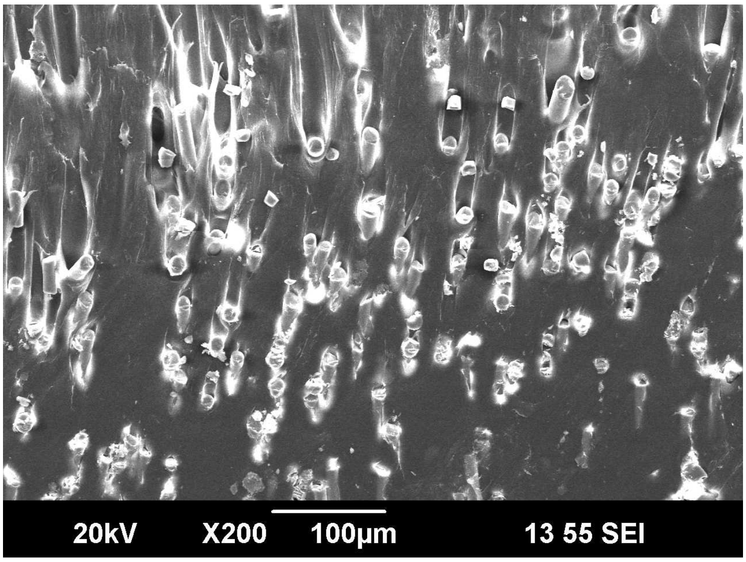


Figure 7.18 SEM image of PP/HDPE/N100A/gf composites

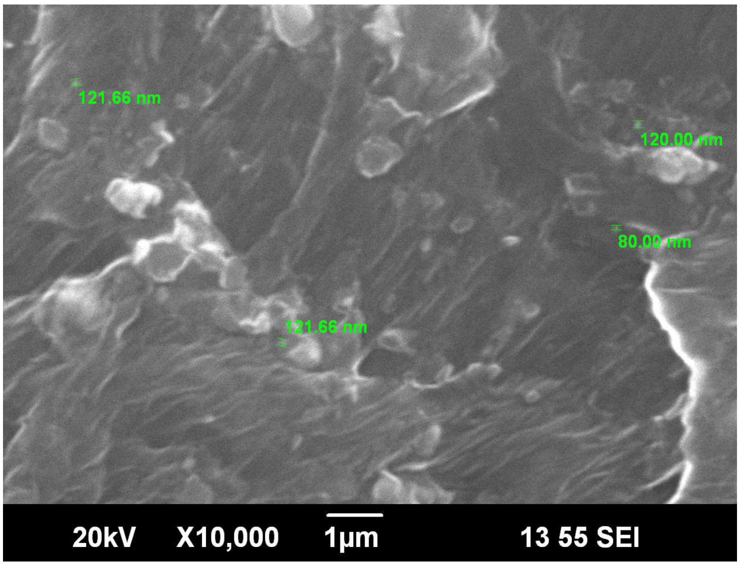


Figure 7.19 SEM image of PP/HDPE/N100A/gf composites at higher magnification

7.3.2 Effect of glass fibre content on PP/HDPE/nanoclay/E-glass fibre hybrid composites

The short glass fibre reinforced composites increase the stiffness and give superior properties but only at higher fibre loadings. This will alter basic polymer properties and reduce toughness and mouldability. In this regard, the incorporation of nanoclay into PP/HDPE/glass fibre composite resulting in the formation of hybrid will be a better option. With the use of nanoclay, the improvement in mechanical properties for a variety of polymers can be achieved at very low filler contents (<=20 wt%), which is far less than those using traditional micro-scaled fillers (approximately 30-60 wt%). Usually, clays are added to thermoplastic polymer matrices to reduce cost but currently modified nanoclays have been used as reinforcing agent to improve the properties of the material. Nanoclays are known to increase the modulus, heat distortion temperature, flame retardancy and dyeability of thermoplastic materials with a reduction in other properties like impact strength. This can be rectified by adding short fibres into the same matrix which improve stiffness and strength. The simultaneous use of both clay and fibre fillers in so-called hybridization, leads in many cases to synergistic effects, improving properties such as wear resistance, stiffness, fracture toughness, dynamic response etc.[65-67] Effect of fibre content on thermal and dynamic mechanical properties of hybrid composites is proposed to be investigated in the study.

Thermal stability

Thermal properties are important for determination of the processing conditions and appropriate use of temperatures. The thermal stability of polymer composites is generally estimated from the weight loss upon heating, which results in the formation of volatile products. The improved thermal stability in the polymer nanoclay composites is due to the clay platelets that hinder the diffusion of volatilities and assist formation of char after thermal decomposition. PP/HDPE/N100A/gf composites show enhanced thermal stability at 20 wt% glass fibre composition (figure 7.20). At 30 wt% filler composition, the thermal degradation profile is a smooth curve, the onset and complete degradation cannot be identified. This may be due to agglomeration and less homogenous dispersion of filler particle at higher filler loadings. Also there is more amount of residue present in the case of higher filler loadings. The formation of residue and char may be the reason for enhanced thermal stability when the filler content is increased from 10 to 20 wt% of glass fibre. Norasmira *et al.*[38] studied the thermal analysis of PP/nanoclay/glass fibre composites and reported similar results.

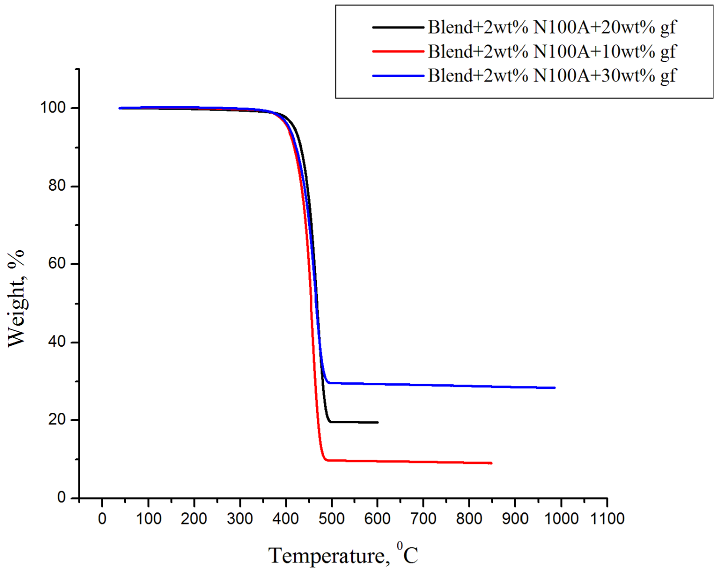


Figure 7.20 **TGA thermograms of PP/HDPE/N100A/gf composites at various micro filler loadings.**

Dynamic mechanical analysis (DMA)

The effect of microfiller content on the storage modulus of nanoclay (both N100A and N100) and gf-filled hybrid composites having 10wt%, 20wt%, and 30wt% loading levels is presented in figures 7.21 and 7.22, respectively. A general trend of increase of the storage modulus with increased filler content in the composites is observed. E′ is more associated with the molecular elastic response of the composites, indicating the stiffness of the material. The increase of E′ with increased filler content was due to mechanical limitation posed by increasing filler concentration embedded in the viscoelastic matrix. The E′ decreased with temperature increase and converged to a narrow range at higher temperatures. The reduction of E′ with increasing temperature was due to the softening of the matrix and initiation of the relaxation process [68].

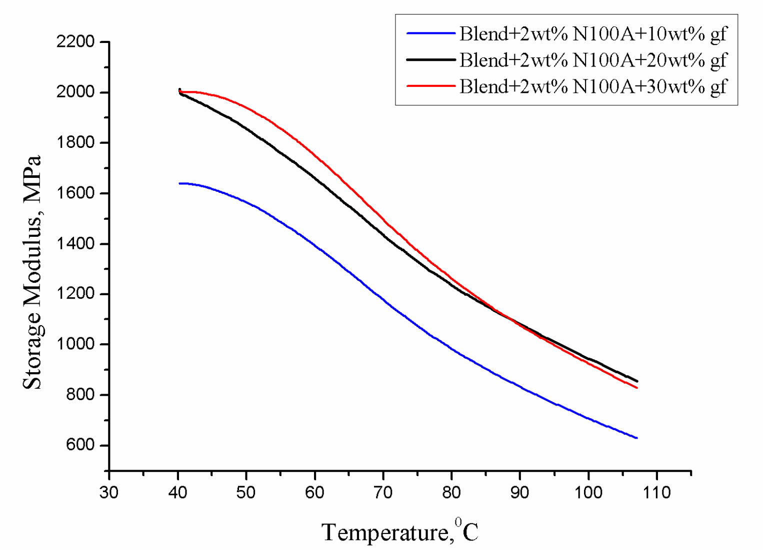


Figure 7.21 Effect of glass fibre content on storage modulus of PP/HDPE/N100A/gf composites.

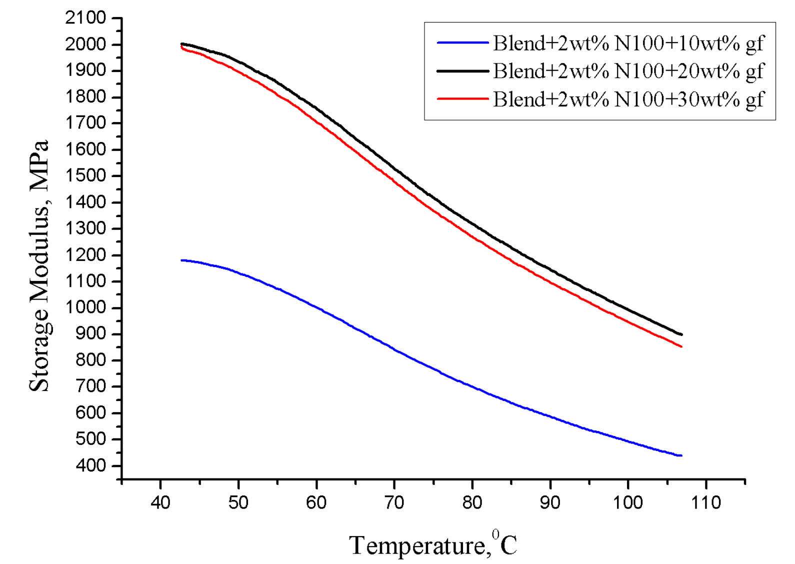


Figure 7.22 Effect of glass fibre content on storage modulus of PP/HDPE/N100/gf composites.

The loss modulus is a measure of the absorbed energy due to the relaxation and is associated with viscous response or the damping effect of the material. Effect of varying filler contents and temperature on loss modulus of the composites on loss modulus is plotted in (figures 7.23 and 7.24). E" increase with the increased filler concentration and had a peak in the transition region around 50°C. This relaxation peak is known as α-relaxation of polymer [69], which is related to a complex multi-relaxation process associated with the molecular motion of the PP/HDPE crystalline region[70, 71]. The E″ at this relaxation temperature is markedly increased with the increase of filler loading level. The presence of filler in the plastic resin reduces the flexibility of the material by introducing constraints on the segmental mobility of the polymer molecules. The α-relaxation peaks of gf-filled composites at 20 wt% shift to the higher temperature region as compared to that at 10 wt%.

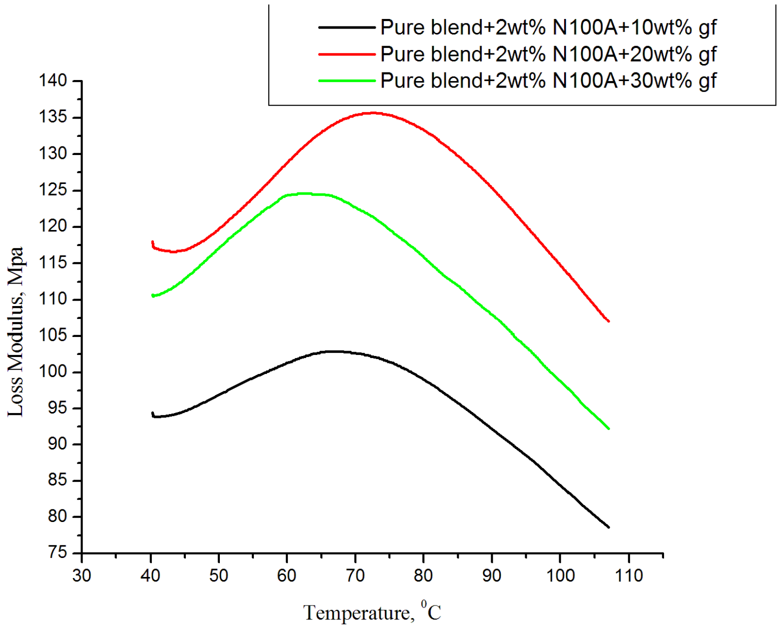


Figure 7.23 Effect of glass fibre content on loss modulus of PP/HDPE/N100A/gf composites.

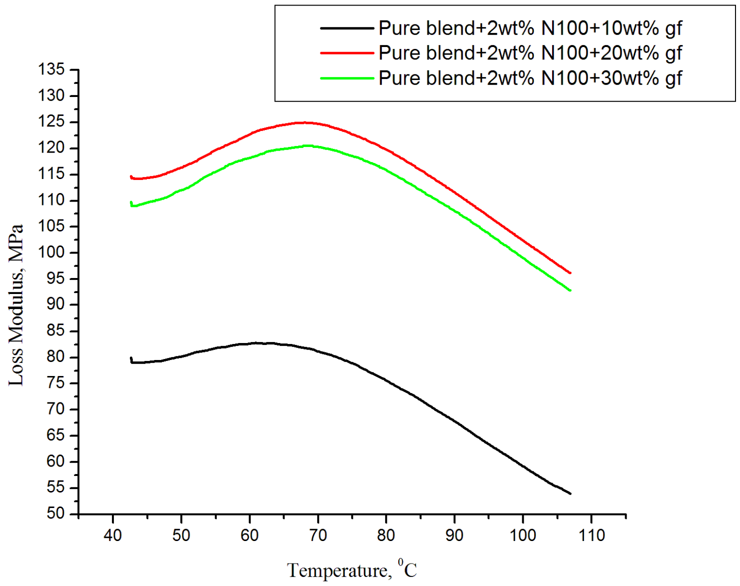


Figure 7.24 Effect of glass fibre content on loss modulus of PP/HDPE/N100/gf composites.

The tan δ, damping factor, is a ratio of the loss modulus to the storage modulus. The parameter is independent of the material's stiffness and is widely used to study visco-elastic response of the materials. For gf-filled hybrid composites, the damping curves shift toward lower values as the filler content level increases. This indicates that the damping effect reduced with the increased filler content in the matrix. The result suggests that certain degree of interfacial bonding existed between the fillers and matrix in gf-filled hybrid composites. The higher glass fibre levels induce a better fibre packing in the matrix and result in more efficient stress transfer from the resin matrix to the fibres, leading to decreased damping effect. Composites show interfacial adhesion, leading to change in the damping effect. At further increased level of fibre content, tan δ again increases due to agglomeration. The results of modified and unmodified nanoclays are shown in figures 7.25 and 7.26

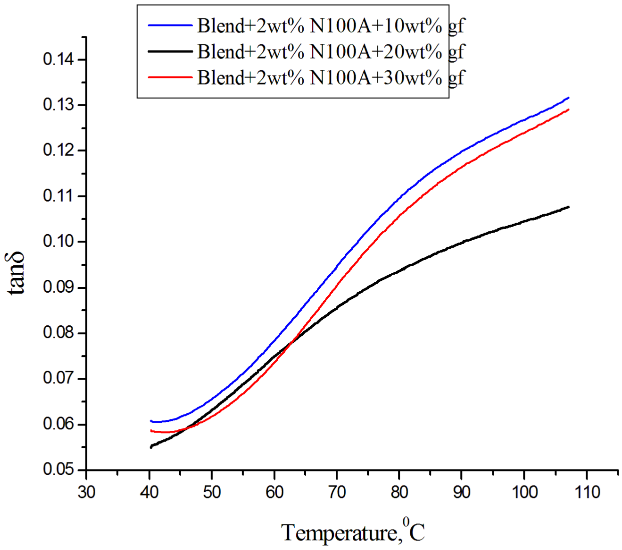


Figure 7.25 Effect of glass fibre content on damping ratio of PP/HDPE/N100A/gf composites.

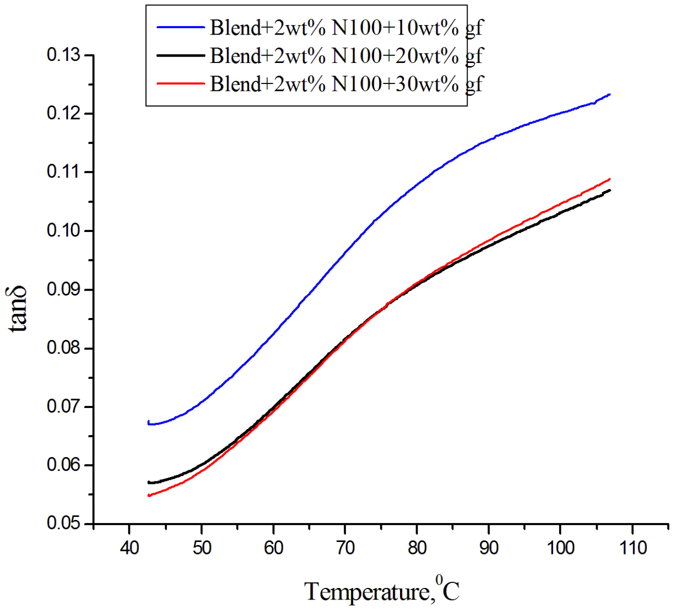


Figure 7.26 Effect of glass fibre content on damping ratio of PP/HDPE/N100/gf composites.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry is one of the most widely accepted methods of thermal analysis for studying the crystallization characteristics of polymers and their composites. The materials undergo temperature changes, their chemical and physical properties are also changed, detected by transducers, which convert the changes into electrical signals that are collected and analyzed to give thermograms. The crystallization and melting behaviour of hybrid composites during heating and cooling scans are depicted in figures 7.27 and 7.28. Two crystallization peaks are observed showing immiscibility of the blend. The nucleating power of nanoclay is not pronounced in the hybrid blend samples. The crystallization behaviour of hybrid composite is more complex due to existence of a second crystallizing or non-crystallizing component.

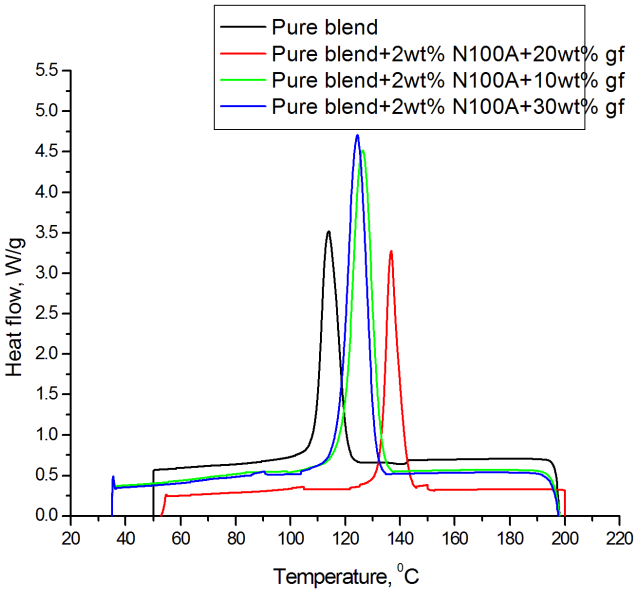


Figure 7.27 **DSC cooling scan curves of pure PP/HDPE, and its hybrid composites with modified nanoclay, at various glass fibre loadings**

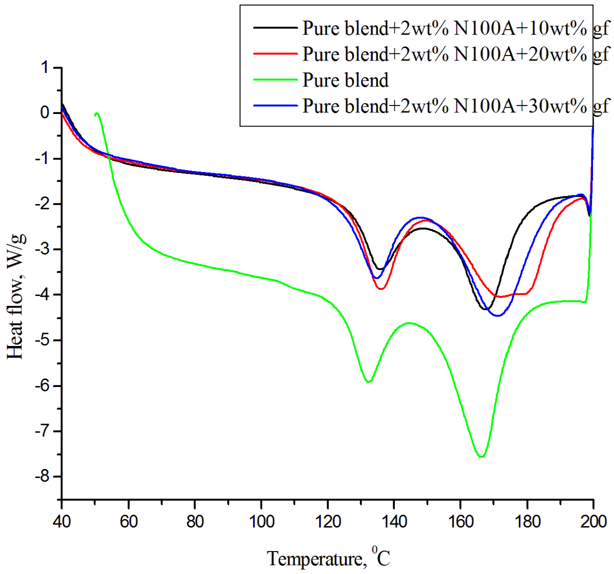


Figure 7.28 **DSC heating scan curves of pure PP/HDPE, and its hybrid composites with modified nanoclay, at various glass fibre loadings**

Dynamic rheological analysis (DRA)

By means of rheological measurements, some valuable and pertinent information responsible for the evolution of morphology and structure development, dealing with these polymer systems can be obtained. Also the corresponding results are in favour of designing and preparing novel polymer-based composites and functional materials. Although rheological behaviour of blend and nanocomposites are studied by many researchers [72-75], the same information of hybrid composite containing both micro and nano fillers are scarcely evaluated. Hence in the following section, the rheological behaviour of both nano and hybrid composites are studied.

Effect of adding short glass fibre on the rheological properties of PP/HDPE blend is depicted in figures 7.29 and 7.30. In figure 7.29, the variations of storage modulus with frequency on PP/HDPE blend containing different amount of E-glass fibre is manifested. As the fibre content increases, the storage modulus and hence strength increases and after 20wt% gf level the modulus slightly decreases. Based on the above observation, PP/HDPE blend containing 20wt% glass fibre is selected as the optimum micro composite for the further study and for the preparation of hybrid composite.

In figure 7.30 the complex viscosity of above mentioned composites are plotted against frequency on a log-log plot. As the fibre content increased from 10 wt% to 20 wt%, the viscosity increases showing more enhancement in mechanical properties. There is no significant increase in viscosity on further increase in glass fibre content, which may be due to improper dispersion and fibre-matrix adhesion at high filler content.

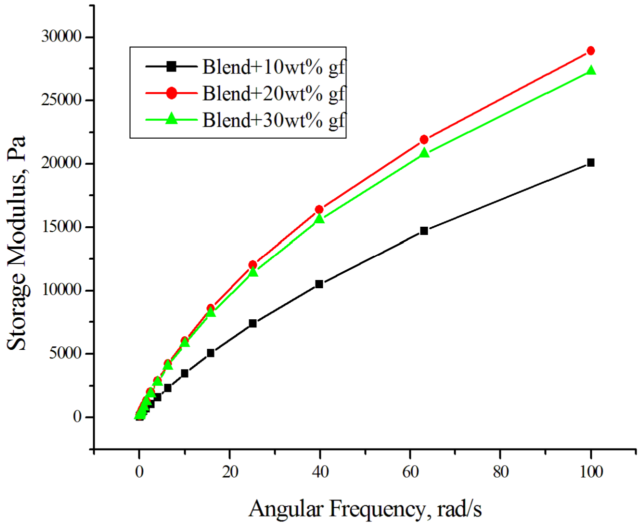


Figure 7.29 **Effect of filler content on storage modulus of PP/HDPE/E-glass fibre micro composites.**

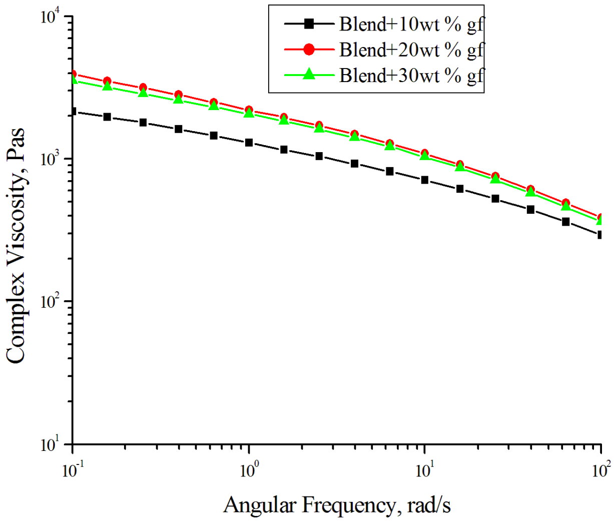


Figure 7.30 **Effect of filler content on complex viscosity of PP/HDPE/E-glass fibre micro composites.**

Scanning electron microscopy (SEM)

SEM analysis is performed to study the effect of filler content on the morphological properties of PP/HDPE blend. As already discussed, the inclusion of modified nanokaolinite clay ensures better dispersion and compatibility in the PP/HDPE blend. This improves the mechanical and thermal properties of polymer matrix. The inclusion of E-glass fibre into the polymer clay matrix lead to significant change in morphological properties and is illustrated in the hybrid composite containing 10wt% glass fibre (figure 7.31). More amount of matrix is not occupied by fibre and this result in less efficient stress transfer between filler and matrix. As the glass fibre content is increased from 10 wt % to 20 wt% (figure 7.32) polymer matrix is optimally filled with fibre and there is strong filler-matrix adhesion that results in enhancement of composite properties. As the fibre content is further increased to 30 wt% (figure7.33), the filler is not fully enveloped by polymer matrix and there is fibre pullout seen in the morphological images.

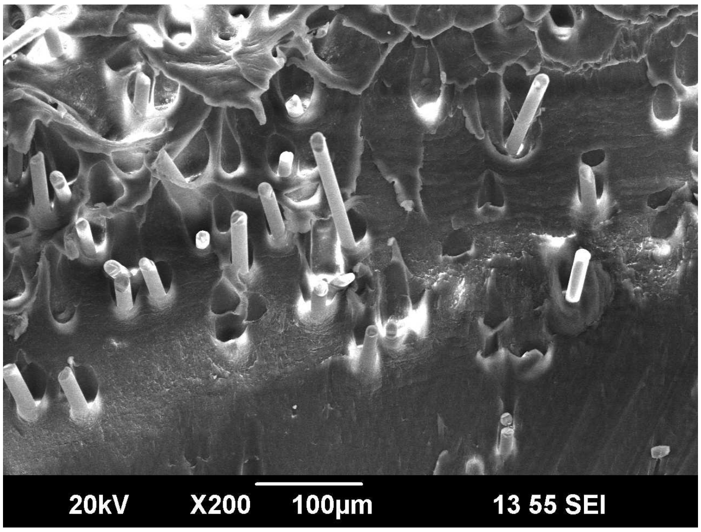


Figure 7.31 SEM fracture surface image of PP/HDPE/N100A/10wt% gf hybrid composites

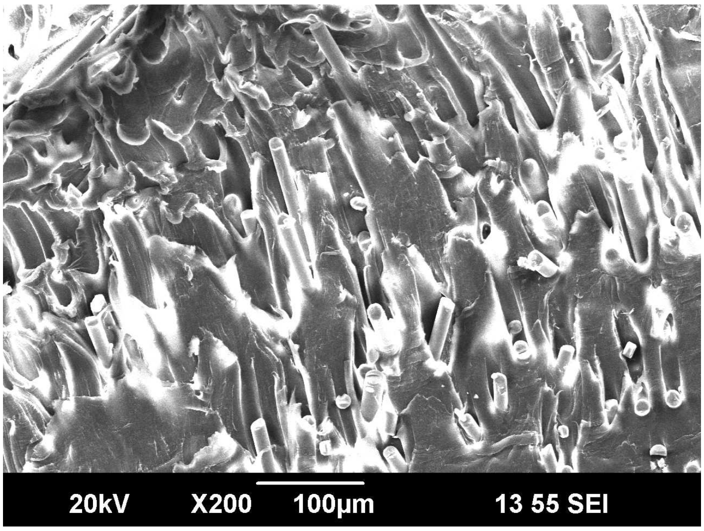


Figure 7.32 SEM fracture surface image of PP/HDPE/N100A/20wt% gf hybrid composites

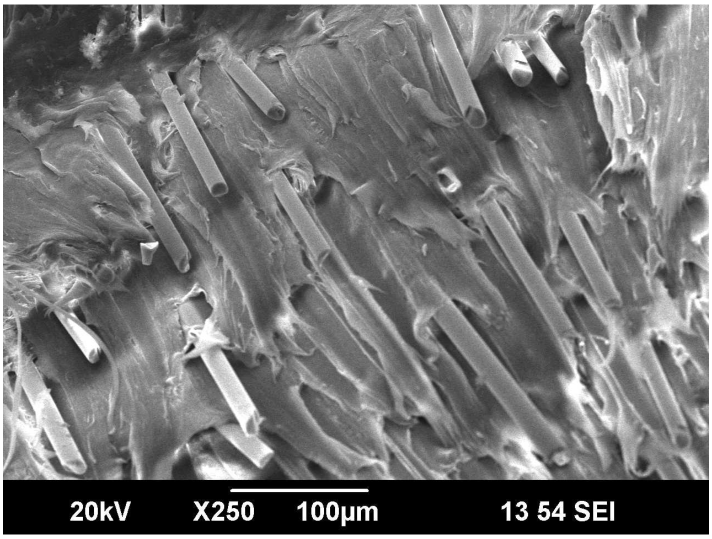


Figure 7.33 SEM fracture surface image of PP/HDPE/N100A/30wt% gf hybrid composites

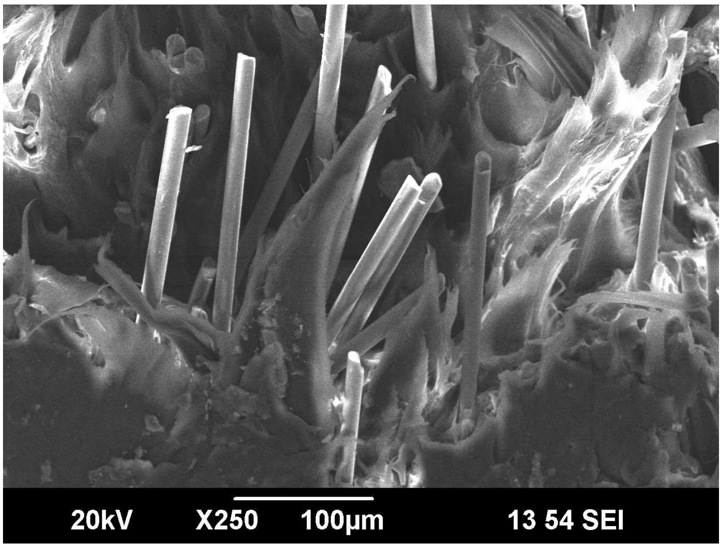


Figure 7.34 SEM fracture image of PP/HDPE/N100A/30wt% gf hybrid composites-another view

7.3.3 Effect of melt compounding temperature on the properties of hybrid composites

Nanoscale dimensions can increase significantly the physical interactions, physico-chemical and chemical interfaces in materials. The morphologies obtained for the nanocomposites and the ability to modify the interfaces are essential to maximize the properties. For all charges, surface treatment and mixing are key points dictating the performance of nanomaterials. As we have seen in the previous sections, the melt compounding temperature is a significant variable that determine the properties of the hybrid composite. In this section the influence of melt compounding temperature on thermal and dynamic mechanical properties of PP/HDPE/nanoclay/gf hybrid composite is analysed

Thermal stability

The improvement in the quality of fillers and progress in production processes will lead to an increasing diffusion of such nanocomposites in a wide range of applications with strong requirements. Since the first studies on organomodified clays[76, 77], various studies have highlighted the interest of various types of nanoparticles, as nano-oxides [77], polyorganosesquioxanes [78], carbon nanotubes [79], natural organo-modified phyllosilicates, delaminated talc and kaolin submicron[80]. The enhanced thermal resistance in such composites are attributed to the formation of a compact and superficial layer of clay shells during the exposure to heat, which thus act as a thermal barrier. The thermal behaviour of the matrix will obviously be dependent upon the way the nanocomposites fillers are dispersed within such matrix. Fillers should be evenly dispersed to confer temperature-resistant properties. The mechanism of action according to which the nanoparticles confer heat-resistant properties is attributable to the accumulation of inorganic material upon the composite surface together with the formation of char. This shield will reduce the material and heat transfers between the heating source and the polymer. It then reduces the radiative flux directed towards the substrate by diffusing the incident radiation towards the gaseous phase and as a result, limits the degradation rate of the material [81]. The synergy existing between the traditional reinforcements, such as glass fibres and nanoclays, is of particular interest. The association of glass fibres and nanoclay produces a much more rigid material with a larger temperature range than the traditional composite material that has the same reinforcement rate [82]. The dispersion of nanoclay in hybrid composite is dependent on the dispersion of nanoclay in the polymer matrix, which in turn will depend on the processing conditions. Hence, in this section, the effect of melt compounding temperature on the thermal stability of PP/HDPE/2 wt% amino modified nanoclay/20 wt% E-glass fibre (fig.7.35) is illustrated.

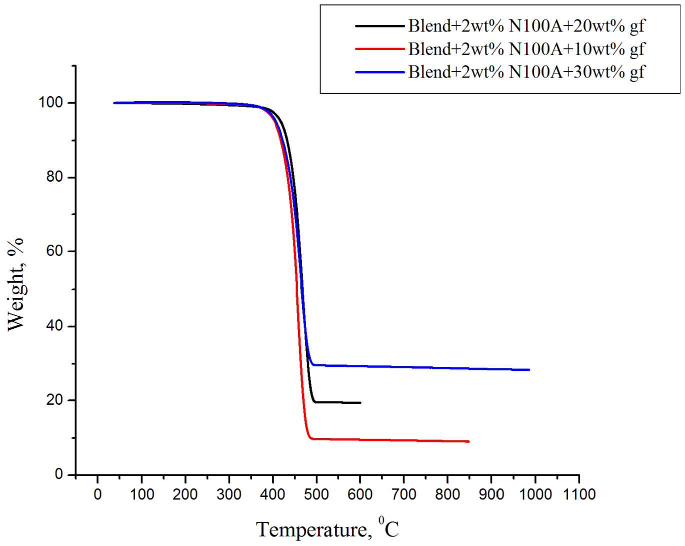


Figure 7.35 Effect of melt compounding temperature on thermal stability of PP/HDPE/N100A/gf hybrid composites

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis measures the response of a material to cyclic deformation as a function of temperature. The storage modulus and tanδ curves of PP/HDPE/N100A/GF hybrid composites are shown in figures 7.36 and 7.37. There is considerable increase in the storage modulus for the composite processed at 160°C, below which leads to improper mixing and above which occurs polymer matrix degradation. Damping curve of the hybrid composite processed at 160°C is having lower values, which indicates more reinforcement. The values of storage modulus at various temperatures are given in table 7.3.C.2

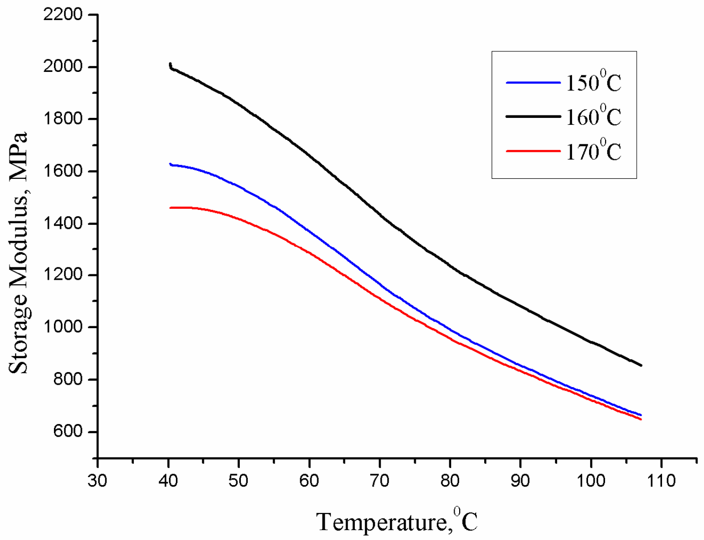


Figure 7.36 Effect of melt compounding temperature on storage modulus of PP/HDPE/ N100A/gf hybrid composites

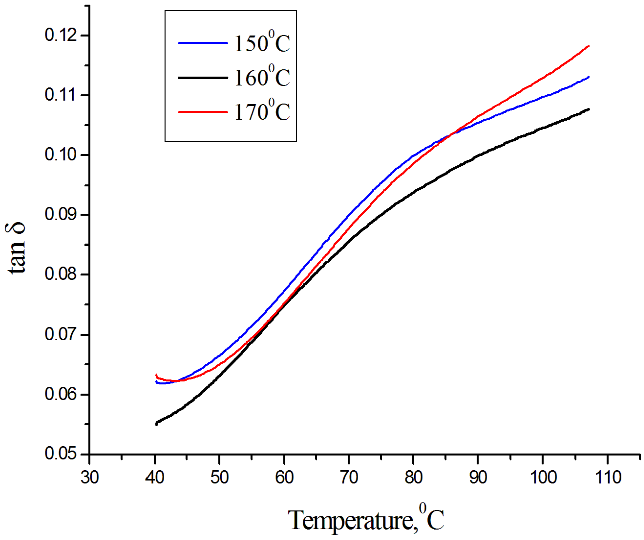


Figure 7.37 Effect of melt compounding temperature on damping coefficient of PP/HDPE / N100A/gf hybrid composites

The dynamic mechanical properties of neat PP and PP clay nanocomposites prepared with modified-MMT are studied by Liu *et al.*[83] Their results clearly show that the incorporation of modified- MMT into the PP matrix results in a remarkable increase in stiffness and a decrease in tan δ. An enhanced rubbery plateau is present in E' curves, indicating that the addition of modified MMT induces a reinforcement effect; at very high temperatures this reinforcement effect strengthens. This behaviour further indicates enhancement of the thermal and mechanical stability of these materials at high temperature[84]. The remarkable improvement in E'; related to the strong interaction between the matrix and nanoclay, is clearly observed in PNC based on nylon-6 [85]. All PNCs show a greater increase in E' at high temperature compared to that of the polymer matrices. This is due to both mechanical reinforcement by the clay particles and extended intercalation at high temperature [86]. Above Tg; when materials become soft, the reinforcement effect of the clay particles becomes prominent due to the restricted movement of the polymer chains. This is accompanied by the observed enhancement of E'.

Table 7.4 Storage modulus of PP/HDPE/modified nanokaolinite clay composites prepared at different melt compounding temperature

Sample	Storage Modulus at 40°C (MPa)	Storage Modulus at 60°C (MPa)	Storage Modulus at 80°C (MPa)	Storage Modulus at 100°C (MPa)
Composite prepared at 150°C	1630	1370	992.3	738.8
Composite prepared at 160°C	2014	1661	1236	945
Composite prepared at 170°C	1460	1285	958.2	722

7.4 Conclusions

- The effect of surface modification of nanoclay, glass fibre content and melt processing temperature on thermal, dynamic mechanical, crystallization and morphological properties of both modified and unmodified PP/HDPE nano kaolin clay composites are studied.
- The inclusion of nanofiller and glass fibre synergistically improves the thermal, crystallization and dynamic mechanical properties
- The surface modified nanoclay enhances the properties much better than unmodified nanoclay. Surface modification can act as a molecular bridge between the non polar polymer and polar glass fibre. It enhances filler matrix adhesion and effective dispersion of clay galleries. Addition of N100A clay and E glass fibre improves degradation temperature by 70°C, storage modulus by 1150 M Pa.
- As the fibre content is varied from 10 to 20 wt% thermal, mechanical and crystallization properties increase and then decreases at 30wt%. The decrease may be due to agglomeration of fibres and fibre pullout from matrix reducing the effect of filler-matrix adhesion. The optimum properties are obtained at 20 wt% glass fibre content.
- The effect of processing temperature on the properties of hybrid composites is illustrated in section C. The processing temperature has significant effect on thermal stability and dynamic mechanical properties. The optimum properties are obtained at 160°C melt processing temperature.

- Dynamic rheological studies reveal that both storage modulus and complex viscosity increases for composite containing both nanoclay and glass fibre than that of short glass fibre composites. The maximum enhancement in properties is obtained for composites containing 2wt% amino modified nanoclay and 20 wt% E glass fibre.
- High degree of intercalation with improved d-spacing (of 8.29nm in hybrid composites where as N100A has a d-spacing of 7.2nm) with composites containing 2 wt% amino modified nanokaolinite clay and 20 wt% E glass fibre is reported in XRD results.
- Morphological characterization using SEM also substantiates the enhancement in thermal and mechanical properties of hybrid composites containing amino modified nanoclay (N100A) and E-glass fibre.
- PP/HDPE blends can be effectively upgraded using modified nano kaolinite clay and E-glass fibre by melt processing technique. Both the filler can synergistically modify the polymer properties and the resultant hybrid composite can replace fibre glass and short glass fibre reinforced polymer composites in many strategic applications like body parts of aircrafts, submarines, ships and space vehicles. It can also be used as a replacement for conventional automobile parts, construction materials etc.

References

[1] Drzal L.T, Rich M.J. & Koenig M.F. “Adhesion of graphite fibers to epoxy matrices: II. The effect of fiber finish. Journal of Adhesion, 1983, 16 (2), 133-152.

[2] D.R. Paul, L.M. Robeson (2008) “Polymer nanotechnology: Nanocomposites”. Journal of Polymer 49: 3187–3204.

[3] I.Ghasemi, M Karrabi, M Mohammadi, H Azizi (2010) “Evaluating the effect of processing conditions and organoclay content on the properties of styrene-butadiene rubber/organoclay nanocomposites by response surface methodology” eXPRESS Polymer letters Vol 4, No.2 62-70.

[4] Homminga D, Goderis B, Hoffman H, Reynaers H, Groeninckx G (2005) “Influence of shear flow on the preparation of polymer layered silicate nanocomposites”. Polymer 46: 9941-9957.

[5] Borse K.N., Kamal M.R (2006) “Melt processing effects on the structural and mechanical properties of PA-6/clay nanocomposites”. Polymer Engineering and Science, 46: 1094-1108.

[6] Zhu L, Xanthos M (2004) “Effects of process conditions and mixing protocols on structure of extruded polypropylene nanocomposites”. Journal of Polymer Applied Science, 93:1891-1899.

[7] M Modesti, A Lorenzetti, D Bon, S Besco (2006) “Thermal behaviour of compatibilised polypropylene nanocomposite: Effect of processing conditions”. Polymer degradation and stability 91:672-680.

[8] M.A.Mohd Salleh, J.Abd.Razak, N.A.Ibrahim, A.Fakhru’l Razi, A.R.Suraya (2008) “The influence of melt compounding parameters on the tensile properties of low filler loading of untreated-MCNTs-polyproplene (pp) nanocomposites”. Journal of Engineering Science and Technology Vol. 3 No.1 97-108.

[9] Vaia R.A, Giannelis E.P (1997) "Polymer melt intercalation in organically-modified layere silicates: Model predictions and experiment. Macromolecules 30:8000-8009.

[10] Chen X, Guo Q. & Mi Y. (1998). "Bamboo fiber-reinforced polypropylene composites: A study of the mechanical properties". J. Appl. Polym. Sci. 69(10): 1891-1899.

[11] Hong C.K, Kim M.J, Oh S.H, Lee Y.S. & Nah C (2008) "Effects of polypropylene-g-(maleic anhydride/styrene) compatibilizer on mechanical and rheological properties of polypropylene/clay nanocomposites". J. Ind. Eng. Chem. 14(2): 236-242.

[12] Vilaseca F, Valadez-Gonzalez A, Herrera-Franco P.J, P lach M, López J.P. & Mutjé P (2010) "Biocomposites from abaca strands and polypropylene. Part I: Evaluation of the tensile properties". Bioresource Technol. 101(1): 387-395.

[13] Jordan J, Jacob K.I, Tannenbaum R, Sharaf M.A. & Jasiuk, I (2005) "Experimental trends in polymer nanocomposites-a review". Mater. Sci. Eng. A. 393(1-2): 1-11.

[14] Samal S.K, Nayak S.K. & Mohanty S (2008) "Polypropylene nanocomposites: Effect of organo-modified layered silicates on mechanical, thermal & morphological performance". J. Thermoplast. Compos. Mater. 21(3): 243-263.

[15] Isik I, Yilmazer U and Bayram G (2003) "Impact modified epoxy/ montmorillonite nanocomposites: Synthesis and characterization". Polymer 44: 6371–6377.

[16] Lin JC, Chang LC, Nien MH and Ho HL (2006) "Mechanical behaviour of various nanoparticle filled composites at low velocity impact". Compos Struct . 74(1): 30–36.

[17] Dorigato A, Fambri L, Pegoretti A, Slouf M and Kolarik J (2011) "Cycloolefin copolymer (COC)/fumed silica nanocomposites". J Appl Polymer Sci 119: 3393–3402.

[18] Dorigato A and Pegoretti A (2010) “Tensile creep behaviour of poly(methylpentene)-silica nanocomposites”. Polymer Int 59: 719–724.

[19] Avlar S and Qiao Y (2005) “Effects of cooling rate on fracture resistance of nylon 6-silicate nanocomposites”. Compos A. 36(5): 624–630.

[20] Liu W, Ho SV and Pugh M (2005) “Fracture toughness and water uptake of high-performance epoxy/nanoclay nanocomposites”. Compos Sci Technol 65: 2364–2673.

[21] Ragosta G, Abbate M, Musto P, Scarinzi G and Mascia L (2005) “Epoxy-silica particulate nanocomposites: Chemicalinteractions, reinforcement and fracture toughness”. Polymer 46(23): 10506–10516.

[22] Yao XF, Yeh HY and Zhao HP (2005) “Dynamic response and fracture characterization of polymer–clay nanocomposites with Mode-I Crack”. J Compos Mater 39(16): 1487–1496.

[23] Dorigato A, Pegoretti A and Kolarik J (2010) “Nonlinear tensile creep of linear low density polyethylene/fumed silica nanocomposites : Time-strain superposition and creep prediction”. Polymer Compos 31: 1947–1955.

[24] Kim JK, Hu C, Woo RSC and Sham ML (2005) “Moisture barrier characteristics of organoclay–epoxy nanocomposites”. Compos Sci Technol 65: 805–813.

[25] Varghese S, Gatos KG, Apostolov AA and Karger- Kocsis J (2004) “Morphology and mechanical properties of layered silicate reinforced natural and polyurethane rubber blends produced by latex compounding”. J Appl Polymer Sci 92: 543–551.

[26] Zhang J, Jiang DD and Wilkie CA (2005) “Fire properties of styrenic polymer–clay nanocomposites based on oligomerically-modified clay”. Polymer Degrad Stabil 91(2): 358–366.

[27] Dzenis Y (2008) “Materials science - Structural nanocomposites”. Science 319(5862): 419–420.

[28] Lin LY, Lee JH, Hong CE, Yoo GH and Advani SG (2006) “Preparation and characterization of layered silicate/glass fiber/epoxy hybrid nanocomposites via vacuum-assisted resin transfer molding (VARTM)”. Compos Sci Technol 66(13): 2116–2125.

[29] Subramaniyan AK and Sun CT (2006) “Enhancing compressive strength of unidirectional polymeric composites using nanoclay”. Compos A Appl Sci Manuf 37(12):2257–2268.

[30] Siddiqui NA, Woo RSC, Kim JK, Leung CCK and Munir A (2007) “Mode I interlaminar fracture behaviour and mechanical properties of CFRPs with nanoclay-filled epoxy matrix”. Compos A Appl Sci Manuf 38(2):449–460.

[31] Kornmann X, Rees M, Thomann Y, Necola A, Barbezat M and Thomann R (2005) “Epoxy-layered silicate nanocomposites as matrix in glass fibre-reinforced composites”. Compos Sci technol 65(14):2259-2268.

[32] Vlasveld DPN, Bersee HEN and Picken SJ (2005) “Nanocomposite matrix for increased fibre composite strength”. Polymer 46(23): 10269–10278.

[33] Vlasveld DPN, Daud W, Bersee HEN and Picken SJ (2007) “Continuous fibre composites with a nanocomposite matrix: Improvement of flexural and compressive strength at elevated temperatures”. Compos A Appl Sci Manuf. 38(3): 730–738.

[34] Rozman H.D, Tay G.S, Kumar R.N, Abusamah A, Ismail H and Ishal Z.A (2001) “Polypropylene oil palm empty fruit bunch-glass fiber hybrid composites:A preliminary study on the flexural an tensile properties”. Journal of European polymer 37:1283-1291.

[35] Thwe M and Liao K (2002) “Effects of environmental ageing on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites”. Journal of composite 33:43-52.

[36] Mohan T.P. & Kanny K (2011) “Influence of nanoclay on rheological and mechanical properties of short glass fiber-reinforced polypropylene composites”. J. Reinf. Plast. Compos. 30(2): 152-160.

[37] Chandradass J, Ramesh Kumar M. & Velmurugan R (2008) "Effect of clay dispersion on mechanical, thermal and vibration properties of glass fiber-reinforced vinyl ester composites". J. Reinf. Plast. Compos. 27(15): 1585-1601.

[38] Normasmira A Rahman, Aziz Hassan, R. Yahya and R.A Lafia-Araga (2013) "Glass fiber and Nanoclay Reinforced Polypropylene Composites: Morphological, Thermal and Mechanical Properties.

[39] Andrea Dorigato, Stefano Morandi and Alessandro Pegoretti (2013) "Effect of nanoclay addition on the fiber/matrix adhesion in epoxy/glass composites". Journal of Composite Materials 46:1439–1451.

[40] ASTM D 1238-10. Standard test method for melt flow rates of thermoplastics by extrusion plastometer, volume 08.01. ICS number code 83.080.20 (thermoplastic material)

[41] Y. Xu and S. Van Hoa (2008) "Mechanical Properties of Carbon Fibre Reinforced Epoxy/Clay Nanocomposites," Composites Science and Technology, Vol. 68, No. 3-4 pp. 854-861.

[42] Ray S.S. & Bousima M (2005) "Biodegradable polymers and their layecred silicatenanocomposites: in greening the 21st century materials world". Prog. Mater. Sci., Vol.50:962–1079.

[43] Becker O, Varley R.J. & Simon G.P (2004) "Thermal stability and water uptake of high performance epoxy layered silicate nanocomposites". Euro. Polym. J., Vol. 40"187–195.

[44] Zanetti M, Bracco P. & Costa L (2004) "Thermal degradation behaviour of PE/clay nanocomposites". Polym. Degrad. Stab., Vol. 85:657–665.

[45] Wang S, Hu Y, Song L, Wang Z, Chen Z, & Fan W (2002) "Preparation and thermal properties of ABS/montmorillonite nanocomposite". Polym. Degrad. Stab., Vol. 77:423-426.

[46] Zhu J, Uhl F.M, Morgan A.B & Wilkie C.A (2001) "Studies on the mechanism by which the formation of nanocomposites enhances thermal stability". Chem. Mater., Vol. 13:4649–4654.

[47] Ray S.S, Yamada K, Okamoto M, Ogami A & Ueda K (2003) "New polylactide/layered silicate nanocomposites. 3. High performance biodegradable materials". Chem. Mater., Vol. 15:1456–1465.

[48] Gilman J.W (1999) "Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites". Appl. Clay Sci., Vol. 15:31-49.

[49] X. Kornmann, L. A. Berglund, J. Sterte, and E. P. Giannelis (1998) "Nanocomposites based on montmorillonite and unsaturated polyester". Polymer Engineering and Science, vol. 38, no. 8, pp.1351–1358.

[50] Jan Golebiewski, Andrzej Galeski (2007) "Thermal Stability of nanoclay polypropylene composites by simultaneous DSC and TGA". Composites Science and Technology 67:3442-3447.

[51] Huang R, Xiong W, Xu X, Wu Q (2012) "Effect of hybrid mineral and bamboo fillers on thermal expansion behaviour of bamboo fibre and recycled polypropylene-polyethylene composites". Bio Resources, 7, 4563–4574.

[52] Jang Oo Lee, Bong-Kwan Kim, Chang-Sik Ha, Ki-Won Song, Jin-Kook Lee and Won-Jei Cho (1994) "Rheological and mechanical properties of PP/PE binary and PP/PE/EPDM ternary blends". Polymer Vol, 18, No 1, pp 68-77.

[53] Peymen Ezzati, Ismaeil Ghasemi, Mohammed Karrabi and Hamed Azizi (2008) "Rheological behaviour of PP/EPDM blend: The effect of compatibilization". Iranian Polymer Journal 17(9): 669-679.

[54] R. I. Tanner (2000) "Engineering Rheology," Oxford University Press, New York.

[55] C. W. Macosko (1994) "Rheology: Principle, Measurement and Application," VCH, New York.

[56] H. A. Barnes, J. F. Hutton and K. Walters (1989) "An Introduction to Rheology," Elsevier, Amsterdam, London, New York.

[57] Sinha Ray S and Okamoto M (2003) "New Polylactide/Layered Silicate Nanocomposites, 6". Macromolecular Materials and Engineering, 288:936-944.

[58] Pluta M (2006) "Melt compounding of polylactide/organoclay: Structure and properties of nanocomposites". Journal of Polymer Science Part B-Polymer Physics, 44:3392-3405.

[59] Carreau PJ, Kee DD and Chhabra RP (1997) "Rheology of polymeric systems: principles and applications". Hanser publishers.

[60] Krishnamoorti R, Ren J and Silva AS (2001) "Shear response of layered silicate nanocomposites". The journal of chemical physics, 114:4968-4973.

[61] Prasad R, Gupta RK, Cser F and Bhattacharya SN (2006) "Experimental investigation of the linear viscoelastic response of eva-based nanocomposites". Journal of applied polymer science, 101:2127-2135.

[62] Singh S, Ghosh AK, Maiti SN, Raha S, Gupta RK and Bhattacharya S (2012). "Morphology and rheological behavior of polylactic acid/clay nanocomposites". Polymer engineering & science, 52:225-232.

[63] Vikas Mittal (2010) "Polymer nanocomposites: Synthesis, microstructure and properties". Institute of chemical and bioengineering, Department of chemistry and applied science, 8093 Zurich, Switzerland.

[64] Ramsaroop, K. Kanny, T. P. Mohan (2010) "Fracture Toughness Studies of Polypropylene-clay Nanocomposites and Glass Fibre Reinfoerced Polypropylene Composites". Material Sciences and Applications, 1:301-309.

[65] Runzhou Huang , Xinwu Xu , Sunyoung Lee , Yang Zhang , Birm-June Kim and Qinglin Wu (2013) "High Density Polyethylene Composites Reinforced with Hybrid Inorganic Fillers: Morphology, Mechanical and Thermal Expansion Performance". Materials 6:4122-4138.

[66] NRR. Anbusagar and P.K. Giridharan (2013) "Influence of Nanoparticles on Impact Properties of Polystyrene Foam Sandwich GFRP Composites". International Journal of Research in Engineering and Technology (IJRET) Vol. 2, No. 2, ISSN 2277 – 4378.

[67] Javad Moftakharian Esfahani, Masoud Esfandeh, Ali Reza Sabet (2011) "High-Velocity Impact Behavior of Glass Fiber-Reinforced Polyester Filled with Nanoclay". DOI 10.1002/app.36605.

[68] Huda M.S, Mohanty A.K, Drzal L.T, Misra M, and Schut E (2005,) "Green composites from recycled cellulose and poly(lactic acid): Physico-mechanical and morphological properties evaluation". J. Mater. Sci. 16: 4221–4229.

[69] Matuana L.M, Balatinecz J.J, and Park C.B (1998) "Effect of surface properties on the adhesion between PVC and wood veneer laminates". Polym. Eng. Sci. 38:765–773.

[70] Danyadi L, Renner K, Moczo J, and Pukanszky B (2007) "Wood flour filled polypropylene composites: Interfacial adhesion and micromechanical deformations". Polym. Eng. Sci. 47:1246–1255.

[71] Mohanty S, Nayak S.K (2006) "Interfacial, dynamic mechanical, and thermal fiber reinforced behaviour of MAPE treated sisal fiber reinforced HDPE composites". J. Appl. Polym. Sci. 102:3306–3315.

[72] Dumoulin M.M, Carreau P.J, Utracki L.A (1987) "Rheological properties of linear low density polyethylene/polypropylene blends. Part 2: Solid state behaviour". Poly. Eng. Sci. 27:1627–1633.

[73] Blom H.P, The J.W, Rudin A. (1996) "i-PP/HDPE blends. III. Characterization and compatibilization at lower i-PP contents". J. App. Poly. Sci. 61:959–968.

[74] Dealy J.M, Wissburn K.F.(1996) "Melt rheology and its role in plastic processing". Chapman & Hall: London.

[75] Gu S.Y, Ren J, Wang Q.F (2004) "Rheology of poly (propylene)/clay nanocomposites". J. App. Poly. Sci. 91:2427–2434.

[76] Giannelis E (1996) "Polymer layered silicate nanocomposites", Advanced Materials 8: 29.

[77] LeBaron P, Wang Z & Pinnavaia T (1999) "Polymer layered silicates nanocomposites : an overview". Applied Clay Science 15: 11–29.

[78] Finaa A, Abbenhuisb H, Tabuania D. & G.C (2006) “Metal functionalized poss as fire retardants in polypropylene”. Polymer Degradation and Stability 91: 2275–2281.

[79] Peeterbroech S L. B., Alexandre M, Bnagy J, Viville P, Lazzaroni R & Dubois P (2007). “The influence of the matrix polarity on the morphology and properties of ethylene vinyl acetate copolymers-carbon nanotube nanocomposites”, Composites Science and Technology 67: 1659–1665.

[80] Le Bras M, Wilkie C, Bourbigot S, Duquesne S & Jama C (2005) “New applications of mineral fillers,: the use of mineral fillers in micro and nano-composites”. Fire Retardancy of Polymers, The Royal Society of Chemistry.

[81] Gilman J (2000) “Flammability properties of polymer layered silicate nanocomposites polypropylene and polystyrene nanocomposites”. Chemistry of Material 12: 1866–1873.

[82] Damien M. Marquis, Éric Guillaume and Carine Chivas-Joly “Properties of Nanofillers in Polymer”.www.intechopen.com

[83] Liu X, Wu Q (2001) “PP/clay nanocomposites prepared by grafting melt intercalation”. Polymer 42:10013–9.

[84] Okamoto M, Nam PH, Hasegawa N, Usuki A “Uniaxial flowinduced alignment of silicate layers in polypropylene/clay nanocomposites”. Macromol Mater Engng. Submitted for publication.

[85] Maiti P, Nam PH, Okamoto M, Kotaka T, Hasegawa N, Usuki A (2002) “Influence of crystallization on intercalation, morphology, and mechanical properties of propylene/clay nanocomposites”. Macromolecules 35:2042–9.

……

Chapter 8

MICROMECHANICAL MODELLING OF PP/HDPE/KAOLINITE CLAY NANOCOMPOSITES AND PP/HDPE/ KAOLINITE CLAY/GLASS FIBRE HYBRID COMPOSITES

Contents

8.1 Introduction

Nanoscience and nanotechnology refer to the understanding and control of matter at the atomic, molecular or macromolecular levels, at the length scale of approximately 1 to 100 nanometers, where unique phenomena enable novel applications. Applications of nanotechnology involve design, characterization, production and application of structures, device and systems by controlling shape and size at nanometer scale. According to Braun *et al.*[1], from 1980s, the growth of research papers dealing with the prefix called ‘nano’ is exponential. Among all the work, synthesise and characterization of nanocomposites are the most important subjects. Nanosized fillers pose challenges in the processing and characterization techniques for composites. Also, it is a great challenge to understand the mechanics at the nanolevel. Fundamental studies in processing, characterization and modelling are needed to obtain fully optimized nanocomposites.

Comparing to the conventional micro-composites, nanocomposites greatly improve the physical and mechanical properties. The nanoscale reinforcements over traditional fillers have the following advantages [2,3]:

1) Low-percolation threshold (~0.1–2 vol.%).
2) Large number density of particles per particle volume (106–108 particles/μm3).
3) Extensive interfacial area per volume of particles (10_3–10_4 m_2/ml).
4) Short distances between particles (10–50nm at ~1–8 vol.%).

Although any kind of material can be produced to appear in a nanoscaled shape and size, carbon nanotubes and nanoplatelets are the two kinds of nanoparticles that gained the most attention[4].

It is well known that composite materials have advantages over traditional materials. Nanocomposites, where nano-sized reinforcements (fillers) are dispersed in the base material (matrix), offer a novel class of composites with superior properties and added functionalities[5-8]. Although there have been numerous material syntheses, tests and characterisations of layered silicate-reinforced nanocomposites, as seen from the literature, the fundamental mechanisms for mechanical property enhancement are not fully understood and are rarely discussed[9-11]. As pointed out by Brune and Bicerano[9] a better understanding and prediction ability is very important in accelerating the development of nanocomposites. The discipline of composite materials is constantly providing engineers with stiffer, stronger, yet lighter materials. The design of composite material yield great flexibility in choosing a material. In fact, many times materials may be custom tailored to meet the design needs of a particular engineering task. This flexibility has the end led to vastly improved products. However, not everything about composite materials makes life easier for the design engineer. Composite materials are generally anisotropic or at best, transversely isotropic. This fact greatly complicates the analysis of their behaviour necessary to the design process. In addition, not only are the most composites anisotropic, but often the reinforcement material, the matrix material, or both may be non elastic or even nonlinear in their behaviour. This complicates the analysis even further. Finally the properties of the composite itself are often not known, particularly if it is a new layup of materials or if the constituent materials themselves have been changed. As a result extensive testing must often be performed before the composite will be usable. In short, the analysis of composite material requires the knowledge of not only anisotropy, but also appropriate structural theory to derive the laminate properties.

Modelling and simulation of properties is important for the development of polymeric materials for engineering applications. To develop and optimize the use of nanostructured materials, it is essential to determine and model the properties, either by applying existing models or developing new models. But the field of modelling nanocomposites is still in its infancy as most of the models are based on several idealistic assumptions

Many composite analyses are performed using a macroscopic approach. In this approach, the properties of the composite are homogenized to produce an anisotropic, yet homogenized continuum before the analysis is conducted[12]. The true nature of the composite is generally one of a randomly spaced anisotropic reinforcement material in an isotropic medium. In contrast to the macroscopic approach, the micromechanical approach, to analysing composite instead considers the properties of the filler and matrix separately and applies the loading and boundary conditions at individual filler and matrix level. The overall properties of the composite are developed by relating the average stresses and strains. Hence the micromechanical approach may provide much more detail into true interactions between the filler and matrix, potentially leading to a more accurate model of the composite behaviour.

The advantages of micromechanical behaviour are as follows:

- Effective material properties arise from the fact that many composites are formed of layers in addition to being anisotropic. Micromechanical approach can be performed on the composite provided that the individual phase properties are known; effective material properties are obtained as a result of analysis. A macroscopic analysis on the other hand requires the effective material properties to be known before the analysis may be performed.
- Another advantage of micromechanical analysis falls in the area of failure. Failure in composites usually occurs at the micromechanical level and is difficult to capture in a macroscopic model using macroscopic failure criteria. Failure at the microscopic level can take many forms including filler breakage, matrix cracking and matrix filler interface debonding or damage. Failure at interface between phases is of particular interest due to the fact that it is this type of damage that is most common in composites.

In nanocomposite materials, in addition to the filler content, factors like the extent of dispersion, interfacial interactions and processing methods are key factors in determining nanocomposite properties. Hence predictions of these models often deviate from experimental results. The mechanics of polymer composites in micromechanical models usually follows the fundamental assumptions including (i) linear elastic material behaviour of fillers and the polymer matrix; (ii) axisymmetric fillers in identical shape and size, characterised by material parameters such as aspect ratio and shape parameter and (iii) well-bonded filler-polymer interfacial area with neglecting interfacial slip and filler-polymer debonding or matrix cracking. Although the applicability of continuum mechanics (including micro mechanics) to nanocomposites has been subjected to debate[5,13], many recent works directly applying continuum mechanics to nanostructures and nanomaterials have reported meaningful results and elucidated many issues[14-23]. Thus, mechanics-based formulas for predicting the mechanical properties will be reviewed. In nanocomposites, there are typically three kinds of fillers. They are cylinder-like nanofibers (nanotubes), flake-like (disk-like) platelets (nanolayers, nanoclays), and spheroid-like particulates, For the fiber-reinforced nanocomposites, there are two cases depending on the orientation of the fibers, i.e. aligned fibers and randomly oriented fibres. Micromechanical-based models have been used in the case of composites to analyse the effect of filler's structural parameters, such as shape, aspect ratio, and orientation, on the mechanical properties. Although these micromechanical models cannot be used to fully account for the exact mechanical behaviour of polymer nanocomposites, they generally give satisfactory correlations. The popular micromechanical models used in this section for prediction of modulus of elasticity are Halpin-Tsai Model, Voigt Upper Bound and Reuss Lower Bound Model, Ji Model and Takayanagi Model

8.2 Methodology

The first results obtained by Toyota Research group[24,25] in the 90s, on the dispersion of nanoscopic platelet silicates (montmorillonite, MMT) in a polyamide 6 matrix have induced considerable worldwide research in the field of nanocomposites consisting of a thermoplastics and clay platelet reinforcement [23,26-28]. For very low mass fraction of platelets (less than 5%), some remarkable mechanical properties as well as thermal barrier to gases, etc. have led to a great industrial and academic interest [27,29-34]. Most of these publications investigated only experimental processing and characterization or theoretical modelling, and often in the linear regime. The present study is concerned with the experimental characterization and the prediction of the elastic properties of a class of platelet-reinforced nanocomposites. The main objective is a better understanding of the effect of the nanoscopic reinforcements on the mechanical behaviour: Young's modulus. The experimental characterization of the mechanical behaviour is performed through tensile tests as described in chapters 4 and 6.

The analysis of stress transfer efficiency of nanocomposites and hybrid composites has been carried out by adopting several successful theoretical models for particle/particulate filled polymer systems as reported in many literatures[35-38]. The models considered for studying the effect of nanoscopic reinforcement on the mechanical properties of nanocomposite are Halpin-Tsai model, modified Halpin-Tsai model, Vogit rule of mixtures, Reuss inverse rule of mixtures, Takayanagi model and Ji's model. The modulus of the composite is calculated using the micromechanical models and compared with the experimental data.

When both microscopic and nanoscopic reinforcements are considered simultaneously, the matrix–reinforcement interface energy cannot be neglected, as is the case for classical composites. Several authors[31,39] have shown that nanoscopic size of the reinforcement can strongly modify the properties of the matrix which surrounds the reinforcement. This part of the matrix, termed the interphase, has already been modelled in the case of nanocomposites [31,34]. We propose, in the second section to analyse the macroscopic elastic and non linear properties of the PP/HDPE/nanoclay/E-glass fibre hybrid composite by taking into account this interphase. It is considered that modulus of matrix, that E_m = 854 MPa and modulus of nanoclay, E_f = 16 GPa, clay-platelet thickness as 7.2 nm (obtained from the XRD data and literature) and fibre thickness is taken as 10μm(as shown in SEM images of fig. 8.1&8.2).

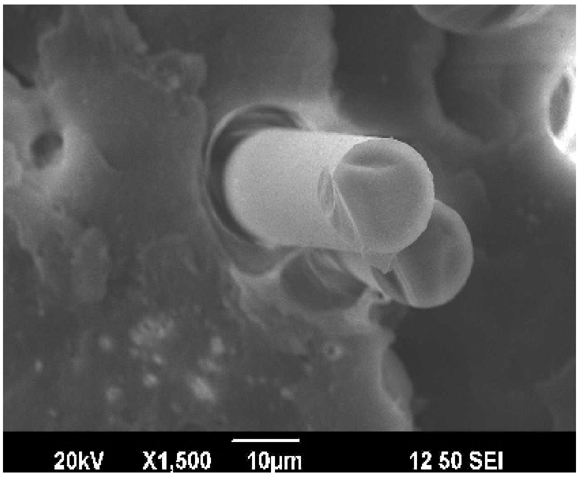


Figure 8.1 SEM image of E-glass fibre in PP/HDPE/ N100A/ E-glass fibre hybrid composite

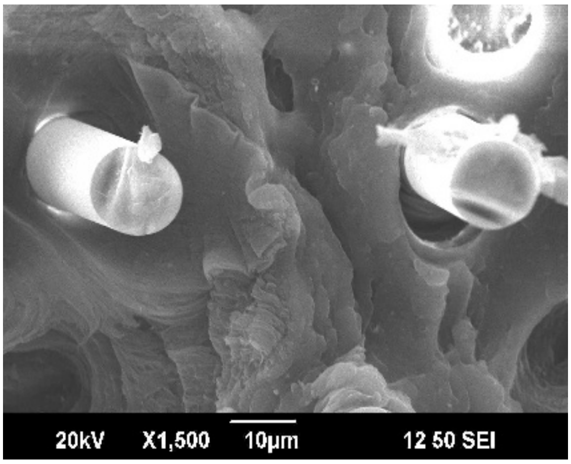


Figure 8.2 SEM image of E-glass fibre in PP/HDPE/ N100/ E-glass fibre hybrid composite

8.3 Results and discussions

8.3.1 Theoretical modelling of mechanical properties of PP/HDPE/ kaolinite clay nanoparticles

Micromechanical modelling of filled polymer composites have revealed that the particle induced toughening in polymers functionally originate from locally induced anisotropy[40]. In the present investigation Halpin-Tsai model, Takayanagi model, Vogit upper-bound model, Reuss lower bound model and Ji's prediction models for elastic moduli of filled polymer systems have been explored regarding their validity to predict the elastic mechanical response of PP/HDPE/kaolin clay nanocomposites.

The versatility of well accepted Halpin-Tsai model is associated with its ability to predict the elastic modulus of a variety of reinforcement geometries, including discontinuous filler reinforcements such as fibre-like or flake like fillers[23,41]. The composite equation to theoretically predict Young's modulus of a composite material as per the Halpin-Tsai model may be expressed as

$$\frac{E_c}{E_m} = \frac{1+\zeta\eta\phi_f}{1-\eta\phi_f} \quad \text{...} (1)$$

$$\text{where,} \quad \eta = \frac{\frac{E_f}{E_m}-1}{\frac{E_f}{E_m}+\zeta} \quad \text{..} (2)$$

where E_c, E_f and E_m are Young's moduli of composites, inclusions and polymer matrix respectively(MPa), φf is the filler volume fraction and ζ is the shape parameter dependent on filler geometry loading direction. In a particular direction, ζ= 2(l/d) for fibres or 2(l/t) for disk-like platelets where l, d, t are the length, diameter and thickness of the dispersed fillers. In the present investigation l/t is assumed to be 100. However, 2-D disk-like clay platelets theoretically contribute less to modulus than 1-D fibre-like inclusions. In order to accommodate such effects, a modulus reduction factor (MRF) [21] was also reported to be introduced to modify the Halpin-Tsai model which may be stated as,

Based on the studies of You-ping Wu *et al*. the MRF value for clay platelets was chosen as 0.66

$$\frac{E_c}{E_m} = \frac{1+\zeta(MRF)\eta\phi_f}{1-\eta\phi_f} \quad \text{...} (3)$$

Based on the conventional rule of mixture principle the elastic modulus may also be predicted by using a modified form of a Halpin-Tsai model, especially in the case when ζ→infinity. In such a scenario the Halpin-Tsai model predictions concerning the elastic modulus reach the upper-bound.

Such an iso-strain (i.e. when filler and matrix undergo the same uniform strain under a certain applied stress) approximation based solution is normally referred as Voigt rule of mixtures (ROM) [42,43]. The Voigt rule may be stated as,

$$E_c = \phi_f E_f + (1-\phi_f)E_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Conversely, when ζ→0, the Halpin-Tsai model equation reaches at the lower bound elastic modulus value corresponding to the elastic response, when the reinforcement and the matrix phases undergo equal stress (i.e., iso-stress approach), the situation so arrived is normally called as Reuss inverse rule of mixtures (IROM) [43,44]. The Reuss model may be stated as

$$\frac{1}{E_c} = \frac{\phi_f}{E_f} + \frac{(1-\phi_f)}{E_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

Takayanagi model is initially used to describe the visco-elastic properties of a variety of heterogeneous materials with two visco-elastic constituent phases based on simple mechanical models including elements connected partly in series and partly in parallel[32] .The tensile modulus of polymer nanocomposites with random oriented plate-like dispersed phase can be expressed as

$$E_c = \left[\begin{array}{l} \left[\dfrac{1-\sqrt{[2(\tau/t)+1]\phi_f}}{E_m}\right] + \dfrac{\sqrt{[2(\tau/t)+1]\phi_f}-\sqrt{\phi_f}}{\{1-\sqrt{[2(\tau/t)+1]\phi_f}\}E_m + \sqrt{[2(\tau/t)+1]\phi_f}\,(k-1)E_m/\ln k} \\ + \dfrac{\sqrt{\phi_f}}{\{1-\sqrt{[2(\tau/t)+1]\phi_f}\}E_m + \{\sqrt{[2(\tau/t)+1]\phi_f}-\sqrt{\phi_f}\}(k+1)E_m/2+\sqrt{\phi_f}E_f} \end{array}\right]^{-1} \quad \ldots(6)$$

where τ is the thickness of interfacial region, and *t* is the thickness of plate-like dispersed phase. *k* represents the modulus ratio of interface neighbouring on the surface of a particle. It is assumed that the modulus of the interfacial region tends to have a linear decreasing gradient along the normal direction to the surface of dispersed phase.

A simplified two phase version of Takayanagi model is obtained when the interphase effects are neglected which can be described as follows. Here $\beta = \sqrt{\Phi_f}$

$$E_c = E_m \left[(1-\beta) + \frac{\beta}{(1-\beta) + \beta \frac{E_f}{E_m}} \right] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Ji proposed a three phase micromechanical model taking into consideration of interfacial effects also. The model can be stated as follows:

$$E_c = \left[(1-\alpha) + \frac{\alpha-\beta}{(1-\alpha) + \frac{\alpha(k-1)}{\ln(k)}} + \frac{\beta}{(1-\alpha) + \frac{\beta E_f}{E_m} + \frac{(\alpha-\beta)(k+1)}{2}} \right] E_m \ldots (8)$$

where $k=E_i/E_m$

$$\beta = \sqrt{\phi_f} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$\alpha = \sqrt{[2(\tau/t)+1]\phi_f} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

In another approximation where the effects of interface are neglected (t = 0), the well known Ji's model[45] for tensile modulus prediction reduces to the two-phase Takayanagi model[46,47]. Typically, the Takayanagi model prediction underestimates the Young's modulus since the interfacial contribution which plays a functional role in stress-transfer mechanism is ignored.

However, by considering that E_m = 854 MPa and E_f = 16 GPa, and clay-platelet thickness as 7.2 nm, the tensile modulus reduction tends to follow a trend with the closest proximity to the experimentally determined trend. The predictions from the above models vis-à-vis the experimental moduli are shown in fig 8.3. It is observed that the predictions from IROM and Takayanagi model have a closer proximity to the experimental value, though their absolute magnitude converged to the lower-bound predictions. Halpin-Tsai, Modified Halpin-Tsai (with a modulus reduction factor) and VROM models stay largely deviated away on the higher side of the predicted moduli. Comprehensively, these theoretical analyses indicate that the polymer-nanoclay interfacial characteristics partially converge to a state of perfect interfacial bonding (Takayanagi model) with an iso-stress (Reuss IROM) response.

Although in the literature[36], the tensile modulus of the nanoclay (MMT) is usually taken as 170-180GPa, in the case of kaolinite clay it is taken as 16GPa. Due to strong interfacial bonding the clay layers remain in the state of partially intercalated form in the composite (in case of kaolin clay when compared with MMT in unmodified form and hence there is significant reduction in the resultant modulus. Arpitha Bal[48] in her thesis substantially showed that the tensile modulus of unmodified nanokaolinite clay remain in the range of 12-16GPa.

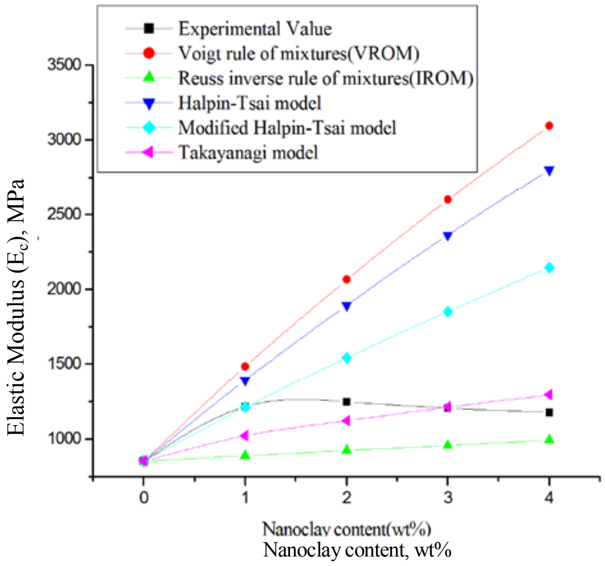


Figure 8.3 Theoretical modelling of elastic modulus as a function of nanoclay content(N100) using various equations/models based on micromechanics and composite theories.

Polymer composites containing particles with a small aspect ratio of 1 or thereabout have also been studied extensively because of their technological and scientific importance. Many studies have been conducted on the mechanical properties of these particulate-filled polymer composites. Stiffness or Young's modulus can be readily improved by adding either micro- or nano-particles since rigid inorganic particles generally have a much higher stiffness than polymer matrices [49-57]. However, strength strongly depends on the stress transfer between the particles and the matrix. For well-bonded particles, the applied stress can be effectively transferred to the particles from the matrix [58]; this clearly improves the strength[49,59-63]. However, for poorly bonded micro-particles, strength reductions occur by adding particles [39-51,64-70]. There are, however, several studies that show toughness increase with introduction of rigid particles in polypropylene [71,72] and polyethylene [72-79] even in the presence of micro fillers. This clearly shows that PP and HDPE are effective candidates for up gradation with nano/micro fillers. Sumita *et al.* [80] underlined the interest of replacing microscale silica by its nanoscale counterpart, since nanoscale silica particles possess superior mechanical properties. They found that these nanoparticles give higher rigidity and superior yield strength to the polymers. Smaller particle size yields higher fracture toughness for calcium carbonate filled high density polyethylene (HDPE)[79]. Particle– matrix interface adhesion and particle loading are two important factors that also affect mechanical properties Thus, the use of coupling agents/ surface modifiers that increase the particle–matrix adhesion leads to higher strength [54,81-86]. When chemical treatment was applied to the silica particles in HDPE, the toughness of the filled polymer was significantly improved. [87]

In particulate filled polymers (especially in the case of nanoscale materials) two types of interactions may be distinguished. Particle–particle interactions lead to aggregation, while matrix–filler interactions determine micromechanical deformation processes as well as the macroscopic behaviour and performance of the material [38]. The detection and quantitative characterization of aggregation is difficult, unambiguous methods do not exist yet. Although general tendencies, i.e. the increase in the extent of aggregation with decreasing particle size and increasing filler content, are known, exact correlations do not exist in spite of the fact that aggregation is one of the major issues in the production of particulate filled polymers[36]. The usual purpose of the surface treatment of particulate fillers is to decrease their surface free energy in order to hinder particle/particle interactions and aggregation[88]. Under the effect of external load stress concentration develops around the inclusions, which induces local deformations. In particulate filled polymers the dominating micromechanical deformation process is thought to be debonding, but considerable shear yielding also takes place. Other deformations like matrix cracking or crazing may also occur in these systems. Interfacial adhesion is one of the factors determining debonding and its control makes possible the improvement of product quality[89].For reducing particle-particle interaction that lead to aggregation and increasing particle-matrix interaction, surface treatment of nanoclay is carried out. The increase in the state of dispersion and filler matrix adhesion in the presence of modified nanoclay is evident from morphological studies and enhancement in mechanical properties as discussed in previous chapters. As a result of this modulus of modified nanoclay is taken as 20GPa and the resultant micromechanical models are compared with the experimental data in fig. 8.4.

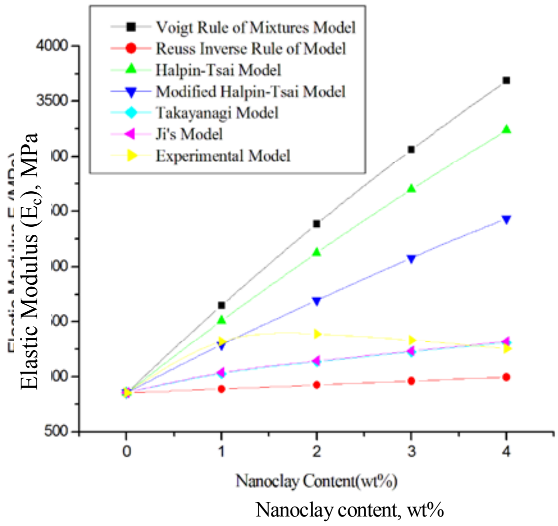


Figure 8.4 Theoretical modelling of elastic modulus as a function of modified nanoclay content(N100A) using various equations/ models based on micromechanics and composite theories.

Even though the experimental data fits also well with Halpin-Tsai and Vogit rule of mixtures at lower nanoclay loadings, it deviate extensively at higher loadings. It is observed that the predictions from IROM and Takayanagi model have a closer proximity to the experimental value, as is the case of unmodified clay composites. So a perfect interfacial bonding with isostress approach is observed in the case of PP/HDPE/modified nanoclay composites

8.3.2 Theoretical modelling of mechanical properties: PP/HDPE/ nanoclay/E-glass fibre hybrid composites.

Fibre reinforced composites represent an attempt to improve the properties of engineering plastics by the inclusion of stiff, strong fibres. Continuous fibre reinforcements represent the optimum geometric solution, but restrict the processing options available to manufactures[91]. The inclusion of short reinforcing fibres into a plastic matrix generally increases the viscosity of the polymer melt, but enables rapid, high-volume manufacture using injection moulding. Higher fibre volume fractions lead to higher viscosity, so there is a practical limit on fibre volume fraction of around 40%, which limits the application of such materials for structural composite components. It is an established fact that PP and HDPE matrices can be effectively modified using nanoclay platelets. It is therefore interesting to consider a polymer with reinforcement on two scales; microscopic fibre reinforcement, combined with exfoliated nanoscale platelets.

Polymer composites made from polymeric matrices, nanomaterials and fibres appeared during the last decade as a sustainable alternative material for many applications related to aerospace, automotive and structural engineering. Interest towards an increased use of those hybrid composite structural materials has grown from the surging demand for low cost, light weight, high strength materials and the possibility of finding an alternative to traditional composites made of synthetic fibres.

It is well-known that including a modest amount of nanocomposites into a polymer matrix can increase the tensile modulus. This improvement is governed by two factors: the strong interaction between polymers and the clay surface, and the modulus and geometry of the clay reinforcement. A good interface increasing the bond strength, is important for applying modulus prediction models. It is reasonable to assume that a strong interface provides no interfacial sliding in the elastic range. Thus, the reinforcement mechanism in nanocomposites could be similar to that in traditional composites.

The properties of polymer/clay composites are dependent on the filler modulus, the volume fraction and the degree of exfoliation of the clay particles. An improvement of the exfoliation increases the aspect ratio and the numbers of particles. These factors are related to the properties of clay layers, which can contribute to the mechanical properties of nanocomposites.

A simple and crucial question is whether the significant improvements in mechanical properties can be explained by conventional composites theory. For example, important factors such as aspect ratio, modulus and volume fraction are already well explained and demonstrated in fibre composites, and many composites models take these factors into account. An assumption inherent in all of these theories is that each component of a composite acts independently of the other. Aspect ratio is an important factor in nanocomposites, and is related to the level of the exfoliation. As it cannot be accurately measured, a shape factor is introduced. However, the aspect ratio of the clay layers need not be measured since we use shape factor ξ to predict the effect on the modulus[35,91].

One of the main difficulties when dealing with polymer composites is the adhesion between fibres and matrices[92-93] mainly due to the hydrophilic and hydrophobic characteristics showed by the fibres and the polymers, respectively. However, the chemical affinity between the glass fibre and the polymeric matrix can be improved by the modification of the fibre surface[94-95] or the polymer [41, 96-98] by adding a third component like surface modified nanoparticle or using chemical additives like maleic anhydride. Hence in this section the modelling is carried out for modified clay nanocomposites only. Hence the objective of this section is to model the modulus of PP/HDPE/nanoclay/glass fibre hybrid composites and to evaluate the synergy (if any) in combing the two scales of reinforcement.

To simplify the scenario, we assume that there is no interaction between clay and glass fibres. Polymer/clay as a matrix is reinforced by glass fibre. The Halpin-Tsai model is applied to predict the modulus of hybrid composites. Mike *et al.* carried out the micromechanical modelling of PA/clay/gf composites using a three phase model developed from the well known Halpin-Tsai model. As the glass fibres may align in longitudinal and transverse directions of applied load in the case of hybrid composites prepared by melt compounding, two equations are developed to calculate the modulus in both longitudinal and transverse directions.
The equations may be stated as follows:

a) For fibres aligned in longitudinal direction

$$\frac{E_{IIhc}}{E_m}=\frac{(1+V_{fgf}\xi_{gf}\eta_{gf})}{(1-\eta_{gf}V_{fgf})}\times\frac{E_c}{E_m}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(11)$$

b) For fibres aligned in transverse direction

$$\frac{E_{\perp hc}}{E_m}=\frac{(1+2V_{fgf}\eta_{gf})}{(1-\eta_{gf}V_{fgf})}\times\frac{E_c}{E_m}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(12)$$

$$\text{where } \eta_{gf}=\frac{(E_{gf}/E_{clay})-1}{(E_{gf}/E_{clay})-\xi_{gf}}\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(13)$$

The relative modulus of the hybrid composite is then carried out by Krenchel's approach using the following equation:

$$\frac{E_{hc}}{E_m}=\eta_0\left(\frac{E_{IIhc}}{E_m}\right)+(1-\eta_0)\left(\frac{E_{\perp hc}}{E_m}\right)\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(14)$$

where η_0 is the orientation efficiency which is taken as 0.25 [91]. ξ_{gf}, the shape factor of fibres is taken as 2(l/t), length=6mm and thickness=10μm, E_f is the modulus of glass fibres, MPa, E_c is the modulus of nanocomposite, MPa and E_{hc} is the modulus of hybrid composite, MPa.

A three phase model is developed by Ji *et al.*[45] and later tested by Ait Hocine *et al.*[34]. This model links in parallel and in series the matrix, the reinforcement and the interphase (including its size). For platelet reinforcement having a thickness t and both length and width much more than thickness ie (with $\xi >> t$), the effective Young's modulus E is expressed in the following equation:

$$E_c = \left[(1-\alpha) + \frac{\alpha-\beta}{(1-\alpha)+\frac{\alpha(k-1)}{\ln(k)}} + \frac{\beta}{(1-\alpha)+\frac{\beta E_f}{E_m}+\frac{(\alpha-\beta)(k+1)}{2}} \right] E_m \quad ..(15)$$

In the case of three filler system, instead of taking matrix, particulate filler and interphase as the three phases, micro filler is taken as the third phase. Hence $k=E_f/E_m$ ie the ratio between Young's modulus of fibre and the matrix, Φ_f is the volume fraction fibres, τ is the thickness of platelet and t is the thickness of fibre.

$$\beta = \sqrt{\phi_f} \quad \ldots\ldots (17)$$

$$\alpha = \sqrt{[2(\tau/t)+1]\phi_f} \quad \ldots\ldots (18)$$

The results of the above two models along with the experimental data are plotted in fig. 8.5. The experimental data is approaching more or less similar pattern of the Halpin-Tsai model modified for ternary system. The Ji's model is deviating from the experimental values more at higher filler loadings. This implies that matrix and filler is experiencing varying amount of strain[35] and interfacial adhesion between filler and matrix and also between the two fillers play a vital role in determining the modulus of the hybrid composites[91]. The modelling results are in agreement with the findings of Fornes and Paul[23] that the Halpin–Tsai equations retain the same form for discontinuous cylindrical fibres and lamellar shape reinforcements, such as ribbons or rectangular platelets;

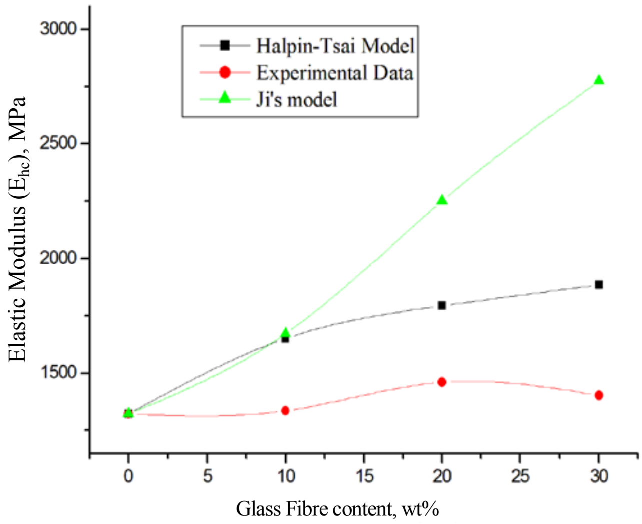


Figure 8.5 **Theoretical modelling of elastic modulus of hybrid composite as a function of glass fibre content using various equations/models based on micromechanics and composite theories.**

8.4 Conclusion

- Micromechanical modelling is carried out to obtain a better understanding of the behaviour of composite under load conditions.
- It is observed that the predictions from IROM and Takayanagi model have a closer proximity to the experimental value in the case of nano composites.
- Halpin-Tsai, Modified Halpin-Tsai (with modulus reduction factor) and VROM models stay largely deviated away on the higher side of the predicted modulii of PNC.
- These theoretical analyses indicate that the polymer-nanoclay interfacial characteristics partially converge to a state of perfect interfacial bonding (Takayanagi model) with an iso-stress (Reuss IROM) response.

- The usual purpose of the surface treatment of particulate fillers is to decrease their surface free energy in order to hinder particle/particle interactions and aggregation and this explain the enhancement of composite modulii
- Modelling the modulus of PP/HDPE/nanoclay/glass fibre hybrid composites is done to evaluate the synergy (if any) in combing the two scales of reinforcement.
- Halpin-Tsai model and Ji's model is used for modelling the hybrid composites.
- Experimental data follows the trend of three phase Halpin-Tsai model.
- This implies that matrix and filler is experiencing varying amount of strain and interfacial adhesion between filler and matrix and also between the two fillers play a vital role in determining the modulus of the hybrid composites.

References

[1] Braun T, Schubert A, Zsindely S (1997) "Nanoscience and nanotechnology on the balance". Scientometrics 38: 321–325.

[2] Kumar AP, Depan D, Tomer NS, Singh RP (2009) "Nanoscale particles for polymer degradation and stabilization-Trends and future perspectives". Progress in Polymer Science 34:479-515.

[3] Vaia RA,Wagner HD (2004) "Framework for nanocomposites". Mater Today 7:32–7.

[4] Liu H, Brinson LC (2008) "Reinforcing efficiency of nanoparticles: A simple comparison for polymer nanocomposites". Compos Sci Technol 68: 1502-1512.

[5] Fisher FT, Brinson LC (2006) "Nanomechanics of nanoreinforced polymers". In: Rieth M, Schommers W, editors. Handbook of theoretical and computational nanoscience. American Scientific Publishers: 253–360.

[6] Moniruzzaman M, Winey KI (2006) "Polymer nanocomposites containing carbon nanotubes". Macromolecules 39(16):5194–5205.

[7] Thostenson ET, Li CY, Chou TW (2005) "Nanocomposites in context". Compos Sci Technol 65: 491–516.

[8] Ajayan PM, Schadler LS, Braun PV (2003) "Nanocomposite science and technology". Weinheim: WILEY-VCH Verlag GmbH & Co. KGaA.

[9] Brune DA, Bicerano J (2002) "Micromechanics of nanocomposites: comparison of tensile and compressive elastic moduli, and prediction of effects of incomplete exfoliation and imperfect alignment on modulus". Polymer 43:369–87.

[10] Lincoln DM, Vaia RA, Wang Z-G, Hsiao BS (2001) "Secondary structure and elevated temperature crystallite morphology of nylon-6/ layered silicate nanocomposites". Polymer 42:1621–31.

[11] Shelley JS, Mather PT, DeVries KL (2001) "Reinforcement and environmental degradation of nylon-6/clay nanocomposites. Polymer 42:5849–58.

[12] J Aboudi (1989) "Viscoelastic behaviour of thermo-rheologically complex resin matrix composites". Composite Science and Technology 36:351-365.

[13] Srivastava D, Wei CY, Cho K (2003) "Nanomechanics of carbon nanotubes and composites". ApplMech Rev 56: 215–30.

[14] Leamy MJ (2007) "Bulk dynamic response modeling of carbon nanotubes using an intrinsic finite element formulation incorporating interatomic potentials". Int J Solids Struct 44: 874–94.

[15] Odegard GM, Gates TS (2006) "Modeling and testing of the viscoelastic properties of a graphite nanoplatelet/epoxy composite". J Intell Mater Syst Struct 17: 239–46.

[16] Sears A, Batra RC (2006) “Buckling of multiwalled carbon nanotubes under axial compression. Phys Rev B 73:085410-1–085410-11.

[17] Arroyo M, Belytschko T (2005) “Continuum mechanics modelling and simulation of carbon Nanotubes”. Meccanica 40(4–6):455–69.

[18] Odegard GM, Clancy TC, Gates TS (2005) “Modeling of the mechanical properties of nanoparticle/polymer composites”. Polymer 46: 553–62.

[19] Arroyo M, Belytschko T (2004) “Finite element methods for the non-linear mechanics of crystalline sheets and nanotubes”. Int J Numer Methods Eng 59(3):419–56.

[20] Zhu LJ, Narh KA (2004) “Numerical simulation of the tensile modulus of nanoclay-filled polymer composites”. J Polym Sci 42: 2391–406.

[21] Wu YP, Jia QX, Yu DS, Zhang LQ (2004) “Modeling Young’s modulus of rubber–clay using composite theories”. Polym Testing 23: 903–9.

[22] Luo J-J, Daniel IM (2003) “Characterization and modeling of mechanical behaviour of polymer/clay nanocomposites”. Compos Sci Technol 63:1607–16.

[23] Fornes TD, Paul DR (2003) “Modeling properties of nylon 6/clay nanocomposites using composite theories. Polymer 44:4993–5013.

[24] Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, O. Kamigaito (1993) “Mechanical properties of nylon-6-clay Hybrid”. J. Mater. Res. 6:1185–1189.

[25] A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, O. Kamigaito (1993) “Swelling behavior ot montmorillonite cation exchanged for u-amino acid bi e-caprolactam”. J. Mater. Res. 8:1174–1178.

[26] M. Alexandre, P. Dubois (2000) “Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mat. Sci. Eng. 28:1–63.

[27] J.M. Gloaguen, J.M. Lefebvre (2001) “Plastic deformation behaviour of thermoplastic/clay nanocomposites”. Polymer 42:5841–5847.

[28] Na Wang, Qinghong Fang, Yawei Shao, Jing Zhang (2009) “Microstructure and properties of polypropylene composites filled with coincorporation of MCM-41(with template) and OMMT nanoparticles prepared by melt-compounding”. Mater. Sci. Eng. A 512:32–38.

[29] C Ding, D. Jia, H. He, B. Guo, H. Hong, (2005) “How organo-montmorillonite truly affects the structure and properties of polypropylene”. Polym. Test. 24:94–100.

[30] J.-I. Weon, H.-J. Sue (2005) “Effects of clay orientation and aspect ratio on mechanical behavior of nylon-6 nanocomposite”. Polymer 46: 6325–6334.

[31] V. Marcadon (2005) “Effets de taille et d’interphase sur le comportement me’ canique de nanocomposites particulaires (in French). Departement Mecaniques et Materiaux de lecole Polytechnique”. Paris, France.

[32] S.A. Garea, H. Iovu, A. Nicolescu, C. Deleanu (2009) “A new strategy for polybenzoxazine-montmorillonite nanocomposites synthesis”. Polym. Test. 28: 338–347.

[33] A.S. Luyt, M.D. Dramicanin, Z Antic, V. Djokovic (2009) “Morphology, mechanical and thermal properties of composites of polypropylene and nanostructured wollastonite filler”. Polym. Test. 28: 348–356.

[34] N. Ait Hocine, P. Mederic, T. Aubry (2008) “Mechanical properties of polyamide- 12 silicate nanocomposites and their relations with structure”. Polym. Test. 27: 330–339.

[35] Dayama N, Sathapathy BK (2010) “Morphological interpretations and micromechanical properties of polyamide-6/polypropylene-grafted-maleic anhydride/ nanoclay ternary nanocomposites”. Mater Des; 31:4693-703.

[36] You-Ping Wu, Qing-Xiu Jia, Ding-Sheng Yu, Li-Qun Zhang (2005) “Modelling Young’s modulus of rubber-clay nanocomposites using composite theories”. Polymer Testing 23:903-909.

[37] Shao-Yun Fu, Xi-Qiao Feng, bernd Lauke, Yiu Wing Mai (2008) “ Effects of particle size particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites”. Composites Part B 39:933-961.

[38] Laszlo Szazdi, Bela Pukanszky Jr, G. Julius Vansco, Bela Pukanszky (2006) “Quantitative estimation of the reinforcing effect of layere silicates in PP nanocomposites”. Polymer 47:4638-4648.

[39] F. Lequeux, L. Monnerie, H. Montes, D. Long, P. Sotta, J. Beriot (2002) “Filler-elastomer interaction in model in filled rubbers, a H NMR study 53”. J. Non-Crystalline Solid. 307–310, 719–724.

[40] Dommelen VJAW, brekelmans WAM, Baaijens FPT (2003) “Micromechanical modelling of particle-toughening of polymers by locally induced anisotropy”. Mech Mater; 35:845-63.

[41] J. C. Halpin and J. L. Kardos (1976) “The Halpin-Tsai equations: A review”. Polym. Eng. Sci. 16:p.344-352.

[42] W. Voigt (1889) “Uber Die Beziehung Zwischen den Beiden Elasticitäts constantan Isotroper Körper”. Ann. Phys., 38:p.573-587.

[43] Bhattacharya D, Fakirov S (2009) “Organoclay, particulate and nanofibril reinforced polymer-polymer composites: manufacturing, modelling and applications, In: Karger-Kocsis J, Fakirov S, editors, Nano and micro-mechanics of polymer blends and composites”. Cincinnati, USA: Hanser Publications; [Chapter 5].

[44] A. Reuss (1929) “Berechnung der fliebgrenze von Mischkristalen auf Grund der Plastizitätsbedingung für Einkristalle”. ZAMM 9:p.49-58.

[45] X. L. Ji, J. K. Jing, W. Jiang and B. Z. Jiang, (2002). “Tensile modulus of polymer nanocomposites”. Polym. Eng. Sci. 42 (5): p.983-993.

[46] Cauvin L, Konodo D, brieu M, bhatnagar N (2009) “Mechanical properties of polypropylene layered silicate nanocomposites; characterization and micro-macro modelling”. Polym test:1-6.

[47] Ahmed S, Jones FR (1990) “A review of particulate reinforcement theories for polymer composites”. J Mater sci; 25:4933-42.

[48] Arpitha Pal Bathija ( ) “Elastic properties of clays”. Ph.D. Thesis Colorado School of Mines.

[49] Zhu ZK, Yang Y, Yin J, Qi ZN (1999) "Preparation and properties of organo soluble polyimide/silica hybrid materials by sol-gel process". J Appl Polym Sci; 73:2977-84.

[50] Dekkers MEJ, Heikens D (1983) "The effect of interfacial adhesion on the tensile behaviour of polystyrene-glass-bead composites". J Appl Polym Sci; 28:3809-15.

[51] Fu SY, Lauke B (1998) "Characterization of tensile behaviour of hybrid short glass fibre calcite particle ABS composites. Composite Part A; 29A:575-83.

[52] Fu SY, Lauke B (1997) "Analysis of mechanical properties of injection molded short glass fibre (SGF)/calcite/ABS composites". J Mater Sci Technol; 13:389-96.

[53] Eirich FR, (1984) "Some mechanical and molecular aspects of the performance of composites". J Appl Polym Sci Appl Polym Symp; 39:93-102.

[54] Radford KC (1971) "The mechanical properties of an epoxy resin with a second phase dispersion". J Mater Sci; 6:1286-91.

[55] Spanoudakis J, Young RJ (1984) "Crack propagation in a glass particle filled epoxy-resin. 1. Effect of particle-volume fraction and size. J Mater Sci; 19:473-86.

[56] Amdouni N, Sautereau H, Gerard JF (1992) "Epoxy composites based on Glass-beats. 2. Mechanical properties". J Appl Polym Sci; 46:1723-35.

[57] Wang M, Berry C, Brade M, Bonfield W (1998) " Young's and shear moduli of ceramic paricle filled polyethylene". J Mater Sci Mater Med; 9:621-4.

[58] Hsueh Ch (1987) "Effect of aspect ratios of ellipsoidal inclusions on elastic stress transfer of ceramic composites". J Am Ceram Soc; 72:344-7.

[59] Young Rj Beaumont PWR (1977) "Effect of composition upon fracture of silica particle-filled epoxy-resin composites". J Mater Sci; 12:684-92.

[60] Pukanszky B, Voros G (1993) "Mechanism of interfacial interactions in particulate filled composites". Compos Interf; 1:411-27.

[61] Nakamura Y, Yamaguchi M. Okubo M, Matsumoto T (1992) “Effects of particle size on mechanical and impact properties of epoxy-resin filled with spherical silica”. J Appl Polym Sci; 45:1281-9.

[62] Reynaud E, Jouen T, Gauthier C, Vigier G, Varlet J (2001) “Nanofillers in polymeric matrix: a study on silica reinforced PA6”. Polymer; 42:8759-68.

[63] Ou Y, Yang F, Yu ZZ (1998) “A new conception on the toughness of nylon 6/silica nanocomposite prepared via in situ polymerization”. J Polym Sci Part B Polym Phys; 36:789-95.

[64] Liang JZ, Li RKY, Tjong SC “.(1997) “Tensile fracture behaviour and morphological analysis of glass bead filled low density polyethylene composite”. Plast Rubber Compos Process Appl; 26:278-82.

[65] Chacko VP, Farris RJ, Karasz FE (1983) “Dynamic mechanical spectrometry of nylon-12”. J Appl Polym Sci; 28:2701-5.

[66] Tjong Sc, Xu SA (2001) “Ternary polymer composites: PA6,6/maleated SEBS/glasss beads”. J Appl Polym Sci;81:3231-7.

[67] Danusso F, Tieghi G (1986) “Strength versus composition of rigid matrix particulate composites”. Polymer; 27:1385-90.

[68] Levita G, Marchetti A, Lazzeri A (1989) “Fracture of ultrafine calcium carbonate/polypropylene composites”. Polym Compos; 10:39-43.

[69] Nicolais L, Narkis M (1971) “Stress-strain behaviour of Styrene-acrylonitrile/glasss bead composites in the glassy region”. Polym Eng Sci; 11:194-9.

[70] Nicolais L. Nicodemo L (1974) “effect of particles shape on tensile properties of glassy thermoplastic composites”. Int J Polym Mater; 3:229.

[71] Pukanaszky B (1995) Composites In: Karger-Kocsis J,editor. “Polypropylene: structure, blends and composites, vol 3, London: Chapman & Hall. p. 1-70.

[72] Baker RA, Koller LL, Kummer PE (1987) Calcium carbonate In: Katz HS, Milevski JL, editors. Handbook of fillers for plastics, 2nd ed. New York: Van Nostrand Reinhold Co; p.119-42.

[73] Badran Bm, Galeski A, Kryszewski M (1982) "High-density Polyethylene filled with modified chalk". J Appk Polym Sci; 27:3669-81.

[74] Hoffmann M, Grellmann W, Zilvar V (1986) "Instumented impact studies on thermoplastic composites, In: Sedlacek b, editor. 28th Micro-symposium on Macromolecules polymer composites. Polymer composites". New York: Walter de Gruyter: p.233-42.

[75] Fu Q, Wang G (1992) "Polyethylene toughened by rigid inorganic particles". Polym Eng Sci; 32:94-7.

[76] FU Q, Wang G, Shen J (1993) "Polyethylene toughened by $CaCO_3$ particles: brittle-ductile transition of $CaCO_3$ –toughened HDPE". J Appl POlym Sci; 49:673-6.

[77] Fu Q, Wang G (1993) "Effect of morphology on brittle-ductile transition of HDPE/$CaCO_3$ blends". J Appl Polym Sci; 49:1985-8.

[78] Fu Q, Wang G (1993) "Polyethylene toughened by $CaCO_3$ particles-percolation in HDPE/$CaCo_3$ blends". Polym Int; 30:309-12.

[79] Bartczak Z, Argon AS, Cohen RE, Weinberg M (1990) "Toughness mechanism in semi-crystalline polymer blends: II. High density polyethylene toughened with $CaCO_3$ filler particles". Polymer; 40: 2347-65.

[80] Sumitha M, Shizuma T, Miyasaka K, Ishikawa K (1983) "Effect of reducible properties of temperature, rate of strain, and filler content on the tensile yield stress of nylon 6 composites filled with ultrafine particles". J Macromol Sci;B 22:601-18.

[81] Moloney AC, Kausch HH, Kaiser t, Beer HR (1987) "Review- parameters determining the strength and toughness of particulate filled epoxide resins". J Mater Sci; 22:381-93.

[82] Spanoudakis J, Young RJ (1984) "Crack propagation in a glass particle filled composite at or near a rigid spherical inclusion". J Mater Sci; 19:487-96.

[83] Broutman LJ, Sahu S (1986) "The effect of interfacial bonding on the toughnesss of glass filled polymers". Mater Sci Eng; 8:98-107.

[84] Kinloch AJ (1986) “Structural adhesives”. London: Elsevier Applied Science Publishers.

[85] Roulin-Moloney AC, Cantwell WJ, Kausch HH (1987) “Parameters determining the strength and toughness of particulate filled epoxy resins”. Polym Compos; 8:314-23.

[86] Sahu S, Broutman LJ (1972) “Mechanical properties of particulate composites”. Polym Eng Sci; 12:91-100.

[87] Kendall K (1978) “Fracture of particulate filled polymers”. Brit Polym; 10:35-8.

[88] Yu Dong, Debes Bhattacharyya, Peter J Hunter (2008) “Experimental characterisation and object-oriented finite element modelling of polypropylene/organoclay nanocomposites”. Composites Science and Technology 68:2864-2875.

[89] V. Pukanszky, E. Fekete (1999) “Adhesion and surface modification”. Adv. Polym. Sci. 139:109–153.

[90] Hull D, Clyne Tw (1981) “An introduction to composite materials”. UK: Cambridge University Press.

[91] Mike J Clifford, Tong Wan (2009) “Fibre reinforced nanocomposites: Mechanical properties of PA6/clay and glass fibre/PA6/clay nanocomposites”. J Polymer doi:101016

[92] Le Baron PC, Wang Z, Pinnavaia TJ (1999). Polymer-layered Silicate Nanocomposites: An Overview, Applied clay science; 15:11-29.

[93] Yasue K, Katahira S, Yoshikawa M, Fujimoto K (2000) “In situ polymerisation route to nylon 6-clay nanocomposites”. In: Pinnavaia TJ, Beall GW, editors. Polymer clay nanocomposites. John Wiley & sons Ltd; p :112-26.

[94] Liu XH, Wu Q (2002). “Phase transition in nylon 6/clay nanocompo- sites on annealing.” Polymer; 43:1933-6.

[95] XU H, Zhao XY (2004). Polymer: 45:3819-25.

[96] Wan T, Clifford MJ, Gao F, Bailey AS, Gregory DH (2005). "Strain amplitude response and the microstructure of PA/clay nanocomposites." Polymer; 46:6429-36.

[97] Loo Ls, Gleason KK (2003). "Insights into structure and mechanical behavior of and crystal forms of nylon-6 at low strain by infrared studies." Macromolecules; 36:2587-90.

[98] Mallik PK (2000) "Particulate and short fibre reinforced polymer composites, in comprehensive composites materials". P 291-331.

…..

Chapter 9

SUMMARY AND CONCLUSIONS

Upgrading two widely used standard plastics, polypropylene (PP) and high density polyethylene (HDPE), and generating a variety of useful engineering materials based on these blends have been the main objective of this study. Upgradation was effected by using nanomodifiers and/or fibrous modifiers. PP and HDPE were selected for modification due to their attractive inherent properties and wide spectrum of use. Blending is the engineered method of producing new materials with tailor made properties. It has the advantages of both the materials. PP has high tensile and flexural strength and the HDPE acts as an impact modifier in the resultant blend. Hence an optimized blend of PP and HDPE was selected as the matrix material for upgradation. Nanokaolinite clay and E-glass fibre were chosen for modifying PP/HDPE blend.

Kaolinite clay (1:1 type clay) is used widely in the industrial sector as filler in paints, varnishes and to make ceramic wares due to its low cost and abundance. It has low cation exchange capacity and is very difficult to disperse in its nanoform in the polymer matrix. This is due to the its 1:1 structure, smaller interlayer spacing and hydrophilic nature. Hence there is scarce amount of literature present on the use of kaolinite clay as precursor for polymer nanocomposites when compared to its counterpart, Montmorillonite clay. To improve miscibility and ensure proper dispersion of nanokaolin clay in the polymer matrix, five different types of commercially available surface modified nanoclays were used to produce polymer nanocomposites with PP/HDPE blend as the matrix material. The filler-matrix adhesion and the dispersion of each surface modified nanoclay in the polymer blend were investigated by analysing the product quality and performance. Melt compounding method was adopted because of its versatility and commercial importance. The presence of compatibilizers has less effect on mechanical properties than the use of surface modified nanoclay

As the first stage of the work, the mechanical, thermal, morphological, rheological, dynamic mechanical and crystallization characteristics of the polymer nanocomposites prepared with PP/HDPE blend and different surface modified nanokaolinite clay were analysed. The mechanical and thermal properties of matrix significantly improve on modification with nanoclay. The clay modified with amino tri-ethoxy silane (N100A) show maximum enhancement in composite properties followed by unmodified clay (N100). With the addition of nanoclay-N100A to the polymer matrix, the tensile strength increases by 22.5% and flexural strength by 19.1%. There is an increase of 62.9% in tensile modulus and 28.5% in flexural modulus. Impact strength on the other hand is found to decrease on the addition of nanoclay. This may be due to increase in crystallinity of polymer phase, which is evident from the results of differential scanning calorimetry. The dynamic mechanical properties of the nanocomposites reveal that a small concentration of nanclay is sufficient to improve the storage modulus. The storage modulus improves by around 30 MPa upon addition of nanoclay N100A. This is due to the stiffening effect of the filler particles and efficient stress transfer between them and the polymer matrix. The TEM images reveal the formation of intercalated composites in the presence of N100 and partially exfoliated composites in the presence of N100A. The maximum enhancement of properties are obtained at the nanoclay content of 2wt%. XRD analysis shows that the interlayer spacing of N100A nanoclay is increased to 8.12 nm from 7.2nm and that N100 is varied from 7.09 nm to 7.85nm in respective polymer nanocomposites. SEM analysis shows more homogeneous and compatibilized composites are formed in the presence of 2wt% N100A.

E-glass fibre or electrical grade glass fibre is the commonly used reinforcing filler to upgrade plastics and the composite is known commercially as fibre-glass. The short glass fibre composites with polymer matrix is extensively being used in aircrafts, ships, automobiles etc., as the incorporation of glass fibre gives excellent mechanical strength, thermal and electrical insulation, chemical, corrosion and weather resistance, optical and radar transparency and durability. The E-glass fibre has excellent cost-performance ratio when compared with other types of glass fibres. Hence it is selected as the fibrous filler for upgrading PP/HDPE blend. But the presence of high filler content (15wt% to 50wt%) in these composites is detrimental to polymer properties like ductility, processibility and low weight. Nanofillers can dramatically improve the polymer performance even at very low filler loadings. Hence the presence of nanofiller along with micron sized short. glass fibres has resulted to the development of a new hybrid composite.

As the second stage of the work, the effect of simultaneous inclusion of nanokaolinite clay(both N100A and N100) and short glass fibres are investigated. The presence of nanofiller has increased the properties of hybrid composites to a greater extent than micro composites. The surface modified nanoclay (N100A) acts as a molecular bridge between inorganic glass fibre and organic polymer surface. Hence there is synergism and enhanced filler-matrix adhesion in the presence of organoclay when compared to unmodified clay hybrid composites. This is evident in SEM image of fracture surface as less fibre pull out, better fibre dispersion and matrix compatibility in these composites. The incorporation of optimum amount of both fillers (20 wt% glass fibre and 2 wt% N100A) has increased the tensile strength by 49.01, flexural strength by 66.9%, tensile modulus by 52.49, flexural modulus by 84.5% and impact strength by 31.8%. The dynamic mechanical and thermal properties are also found to increase considerably. The XRD analysis shows that the interlayer spacing of nanoclay increases in hybrid composites. Rheological analysis of the composites shows interesting results. The linear viscoelastic range specifies the applicability of a material to different processing and operating conditions. The linear viscoelastic range (LVR) of the composites is drastically reduced on the increase of filler content. Hence the reduction of fibre loading in hybrid composites has increased the range of applicability and durability of the same.

For the development of useful nano and hybrid composite, selection of proper materials, optimum design with regard to the particular product and choosing proper processing parameters are most essential. Since there is a co-influence of many parameters, analytical solutions are difficult. Hence, for selecting proper processing parameters and optimum filler content, 'Design of Experiments' and Minitab IV software were utilized in the next section. The optimum processing conditions, significance of each process variable and interaction between these variables and filler content are obtained in the complex multivariable process of producing both nanocomposites and hybrid composites by the use of Box-Behnken Design of Experiments. The optimum processing parameters obtained are – melt compounding temperature of 160°C, melt mixing time of 8 minutes and a mixing shear of 50 rpm. Model equations are developed for all the responses. Response surface and contour plots gave a clear visualization of the response variation. Overlaid contour plots are drawn to find the best operating region. Statistical evaluation is conducted for both nano and micro composites using p-test and ANOVA. The statistical evaluation suggests that there is interaction between the two fillers in the case of hybrid composites with N100A and glass fibres which led the synergistic increase of the composite properties.

As the last stage, micromechanical modelling of both nano and hybrid composites is carried out to analyse the behaviour of the composite under load bearing conditions. These theoretical analyses indicate that the polymer-nanoclay interfacial characteristics partially converge to a state of perfect interfacial bonding (Takayanagi model) with an iso-stress (Reuss IROM) response. In the case of hybrid composites the experimental data follows the trend of Halpin-Tsai model. This implies that matrix and filler experience varying amount of strain and interfacial adhesion between filler and matrix and also between the two fillers which play a vital role in determining the modulus of the hybrid composites

A significant observation from this study is that the requirement of higher fibre loading for efficient reinforcement of polymers can be substantially reduced by the presence of nanofiller together with much lower fibre content in the composite. Hybrid composites with both nanokaolinite clay and micron sized E-glass fibre as reinforcements in PP/HDPE matrix will generate a novel class of high performance, cost effective engineering material.

There is ample scope for future research in this area. A few suggestions are given below:

- To develop the hybrid composite for specific applications.
- Thermal degradation and ultra violet degradation studies can be done to check the performance of the composite under real world conditions
- The E-glass fibre has the property of radar transparency. Hence the evaluation of dielectric constant, reflection and transmission losses for radar frequency wavelength radiation can be evaluated for applying the hybrid composite as high performance radar transparent material in high velocity radar transparent aerospace structures and submarines

* * *

Appendix

Annexure of Figure 3.1; BHIC is the required compound for surface modifying clay and K-BHIC is the surface modified form. In this study BHIC refers to amino silane.

Table 6.6 Variables in Box– Behnken design

Variables	Levels used, actual (coded)		
	Low(-1)	Medium(0)	High(1)
Mixing Temperature(^{o}C)	150	160	170
Mixing Time(min)	4	8	12
Nano clay content(%)	1	2	3
Glass fibre content	10	20	30

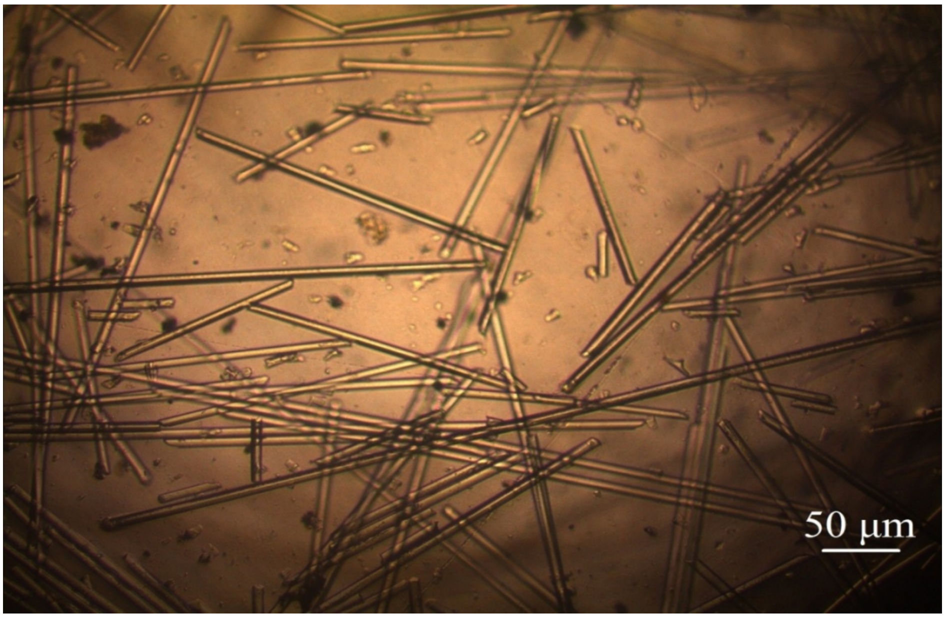


Figure A.1. Optical Microscopy image

Aspect ratio (l/d) is calculated by the optical microscopy image (fig. A.1). Length = 6 mm and d=10μm (from SEM figure 8.1). Hence the aspect ratio= 6000/10 = 600.

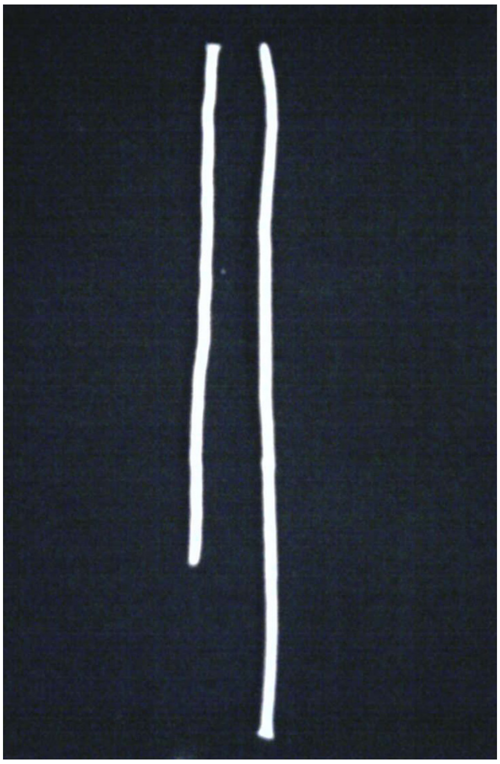


Figure A.2. MFI Extrudate of PP/HDPE Pure blend and that of PP/HDPE/gf composite

Abbreviations and Symbols

AARE	-	Average Absolute Relative Error
ABS	-	Acrylonitrile Butadiene Styrene
AFOSR	-	Air Force Office of Scientific Research
ANOVA	-	Analysis of Variance
ASTM	-	American Society for Testing and Materials
BBD	-	Box-Behnken Design
BS	-	% Break strain
CCD	-	Central Composite Design
DMA	-	Dynamic Mechanical Analysis
DoE	-	Design of Experiments
DMSO	-	Dimethyl sulfoxide
DMTA	-	Dynamic mechanical thermal analysis
DRA	-	Dynamic Rheological Analysis
DSC	-	Differential Scanning Calorimetry
DTA	-	Differential Thermal Analysis
DTG	-	Derivative Thermogravimetric Analysis
EPDM	-	Ethylene- Propylene- Diene – Copolymer
E’	-	Storage modulus
E”	-	Loss modulus
E_c	-	Modulus of composite
E_f	-	Modulus of fibre
E_{hc}	-	Modulus of hybrid composites
E_m	-	Modulus of matrix
FRP	-	Fibre Reinforced Plastic
FS	-	Flexural strength, MPa
FM	-	Flexural modulus, MPa
gf	-	glass fibre
HDPE	-	High Density Polyethylene
IS	-	Impact strength, KJ/mm^2

IROM - Inverse Rule of Mixtures
LVR - Linear Viscoelastic Range
MA/DCP - Maleic Anhydride/ Dicumyl Peroxide
MAPP - Maleic Anhydride – modified Polypropylene
MCR - Modular Compact Rheometer
MFI - Melt Flow Index
MFR - Melt Flow Rate
MMT - Montmorillonite
MPa - Mega Pascal
MRF - Modulus Reduction Factor
MTS - Mica Type Silicates
NC - Nanoclay
NIST - National Institute of Standards and Technology
NMBE - Normalised Mean-Biased Error
N100 - Unmodified nanokaolinite clay-Nanocaliber100
N100A - Amino modified nanokaolinie clay-Nanoclaiber 100A
N100M - Mercapto modified nanokaolinite clay-Nanocaliber 100M
N100V - Vinyl modified nanokaolinite clay-Nanocaliber 100V
N100Z - Dialkyl modified nanokaolinite clay-Nanocaliber 100Z
nm - Nanometre
OFAT - One factor at a time
OMLS - Organo Modified Layered Silicate
OMMT - Organo-Montmorillonite
PE - Polyethylene
PEO - Polyethylene Oxide
PET - Polyethylene Terephthalate
PLA - Polylactic acid
PMMA - Polymethyl Methacrylate
PNC - Polymer Nanocomposites
PP - Polypropylene
PS - Polystyrene
PVA - Polyvinyl alcohol

R - Correlation coefficient
RMSE - Root Mean Square Error
ROM - Rule OF Mixtures
RSM - Response Surface Methodology
rpm - Revolutions per minute
SEBS - Styrene Ethylene Block Polymer
SEM - Scanning Electron Microscope
SI - Scatter Index
sPP - Syndiotactic Polypropylene
$\tan \delta$ - Loss factor
TS - Tensile strength, MPa
TM - Tensile modulus, MPa
τ - Shear stress
TEM - Transmission Electron Microscopy
TGA - Thermogravimetry Analysis
TMA - Thermomechanical Analysis
Tg - Glass transition temperature
UP - Unsaturated Polyester
UTM - Universal Testing Machine
WAXD - Wide Angle X-ray Diffraction
wt% - Weight Percentage
XRD - X-ray Diffraction
ζ - shape parameter
η - complex viscosity
φf - volume fraction of clay

List of Publications

Journals

[1]. **Anjana R**, Asha Krishnan, Tresa Sunitha George and K E George. "Design of experiments for thermomechanical behaviour of PP/HDPE/nanokaolin clay composites". Polymer Bulletin,2014,71,315-335

[2]. **Anjana Ramachandran**, K. E. George, Tresa Sunitha George, Asha rishnan. "Optimisation of processing conditions of PP/HDPE/nanokaolinite clay composites by response surface methodology". Int. J Plast. Technol, 2012 16(2):136–149

[3]. **Anjana R,** Asha Krishnan, Tresa Sunitha George and K E George. Polypropylene/High Density Polyethylene/Glass Fibre/Nanokaolinite Clay Composites-a Novel Material For light Weight Manufacturing Systems. Advanced Materials research, 2013, Vols. 816-817 pp 96-100

[4]. K. Asha Krishnan, **R. Anjana**, K.E. George."Effect of Alkali-Resistant Glass Fiber on Polypropylene/ Polystyrene Blends: Modeling and Characterization". Polym. Composites, 2014, DOI 10.1002/pc.23193

[5]. Asha K Krishnan, Tresa Sunitha George, **Anjana R,** Newly Joseph and K E George. "Effect of modified kaolin clays on the mechanical properties of polypropylene/ polystyrene blends". J Appl. Polym Sci. 2013, 127:2, 1409-1415.

[6]. Tresa Sunitha George, Asha Krishnan. **Anjana R,** K E George. "Effect of maleic anhydride grafting on nanokaolinclay reinforced polystyrene/high density polyethylene blends". Polym. Composites; 2012, 33:9,1465-1472.

[7]. **Anjana R** and K E George."Reinforcing effect of nanokaolin clay on PP/HDPE blends". IJERA,2012, Vol2,Issue4, pp-868-872

[8]. Ranjusha J P, **Anjana R**, K E George. "Effect of moulding temperature on the properties of PP/HDPE/clay/glass fibre composites". IJERA,2012, Vol2, Issue5, pp-1922-1926

[9]. Tresa Sunitha George, Asha Krishnan K, **Anjana R**, K E George. Studies on Nano kaolin Reinforced PS-HDPE Nanocomposites. IJAC,2013, 1(4) 201-206

[10]. Indira V, **Anjana R** and K E George. "Preparation and characterization of pp/hdpe/ nanoclay/short fiber hybrid Composites using response surface methodology". Global Journal of Engineering and Applied Sciences, 2011, PP 88-91.

Conferences

[1]. **Anjana R** and K E George. "Preparation and characterization of high density polyethylene-polypropylene/ nanoclay composites" ICMF 2011, organised by GEC, Thrissur, 23-25th February 2011

[2]. Asha A B, **Anjana R** and K E George. "Modification of PP/HDPE Blends Using Nanoclay". ICMF 2011, organised by GEC, Thrissur, 23-25th February 2011

[3]. **Anjana R** and K E George. "Effect of blend composition and mixing shear on nanoclay modified PP/HDPE blends by Response Surface Methodology". Chemference 2011, organized by Dept. of Chemical Engg., IISC, Bangalore, 23-24th September 2011

[4]. **Anjana R** and K E George."Effect of surface modification of nanoclay in PP/HDPE/ glass fibre/nanoclay hybrid composites". Natcon 2012, organized by CERD and GEC, Thrissur,9-10th February 2012

[5]. Renjusha J P, **Anjana R** and K E George."Review on Polymer short fiber hybrid nanocomposites: Preparation, characterization, application and environmental impact". Natcon 2012, organized by CERD and GEC, Thrissur,9-10th February 2012

[6]. Lovey Jacob, **Anjana R** and K E George. "Review paper on preparation, characterization and application of polymer nanocomposites". Natcon 2012, organized by CERD and GEC, Thrissur,9-10th February 2012.

[7]. **Anjana R** and K E George. "Synergistic effect of nanoclay in the physical properties of PP/HDPE blends". NAIMSAP, organized by DTE and Production Engg Dept of GEC, 5-7September 2012

[8]. **Anjana R** and K E George. "Effect of Compatibilisers on PP/PE/ Nanokaolinite clay Composites". *Proceedings of First National Conference on Advanced Trends In Chemical Engineering(ISBN 978-93-82338-75,2013 Bonfring), organized by Dept of Chemical Engg.,GEC, Thrissur and funded by TEQIP-II in 2013*

[9]. **Anjana R**, Asha Krishnan, Tresa Sunitha George and K E George. "Polypropylene/High Density Polyethylene/Glass Fibre/Nanokaolinite Clay Composites-a Novel Material For light Weight Manufacturing Systems". *4 th International Conference – ICMST 2013 at Dubai, UAE, during 3-4 August 2013*

Funded research project

[1]. **Anjana R.** "Preparation, optimization of parameters, mechanical properties evaluation, thermogravimetric analysis and morphological studies of high density polyethylene and polypropylene-glass fibre- nano clay hybrid composite" Project No. CERD/2010/RSM 32, Research Seed Money Project from Centre for Engineering Research and Development, Govt. of Kerala for Rs. 2 lakhs

Curriculum Vitae

Anjana R
767/7 Panjajanyam
Simple Avenue
Ramavarmapuram P.O
Thrissur – 680631
Kerala, India.

Ph: +91-9446024544
Email: anjan.rnair@gmail.com

Personal Profile

Date of birth : 24-12-1979
Gender & marital status : Female, married
Religion & Caste : Hindu, Nair
Nationality : Indian

Academic Qualification

- M Tech in Chemical Engineering (Process Control): November 2003, University of Calicut
- B Tech in Chemical Engineering : July 2001, University of Kerala

Professional Experience

- Assistant Professor :(June 2004-till date) Department of Chemical Engineering, Government Engineering College, Thrissur

Research Experience

- Doing Ph.D (part time) from August 2009 in the Department of Polymer Science and Rubber Technology, CUSAT under the supervision of Prof. K E George
- Principal Investigator of Research Seed Money Project (Project No. CERD/2010/RSM 32) under CERD, Govt. of Kerala
- Actively participated in various research and developmental projects as TEQIP, DST-FIST, Modrobs etc.
- Successfully guided 11 M Tech research projects and 10 B Tech projects
- Published 10 journal papers and presented 9 conference papers
- Received an incentive of Rs 10,000/- from CERD for publishing research paper in a popular peer reviewed journal

Membership in professional bodies

- Life member of Indian Society for Technical Education (ISTE)
- Life member of Indian Institute of Chemical Engineers (IICHE)
- Life member of International Association for Computer Science and Information Technology (IACSIT)

……