STUDIES ON SHORT POLYESTER FIBER – POLYURETHANE ELASTOMER COMPOSITE WITH DIFFERENT INTERFACIAL BONDING AGENTS

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To
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CERTIFICATE

This is to certify that the thesis entitled ***"Studies on short polyester fiber - polyurethane elastomer composite with different interfacial bonding agents"*** is an authentic report of the original work carried out by **Miss Fathimathul Suhara P.P.**, under my supervision and guidance in the department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin -22. No part of the work reported in this thesis has been presented for any other degree from any other institution.

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DECLARATION

I hereby declare that the thesis entitled *"Studies on short polyester fiber - polyurethane elastomer composite with different interfacial bonding agents"* is the original work carried out by me under the guidance of **Dr. Sunil K. Narayanankutty,** Senior Lecturer, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Cochin, and no part of this thesis has been presented for any other degree from any other institution.

20.02.1998 **FATHIMATHUL SUHARA P. P.**

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PREFACE

Recently short fiber composites, that somewhat exotic and mysterious group of materials, are of great interest to the rubber industry. This thesis is about the short polyester fiber - polyurethane elastomer composite. The properties of the composites are greatly influenced by the interfacial bonding between the fiber and the matrix. Conventionally hexamethylenetetramine, resorcinol and hydrated silica are used to improve the interfacial bonding in short fiber composites. However this bonding agent is not effective in the case of composites based on polyurethane elastomer and short polyester fiber. In this thesis an attempt has been made to develop a new bonding system based on diisocyanate and polyol for this composite. Emphasis has been given to evaluate the new bonding agents with respect to various technological properties of the composite.

The results of the investigation are dealt with separately in different chapters as follows:

Chapter 1 presents a review of the literature in this field and the scope of the present investigation.

Chapter 2 deals with the materials used and the experimental procedures adopted for the study.

Chapter 3 is divided into two sections. Section A is concerned with the evaluation of conventional and newly developed bonding agents by means of the cure characteristics of the composite. Section B covers the optimisation of the -ol to isocyanate ratio in the resin and comparison of the various bonding agents with the help of cure characteristics.

Chapter 4 is divided into two sections. Section A deals with the rheology of the short polyester fiber - polyurethane composite. This is extended to Chapter 4.B. The effect of the various bonding agents on the rheological properties are discussed in this section.

The mechanical properties of the composites with respect to the fiber loading, fiber orientation and the bonding agents are described in Chapter 5.

In Chapter 6 the results of stress relaxation of the composites with respect to fiber loading, fiber orientation and bonding agents are highlighted.

Thermal degradation characteristics of the composites with and without different bonding agents are evaluated in Chapter 7.

Conclusions of the present investigation are described in the last chapter, Chapter 8.

To aid the use of the thesis a lists of abbreviations are also given. At the end of each chapter a list of references is given and it should serve as a useful source of further detailed information at the research level.

ABSTRACT

The work presented in this thesis is regarding the development and evaluation of new bonding agents for short polyester fiber - polyurethane elastomer composites. The conventional bonding system based on hexamethylenetetramine, resorcinol and hydrated silica was not effective as a bonding agent for the composite, as the water eliminated during the formation of the RF resin hydrolysed the urethane linkages. Four bonding agents based on MDI/TDI and polypropyleneglycol, propyleneglycol and glycerol were prepared and the composite recipe was optimised with respect to the cure characteristics and mechanical properties. The flow properties, stress relaxation pattern and the thermal degradation characteristics of the composites containing different bonding agents were then studied in detail to evaluate the new bonding systems. The optimum loading of resin was 5 phr and the ratio of the -ol to isocyanate was 1:1. The cure characteristics showed that the optimum combination of cure rate and processability was given by the composite with the resin based on polypropyleneglycol/ glycerol/ 4,4'diphenylmethanediisocynate (PPG/GL/MDI). From the rheological studies of the composites with and without bonding agents it was observed that all the composites showed pseudoplastic nature and the activation energy of flow of the composite was not altered by the presence of bonding agents. Mechanical properties such as tensile strength, modulus, tear resistance and abrasion resistance were improved in the presence of bonding agents and the effect was more pronounced in the case of abrasion resistance. The composites based on MDI/GL showed better initial properties while composites with resins based on MDI/PPG showed better aging resistance. Stress relaxation showed a multistage relaxation behaviour for the composite. Within the strain levels studied, the initial rate

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of relaxation was higher and the cross over time was lesser for the composite containing bonding agents. The bonding agent based on MDI/PPG/GL was found to be a better choice for improving stress relaxation characteristics with better interfacial bonding. Thermogravimetirc analysis showed that the presence of fiber and bonding agents improved the thermal stability of the polyurethane elastomer marginally and it was maximum in the case of MDI / GL based bonding agents. The kinetics of degradation was not altered by the presence of bonding agents.

CHAPTER I

INTRODUCTION

At the onset of life itself, man unknown to him, has been surrounded by composites in the form of tree trunk rocks, bones, teeth etc. The importance of composites emerged only in the late 1940's and early 1950's, when the availability and utilization of man - made synthetic fibers as structural components along with traditional engineering materials such as steel, wood etc., has increased remarkably. Reinforcement of various matrices can be done to produce structural materials, which require high strength, stiffness and toughness. The very attractive features of composites are their lightweight, low cost and properties that can be tailor- made to suitable for any of the service conditions. Annual production of the composites is over 10 million tonnes and recently the market has been grown ~~upto~~ 5 - 10 % per annum. Now a days, fiber reinforced composites have found wide applications in aerospace industry.

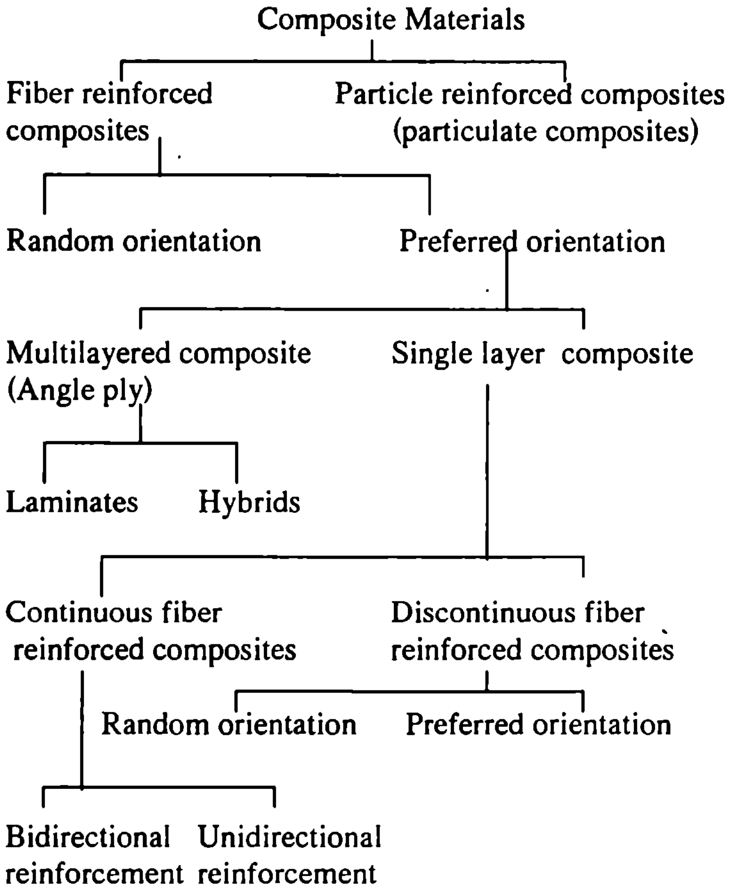
For a material to be a composite, it must consists of two or more distinctive components, of which one usually constitutes a significant majority and atleast some of its properties must be radically different from any of its constituents. Thus a composite can be defined as a combination of two or more distinct phases having significantly different physical properties and the composite properties are noticeably different from the properties of the constituents, which retain~~s~~ their identity. Composites typically have a discontinuous fiber or particle phase (reinforcers) that is stiffer and stronger than the continuous phase (matrix) in which they are embedded.

Properties of the composites are strongly influenced by the properties and proportion of their constituents, their distribution, dispersion and interaction between the matrix and reinforcement. Composite properties may be either the sum of the properties of the distinct phases, or it may be resulted from the synergic action of the different phases that are not accounted for by a simple volume fraction sum of the properties.

1.1. CLASSIFICATION OF THE COMPOSITES

The very broad and important class of these structural engineering composites can be classified on the basis of dimensions of the dispersed phase as macrocomposite (the one in which one or more of the dispersed phases are distinguishable extensively and macroscopically, i.e., are >10 $^{-6}$ m across the widest or longest axis or one in which more than one continuous phase is present) and as microcomposites (composites with all individual phases are between 10 $^{-8}$ - 10 $^{-6}$ m across the widest or longest axis and there is only one continuous phase)[1]. The macrocomposites can again be classified on the basis of geometry of the reinforcer and such a classification is shown in scheme 1.1.[2].

A reinforcer is considered to be a particle if all its dimensions are roughly equal and the composite which contains the particle as the discontinuous phase is said to be a particulate composite. Examples of particle reinforcement are the reinforcement of metallic matrices by ceramics, metallic or inorganic particles. These are mainly used to improve the properties of the matrix material such as ~~to~~ improveed ~~the~~ performance at elevated temperature, to modify thermal and electrical properties, to increase wear and abrasion resistance, to reduce friction, to improve machinability, to increase surface hardness and to reduce shrinkage and then simply used to reduce the cost. For example lead in copper alloys and steels are used to improve machinability, inorganic fillers which can be very effectively improve various properties of plastics without deteriorating the other properties.



Scheme 1.1. Classification of composites

Fiber reinforced composites contain reinforcements having lengths much greater than their cross sectional dimensions and the reinforcing ability of the fiber is restricted to the length wise direction of the fiber. The composites belong to this class include both natural and synthetic fibrous composites. Glass fibers due to its low cost and availability, are the most commonly used reinforcement in man-made composites followed by carbon, boron, aramid, polyester, nylon etc. Examples of natural fibers are cellulose, silk, cotton, jute, sisal, pineapple etc. In these composites fibers are the main load carriers and these composites have exceptional specific mechanical properties that considerably exceeds those of metals. The role of the matrix in the fibrous composites is to bind the fibers together, i.e., it maintains the desired fiber orientations and spacings and transfers the load to the fibers and protect them against environmental attack and damage due to handling.

Continuous fiber reinforced composites are the composites with long fibers and the principle of the continuous fiber composite is that the fibers must support all main loads and limit deformations acceptably[3]. The composites must contain a sufficiently high volume fraction of fibers aligned in directions as needed to support the loads. When the continuous fibers are aligned the composite is said to be unidirectional composite and these are very strong in the fiber direction and generally weaker in the perpendicular direction of the oriented fibers. Composite tensile properties in the fiber direction (L) can be estimated by rule of mixtures based on fiber properties (f) and neglecting the matrix concentration as

$$E_L \cong E_f V_f \text{ and } F_L \cong F_f V_f$$

where E_f, F_f and V_f refers to modulus, strength and fiber volume fraction respectively. The two outstanding features of the oriented fiber composites are their high strength to weight ratio and controlled anisotropy.

Composites in which short or staple fibers are embedded in the continuous matrix are termed as discontinuous fiber reinforced composites. By using short, individual fibers as a reinforcer one can impart drastic changes to the mechanical, thermal and viscoelastic properties of the matrix. These changes obtained even at relatively low loadings go far beyond the levels obtained with the use of particulate fillers. In contrast to the slow process required to place continuous fibers the short fibers can have the advantage of direct incorporation into the matrix. The properties of the composites are affected mostly by the fiber length, distribution, dispersion, orientation, aspect ratio of the fiber (the length to diameter ratio) and the interaction between the fiber and the matrix.

1.2. SHORT FIBER COMPOSITES

The improvement of mechanical properties of the elastomers by the reinforcing ingredients is a major factor in the successful use of elastomers. Among the commercially available reinforcing materials carbon black is the most effective. However, the tensile property improvements obtained through carbon blacks are limited by the processing difficulties encountered at higher filler loadings. The addition of suitable short fibers result in the improvement of mechanical properties and also offers a considerable processing and mechanical advantage such as choice of orientation during extrusion, calendering and molding operations[4]. Reinforcement of elastomers with short fibers combines the rigidity of the fibers with the elasticity of the rubber. Thus short fiber reinforcement of elastomers has got much attention as a viable alternative to particulate filler reinforcement because of the typical advantages associated with fibrous fillers which include design flexibility, high low -strain modulus, anisotropy in technical properties, stiffness, damping and processing economy.

Elastomers find wide utility in many dynamic applications by its low bending and torsional modulus and its high resilience. The incorporation of the dispersed reinforcements throughout the rubber phase would necessarily compromise the attributes of the matrix. A proper use of short fibers in the matrix can generate a degree of reinforcement that is sufficient in many applications.

A short fiber-elastomer composite results from the embedment of short fibers in an elastic matrix. The critical properties of such composites generally relate to the use of the composites against forces in the longitudinal fiber direction and the fibers have a function similar to tensile cords commonly embedded in the rubber.

The reinforcement of elastomers with short fibers has become necessary in many product applications. Composites with low fiber content is useful for improving the hose and belt performance due to an increase in composite stiffness without a great sacrifice of the basic processability characteristics of the compound[5]. (In view ~~of~~ ~~the process~~ing requirements) even though the use of high volume content of fiber in the matrix cause some source of difficulties during the manufacture and product development, the improvement in the mechanical properties resulting from higher fiber loading is important in many applications.

The properties of the composites depend on the type of elastomers used as the matrix, the fiber concentration, fiber aspect ratio and fiber orientation. The fiber must be bonded to the matrix elastomer to get good strength. Composites of good strength can be prepared from a variety of elastomers. Too short fibers are necessarily less effective in reinforcing low modulus materials, for the efficiency of reinforcement, ie, the extent to which a discontinuous fiber can simulate the performance of a continuous filament or cord depends on its modulus ratio relative to that of the matrix. Optimum properties of the composites are obtained by the proper utilisation of fiber and comprises of :[6]

- preservation of high aspect ratio in the fiber
- control of fiber direction to optimally reinforce the fabricated part.
- generation of a strong interface through physico-chemical bonding
- establishment of high state of dispersion
- optimal formulation of the rubber compound itself to accommodate processing and facilitate stress transfer while as much flexibility as possible is maintained to preserve dynamic properties.

The advantages of short fiber-reinforced composite properties are high degree of dimensional stability during fabrication and extreme service environments (high temperature, solvent contact etc.) by restricting matrix distortion, improved creep resistance, better resistance to solvent swelling, good fatigue life under high stress conditions and improved tear and impact strength by blunting the growing crack tips.[7]

Advantages in processing of short fiber reinforced composites arises from direct incorporation of fibers into the rubber compound along with other additives so that the resulting composites are amenable to the standard rubber processing steps of extrusion, calendering and the various types of molding operations (compression, injection and transfer). This is in contrast to the slower processes required for incorporating and placing continuous fibers and so economically high volume out put are feasible with short fiber reinforced composites.

The main application areas of short fibers have been investigated by many workers and suggested that these short fiber reinforced composites ~~had~~ found increasingly growing applications in industry such as paper manufacture, automobile and aerospace sectors.[8] Other applications include belts, hoses, gaskets, tread stocks of the off the road tyre and air craft tyres, V- belts, seals and complex shaped mechanical goods. A Russian review with 25 references deals with the manufacture of composite building materials from rubbers.[9]

The outstanding features and emerging applications of short fiber reinforced composites ~~lead to~~ so many research works in this field. A large number of investigations has been carried out regarding the nature of the fiber, matrices and the properties of the composites.

Both synthetic and natural fibers were used for the reinforcement of elastomers, natural as well as synthetic rubbers. Goodloe and coworkers[10,11] found out the use of finely divided wood cellulose in rubber. The early composites were largely devoid of bonding between the fiber and the matrix[12] so that high degree of strength reinforcement was not possible. Glass fibers and asbestos were very commonly used in polymer industry. Many researchers have indicated the use of short glass fibers as reinforcers for various rubber composites.[13-15] The requirements for a reinforcing fiber in elastomeric matrices were studied by Boustany et.al.[16] The generally available natural fibers are Jute[17], Bagasse[18] and the others include Lignin and Cellulose fibers[19] and synthetic fibers are polyester, nylon, aramid, Rayon and acrylics etc. A review of various types of short fibers, highlighting their short comings as reinforcements for polymers is given by Milewski.[20] Various fibers such as glass, Rayon, Nylon, asbestos, aramid and cellulose have been studied as reinforcement in both natural and synthetic elastomer matrices.[21,22] Moghe discussed[23] the improved performance of the hybrid composites. Coran and Patel[24] used a technology in which reinforcing fibers (nylon fibrils) were generated insitu within an elastomeric matrix (chlorinated polyethylene) on a two roll mill.

Short fibers find applications in essentially all conventional rubber compounds. Examples are NR, EPDM, SBR, NBR, CR.[5,7,8,13-14,25-26] Studies on various speciality rubbers like urethane elastomers, liquid rubbers, thermoplastic elastomers, ethylene vinyl acetate and silicon rubber[15, 27- 30] ha~~s~~ve been reported in detail by Sheeler, Humpidge et.al, Kane, Fettermann and Warrick et al, respectively. A urethane rubber that can be reinforced by glass fibers was introduced by Turner et al.[31] The use of jute fibers and waste silk fiber as reinforcing fillers for NR and carboxylated rubber has been investigated by De and coworkers.[17,32-33] Processing of rubber mixes with chopped fibers in a roller head equipment was done by Lahn.[34] Studies of the short pineapple leaf fiber reinforced composites with respect to the anisotropy of physical properties, processing characteristics, adhesion of fiber to matrix, aging resistance and comparison with carbon blacks have been reported by Bhattacharya and coworkers.[35] Nesiolovskaya et al tried to reinforce the rubber with two polymeric fibers consisting of polyamide fiber and a finely ground rubber powder based on general purpose rubbers and came to the conclusion that very good technical properties could be obtained by the combined treatment of fiber and rubber crumb.[36] Properties of the composites of rubber with chopped coconut fiber have been evaluated by

Arumugam et al.[37] The use of short fibers to reduce rolling resistance of tyres was suggested by Rijpkema.[38]

Foldi[8] pointed out the processing advantage of short fiber reinforcement over carbon black and other common additives. Murty and De have made[39] attempts to assess the role of silica and carbon black in short jute fiber reinforced NR composites and found that the minimum loading required for reinforcement decreased in the presence of carbon black. Akthar et al studied the processing characteristics, properties and fracture behaviour of short fiber reinforced thermoplastic elastomers from blends of NR and polyethylene.[40] Mechanical properties of Kevlar reinforced polyurethane elastomer has been studied by Nando et al and reported that tensile and tear properties were improved with the incorporation of fibers while abrasion resistance decreased with the fiber loading.[41] They also pointed out that a system containing a high amount of sulphur gave [illegible] ~~good~~ mechanical properties than a low sulphur system. Investigations on the cure characteristics and mechanical properties of NR reinforced with short sisal fiber have been made ~~done~~ by Varghese et al [42] and concluded that the minimum volume loading required for reinforcement was about 12 v/v% in the case of treated fibers. The dispersion and orientation of aramid fibers in a Chloroprene rubber vulcanisates were investigated by Wada et al.[43] Kim and coworkers[44] evaluated the physical properties, aging and oil resistance of the CR/NBR blends reinforced with aramid fibers. Zhou et al found that pretreatment of nylon 6 short fibers with Nitrile rubber latex and HRH adhesive solution with or without a tackifier could increase the mechanical properties and fiber dispersion in the matrix and decrease the power consumption in the mixing of Nitrile rubber composite.[45] Mechanical properties of composite materials consisting of short carbon fiber in thermoplastic elastomer have been studied by Ibarra et al[46] and found out that oxidative treatment of carbon fibers exerted a beneficial influence on the properties of material reinforced with such fibers.

A review on the prospects for short fiber reinforcements in tire and rubber technology has been given by Prevorseki et al.[47] The effect of carbon fiber concentration, fiber aspect ratio (L/D) and sample thickness on the electromagnetic shielding of CR, vulcanised by barium ferrite was studied in the frequency range of 100 - 2000 MHz.[48] A study of the dynamic and viscoelastic properties was carried out by Guo et al for thermoplastic elastomer, Styrene - Isoprene copolymers, Hytrel and composites of these rubbers reinforced by PET short fibers.[49] Effect of processing parameters on the mechanical properties of short Kevlar aramid fiber - thermoplastic urethane composite was reported by Nando et al. They reported that the strength, storage and loss moduli of the composites increased while δ_{max} was reduced progressively with fiber loading.[50] Roy et al reported the mechanical and dynamic mechanical properties of short carbon fiber filled Styrene - Isoprene - Styrene block thermoplastic elastomeric composites [51] and showed that tan δ values at the Tg region decreased on filler incorporation, but at room temperature, the values increased with filler loading.

Moghe proposed a simple mathematical model which will predict composite properties for small deformation and the directional properties of elastomers mixed with uniaxially short fiber composite.[4] Shen and Rains predicted the dispersion of short fibers in the internal mixers of different sizes and the mixing time required for a given dispersion rating.[52] Application of short fiber composites in hose technology was investigated by Goettler.[53] The effect of fiber orientation, fiber loading and temperature on the dynamic mechanical properties of NR filled with treated and untreated short sisal fibers were studied by Varghese et al. [54] Mechanism of short nylon rode embedded in rubber block was reported by Gent and Shamberger.[55] The effect of short carbon fiber on the anisotropy in hysterisis loss and tension set of two different thermoplastic elastomers, based on NR, HDPE blend and Styrene - Isoprene - Styrene block copolymer were studied by De and coworkers[56] and established an empirical relationship relating the difference between systems with longitudinal fiber orientation and transverse orientation with the strain present and volume percent of fibers. Rheological, mechanical and electrical properties of NR - white filler mixtures such as $CaCO_3$, Talc, Kaolin and Quartz reinforced with nylon 6 short fibers were studied with respect to filler loading by Saad and Younan.[57] Doherty and coworkers[58] developed a method for activating Kevlar (aramid) fiber surface by fluorination, rendering the fibers more receptive to resorcinol - formaldehyde latex dip treatment and ultimately leading to rubber composites possessing good fiber to matrix adhesion.

Development of sealing materials of jute fiber reinforced cork and butadiene acrylonitrile rubber was done by Xie et al.[59] The vulcanisation behaviour and the properties of a series of short sisal fiber reinforced SBR composites were studied by Thomas and coworkers.[60] Kikuchi showed that tyres from nylon short fibers having 0.2 - 0.3 µm diameter and 100 - 200 µm in length in proper direction and NR showed a reduction in cost and reduced rolling resistance.[61] Stress - strain and stress relaxation in oxidated short carbon fiber thermoplastic elastomer composites were reported by Ibarra et al.[62]

1.3. POLYURETHANE ELASTOMERS

Polyurethanes are a family of materials that can be formulated and designed from hard resins to soft elastomers as well as from solids to low density foams. The invention of such polyurethanes opened up an avenue to a new class of high performance materials. The chemistry of polyurethane makes it [illegible] very versatile polymer and it is their adaptability that allowed them to become successful in a great diversity of applications. Polyurethanes have had a remarkable growth rate since 1950.

Polyurethanes are polar polymers containing many hydrogen bonded groups (- NH- CO -) and are certainly the most developed reactive processing chemical systems available today. The elastomeric properties of polyurethanes have been known since the beginning of industrial research on isocyanate and by the 1940s polyurethane elastomers already had found practical usage. Because of their unique properties, solid polyurethane materials have attained a special importance in widely differing applications. The successful use of polyurethane rubbers in a large number of engineering applications led to demand by the rubber processing industry for PU materials that could be processed on conventional rubber processing equipments. Due to the versatility of PU elastomers, it is possible to prepare a wide range of elastomers with characteristic properties through proper choice of raw materials and proper formulations. The beneficial properties of polyurethane elastomers, i.e., high resistance to wear, high tensile strength, tear properties, hardness etc. are due to the hydrogen-bonded structure. Allport[63] found that at temperatures of 80 -160°C and above, there was a normal gradual equilibrium dissociation of hydrogen bonds and hence consequent reduction in the stiffness and strength properties.

Inorder to posses elastomeric nature of polyurethane the basic materials selected should be in such a way that the resultant polymeric structure has highly flexible segments, so that any crystallinity that may be present is confined to discrete domains and so that there is generally a low level of crosslinking.[64] Bayer et al studied the effect of isocyanate type at an early stage in the development of PU elastomers and established that aliphatic diisocyanates gave unsatisfactory products and that good properties were obtainable by using 2,4 TDI and 1,5 NDI.[65] This has been confirmed by Pigott et al and they concluded that large, rigid, symmetrical, bulky, aromatic diisocyanates free from methyl substituent, favour high modulus, tear strength and hardness.[66] They also found that decreasing value of M_c (molecular weight / branch point) from 21000 to 5300 (i.e., increasing crosslink density) decreased hardness, tensile and tear strength, compression set and further reduction of M_c down to 2100 increased modulus and hardness whilst tensile strength decreased further before beginning to rise. The effect of change in cross link density on the mechanical properties of polyether polyurethane has been studied by Athey[67] and found that increase in crosslink density decreased tensile strength, modulus and compression set. Cluff et al[68] studied the effect of type of crosslink structure on the properties of PU elastomers and found that resilience, hardness and modulus were independent of cross link type but this had some effect on compression set, the effect being higher with sulphur cured materials.

Several studies on the various aspects of polyurethane elastomers have been carried out. Thermal degradation and flammability of urethane elastomers were studied by Saunders et al[69] and suggested that these were well suited to the design of polymers for good ablation and flame resistance. Theocaris[70] studied the relaxation response of

PU elastomers and pointed out that there is a linear relation-ship between the lateral contraction ratio in relaxation and the bulk modulus along the whole response spectrum. A review of urethane elastomers has been given by Smith Vaughn[71] with emphasis on chemistry, components, manufacturing methods, reaction and structure and type of applications. A dielectric study of the Tg in the urethane elastomers modified by ionic bonds has been done by Zielinski et al.[72] Ahmed and coworkers[73] studied the improvements in the stress - strain behaviour of urethane rubbers by bimodal network formation. Equilibrium swelling of PU elastomers with different solvents has been investigated by Adolf.[74] Recently characterisation of polyether polyurethane by inverse chromatography was done by Farooque et al to find out the interaction of elastomer with different solvents.[75]

1.3.1. CLASSIFICATION

The solid elastomers can be divided into cast elastomers, TPU and millable PUs. Cast elastomers are the PU elastomers cast into open moulds. The liquid or other components that contain reactive -NCO and other -NH_2 groups are thoroughly mixed together and poured into open mould. TPUs are block copolymers formed by the reaction of a diisocyanate with - OH terminated polyether or polyester polyol and a low molecular weight glycol chain extender. These can be thermoplastically processed since they contain linear hard segments (diisocyanate and chain extenders) and linear soft segments (long chain diols) and they posses elastomeric character.

Elastomers which can be processed in a similar manner as that of conventional techniques such as traditional mill, internal mixers, extrusion, calendering, molding etc are referred to as millable elastomers.[76] Essential requirements of a millable gum are: it should have sufficient molecular weight to give sufficient strength for handling on mills and other processing equipments, enough stability so that it does not harden on storage and a suitable cure site.[77] The cure sites are deliberately introduced into millable elastomers during their synthesis by the incorporation of unsaturated olefinic groups, commonly allylether group is (CH_2=CH-CH-O-) introduced in the form of glycerylallyl-monoether. The concentration of the allylether must remain limited, since they cause a decrease in elastic properties of the finished vulcanisates.

Millable urethane elastomers are usually based on low molecular weight polymers, about 20,000-30,000 molecular weight, which are essentially linear in nature. However some branching is permissible and these elastomers have a small but positive excess of hydroxyl groups for having storage stability or shelf stability. These were prepared by first making PU with a molar deficiency of diisocyanate. The properties of these prepolymers are too weak to be a useful industrial product. This is then further chain extended to improve the strength to useful value. Different grades of millable urethane elastomers are sulphur curing, peroxide curing and isocyanate curing.[78] Sulphur curing grades are usually preferred by the rubber industry due to its advanced technology and low cost, even though some of their mechanical properties for example, resistance to thermal degradation are inferior to the peroxide and isocyanate cured grades. Sulphur curing rubbers include Adiprene CM, Urepan, Vibrathane 5004, and Millathane HT. Castor oil based millable polyurethane (sulphur curing) was also prepared by Thachil et al.[79]

The cured products of millable elastomers are characterised by good abrasion resistance, good to excellent mechanical strength and resistance to oxidative attack. The essential difference between the properties of the three grades of PU elastomers are found in their hardness value and in compression set at elevated temperature.

Property	Sulphur grade	Peroxide grade	Isocyanate grade
Hardness (Shore A)	50	50	70
Compression Set, (%), 24hrs			
20°C	20 - 40	5 - 10	15 - 20
70°C	25 - 40	8 - 15	40
100°C	70	20 - 30	-
150°C	-	50 - 70	-

The peroxide vulcanised product has relatively low tear strength in comparison to the other product group. The tensile strength, elongation, rebound elasticity and abrasion loss are not substantially different among all the grades.

For many technical applications millable urethane rubber requires reinforcing fillers to develop optimum strength and abrasion resistance. Reinforcement can be done using carbon black, fibers, silica, clay, whiting etc. The properties can be varied with the nature of the filler and was studied by Kellari.[80] Nando et al studied the[41] effect of fiber reinforcement on the mechanical properties of millable polyurethane elastomer and concluded that tensile strength and tear properties could be improved with the incorporation of fibers.

PU elastomers have found wide application in virtually every fields because of their very special properties, the most important of which are their [78]

- high elasticity over the entire hardness range
- flexibility over a wide temperature range
- good weather resistance
- good resistance against oil, grease and many solvents
- excellent wear resistance
- high Young's modulus in comparison to rubbers of similar hardness.

PU elastomers find applications in automobile sectors (for wheel joints, tie and joints etc), general engineering applications (rolls, roll covers, conveyor belts), milling rolls, damping elements, drive components (elastic couplings), gaskets, construction industry, seals, shoe industry (athletic shoes, hiking boots) etc.

1.4. POLYESTER FIBERS [81-83]

The polyester is a synthetic or man made fiber in which the fiber forming substance is any long chain synthetic polymer composed of at least 85 % of an ester of a dihydric alcohol and terephthalic acid. The most widely used polyester is made from linear poly(ethyleneterephthalate). Polyester fibers became commercially available (in the US) in 1953, and production expanded enormously in the 1960s and 1970s. Polyester can be prepared by the polymerisation of terephthalic acid or its dimethyl ester with ethylene glycol. The polymer is melted and extruded or spun through a spinneret forming filaments which are solidified by cooling in a current of air. The spun fiber is drawn by heating and stretching the filaments to several times to their original length to form some what oriented crystalline structure with the desired physical properties.

Drawn polyester fibers may be considered to be composed of crystalline and non-crystalline regions. These fibers have combined property of nylon and rayon. It has high modulus of rayon and high strength and elongation of nylon. Hence it becomes a versatile fiber for rubber products. It does not have flat spooting of nylon and its melting point is also higher than nylon. Due to its high melting point and modulus it is used in tyres, especially radial tyres and beltings. The drawback of polyester is its poor adhesion to rubber. This can be achieved overcome by the use of activated and pretreated fibers.[84] The typical physical and chemical properties of polyester fiber are given below:

Density, g/cc	1.38
Filament diameter, µm	23 - 26
Denier	6 - 7
Tenacity (gpd)	8.8 - 9.2
Elongation at break, %	14 - 16
Moisture, %	≈ 0.5
Shrinkage at 150 °C, %	4 - 8
Wet strength retention, %	≈ 90 +
Heat resistance	220 °C
Melting point	280 °C
Resistance to acids	:Attacked by concentrated acids
Resistance to alkalies	:Attacked by concentrated alkalies
Resistance to solvents	:Soluble in phenol trichloroolefin
Burning resistance	:Burns readily

Application of polyester fiber finds on the blends with cotton, rayon etc. High modulus staple yields light weight fabrics of high strength, sheeting, home furnishings and industrial uses. Use of polyester staple in sewing threads is well established. The staple of lower tex per filament is used in throw rugs and tufted area rugs, the staple of higher tex per filament is used in broad loom carpeting. Other staple products have been engineered for uses as fiber fill for mattresses, sleeping bags, pillows etc., and in the non -

woven area. Industrial, high strength, continuous filament yarn are made for automobile tire reinforcements as tire cord as well as for seat belts, fire hose, V- belts etc. where strength, high modulus, dimensional stability and low creep are important.

1.5. SHORT POLYESTER FIBER REINFORCED ELASTOMER COMPOSITES

Studies on the various aspects of short polyester fiber reinforced elastomers have been disclosed by many researchers. A comparative investigation of the properties of the various polyester fiber and carbon fiber reinforced elastomer composite (CR -PET, EPDM - PET, PUR - PET) was made by Ashida and coworkers.[85-86] The results showed that short PET fibers did not break up during the milling process compared to carbon fibers and they were well dispersed in the matrix and the PET reinforced EPDM (non polar) elastomer gave low value of tensile stress and elongation compared to CR (polar rubber). They also reported the mechanical and dynamic elastic characteristics of PET reinforced CR composites, the variation of these properties with the orientation of short fibers and the condition of the interface between the short fibers. A Japanese work explored the treatment of PET fiber for getting good matrix interaction and hence to get better mechanical properties, for the PET - EPDM composite.[87] Nando et al [88] found out the effect of fiber concentration, orientation and L/D ratio on the mechanical properties and processing parameters of short polyester fiber - natural rubber composites and indicated that an increase of L/D ratio decreased the anisotropy in tensile and tear properties. They also showed that optimum orientation of fibers was obtained by passing through mill at tight nip. Ibarra tried to develop better interfacial bonding between polyester fiber with various matrices by developing new bonding agents and found that short polyester fiber yields best results in SBR matrices when the adhesive system based on resorcinol and formaldehyde, and a bonding agent based on diazide were incorporated. [89]

The effect of short polyester fiber concentration, fiber orientation, aspect ratio of fiber and adhesives on mechanical properties of the reclaimed rubber composite was studied by Chen et al.[90] Use of short polyester, Rayon and polyamide fibers in isoprene rubber for metal cord tyres has been studied by Nesiolovskaya et al.[91] Nando and Kutty evaluated the mechanical properties of short PET fiber reinforced TPU composite.[92] Guo et al studied the mechanical properties of PET short fiber - polyester thermoplastic elastomer (Hytrel TR 2300) composites and suggested that the reinforcement by short fibers mainly depended on the difference of extensibility between the fiber and the matrix, because the difference directly affected the effective transfer of stress from the matrix to fiber.[93] Zhang and coworkers evaluated the rheological and dynamic properties of nylon and short polyester filled rubber with respect to the influence of pretreatment, temperature and fiber content.[94] Rijpkema reported the use of short fibers to reduce the rolling resistance of tyres since the rolling resistance of a truck tyre can be considerably reduced by the addition of small amounts of treated PET and aramid fibers to tire tread compounds.[38] Ibarra determined the physical properties of composite materials consisting of an elastomeric EPDM matrix and short polyester fiber as a function of fiber content and the properties are evaluated in terms of the existence or absence of a matrix - fiber interface. [95] He also reported the dynamic properties of short fiber - EPDM matrix composites with respect to strain amplitudes.[96]

THEORETICAL ASPECTS OF SHORT FIBER REINFORCED COMPOSITES

In composites, loads are not directly applied on the fibers but are applied to the matrix material and transferred to the fibers through fiber ends and also through the cylindrical surface of the fiber near the ends. The end effects in a composite can be neglected when the length of the fiber is much greater than the length over which the transfer of stress takes place and this effect cannot be neglected in the case of short fiber composites and hence the composite properties are a function of fiber length.

A deep investigation of the stress transfer mechanism has been carried out by many research workers.[97-98] The most often quoted theory of the stress transfer is the shear lag analysis applied by Rosen.[99] The average longitudinal stress on an aligned short fiber composite can be calculated by the rule of mixtures and is given by

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \qquad 1.1$$

where σ_f is the average fiber stress (since the fibers cannot be strained to their maximum), σ_m is the matrix stress, V_f and V_m are the volume fractions of the fiber and the matrix respectively. The average fiber stress depends on the fiber length. The rule of mixtures is similar to that of a perfectly aligned and properly bonded unidirectional continuous fiber composite which is

$$\sigma_{cu} = \sigma_f V_f + \sigma_m V_m \qquad 1.2$$

where σ_{cu} is the ultimate composite strength, σ_f is the ultimate fiber strength σ_m is the matrix strength at the maximum fiber strength, V_f and V_m are the volume fraction of fiber and the matrix. Certain empirical equations relating volume fraction and aspect ratio of the fibers to the tensile strength, modulus and elongation at break were postulated by Derringer.[14] In the case of short fiber composites the ultimate strength depends on the fiber length. Many finite element analyses of aligned short fiber composites have been carried out to study the various aspects of the composites. In some of the analyses the matrix material has been assumed to be completely elastic whereas in others it is assumed to be plastic - elastic.[100-103] These analyses provide very useful information regarding the stress distributions in the fibers as well as in the matrix. A critical fiber length or load transfer length is required to obtain the transfer of maximum load from the matrix to the fiber. When the fibers are smaller than the critical fiber length the maximum fiber stress is less than the average fiber strength and in this case the composite failure occurs when the matrix or interface fails. When the fiber length is greater than the critical fiber length the fibers can be strained to their average strength and the fiber failure initiates when the maximum fiber stress is equal to the ultimate strength of fibers. For getting better strength the volume fraction of fiber also should exceed a critical value. These theoretical aspects hold good for unidirectional composites and for randomly oriented composites when the load is applied along the direction of principal fiber orientation.

When the fibers are aligned transversely to the direction of application of stress the fracture of the composite takes place mainly through the matrix and the fibers do not affect the strength properties significantly. Moghe reported the variation of physical properties of the composites with the direction of fiber orientation.[4] An expression in which the orientation parameter had been taken into account for determination of the strength of the composite was given by Fukada and Chow [104] and the ultimate strength was given by

$$\sigma_{cu} = \sigma_{fu} V_f F (L_c / L) C_o + \sigma_m (1 - V_f) \qquad 1.3$$

where σ_{cu} = the ultimate composite strength, σ_{fu} = ultimate fiber strength, V_f = volume fraction of fiber, σ_m = matrix strength at maximum fiber stress, L_c = initial fiber length and C_o is the orientation parameter.

Dzyura used the theoretical diagram proposed by Kelly and Tyson[105] for computing the efficiency of filamentary reinforcement of metals and expressed the strength of rubber - fiber composites which can be expressed by the additivity rule. [106]

$$\sigma_c = \sigma_f V_f (1 - L_i / 2 L) K + \sigma_m V_m \qquad 1.4$$

where σ_m is the strength of the matrix at its maximum attainable deformation, K is the coefficient of fiber orientation, L_i is the ineffective length of fiber and can be calculated on the condition that the force required for breaking the fiber is equal to the maximum shear force on the fiber - rubber boundary.

$$L_i = \sigma_f . d / 2\Gamma \qquad 1.5$$

where d is the diameter of the fiber and Γ is the shear stress on the boundary (interface). It was found that the orientation coefficient depended on various factors such as the method of processing, concentration, type of rubber - fiber composites. A review with 20 references in which different models of continuum theory for the prediction of mechanical properties of composites was presented by Kern et al.[107]

Longitudinal as well as transverse moduli of the aligned short fiber composites are given by Halpin - Tsai equation as

$$E_L / E_m = \frac{1 + 2\, l/d - \eta_L V_f}{1 - \eta_L V_f} \qquad 1.6$$

and

$$E_T / E_m = \frac{1 + 2\, \eta_T V_f}{1 - \eta_T V_f} \qquad 1.7$$

where

$$\eta_L = \frac{E_f / E_m - 1}{E_f / E_m + 2\,(l/d)} \qquad 1.8$$

and

$$\eta_T = \frac{E_f / E_m - 1}{E_f / E_m + 2} \qquad 1.9$$

For a randomly oriented composite the modulus is given by

$$E_{random} = 3/8\, E_L + 5/8\, E_T \qquad 1.10$$

where E_L and E_T are the longitudinal and transverse moduli of an aligned short fiber composite under consideration.

1.7. PROPERTIES OF THE COMPOSITES

1.7.1. RHEOLOGICAL PROPERTIES

Rheological behaviour of polymer melts provides the choice of processing conditions and influences the morphology and mechanical properties of the final product. White et al have made a correlation between rheology and processing and also studied the extrusion characteristics of polymer melts.[108-109] Flow characteristics of the thermoset compounds filled with PET fiber have been studied by Owen and Whybrew.[110] Crowson and Folkes studied the rheology of short glass fiber reinforced thermoplastics and concluded that the fibers in the composite orient along the flow direction during the convergent flow and that the fiber alignment takes place only at high shear rates.[111] Brydson indicated the need for rheological studies and its importance in the selection of processing conditions and in the designing of processing equipments.[112] The dependence of die swell on L/D ratio of the capillary has been studied by many workers and concluded that the die swell decreased with increase of L/D ratio.[113-115] The rheology of short jute fiber filled NR composites has been studied by De and coworkers.[116] Gupta and coworkers reported the flow properties of PP - EPDM blend filled with short glass fibers [117]. Rheological characteristics of short Kevlar fiber reinforced thermoplastic polyurethane has been reported by Kutty et al.[118] Roy et al reported the rheological behaviour of the short carbon fiber filled thermoplastic blends of NR and HDPE. [119] Recently Kuriakose and coworkers reported the rheology of short sisal fiber reinforced NR composites and suggested that the incorporation of a treated fiber increased the melt viscosity and decreased the melt elasticity.[120] Rheological properties of nylon polyester short fiber filled rubber were studied by Zhang et al.[121] A Chinese review with 45 references deals with the dependence of rheological properties of short fiber reinforced composites on the characteristics of short fibers and matrix , the amount and length of short fiber, temperature and shear rate in the flow field.[122] The melt behaviour of NR composites containing untreated, acetylated and γ- irradiated coir fiber was studied by Thomas and coworkers.[123] Many other works have been reported on the rheological behaviour of short fiber reinforced polymer melts.[124-125]

1.7.2. MECHANICAL PROPERTIES

Mechanical properties of composites containing natural as well as synthetic elastomers have been studied [4,16,21,26,126] extensively. A general relationship between fiber loading, tensile strength and elongation at break was reported by Coran.[7] De found that[18] a minimum tensile strength occurred for strain crystallising rubbers at low fiber concentration and was due to the dilution effect caused by the fibers ie, when the matrix was not strained by enough fibers high matrix strain resulted at relatively low composite stresses. This fiber concentration depended upon the type of matrix and fiber. Once enough fibers were present in the matrix to constrain it the addition of more fibers increased the strength. With excessive fibers again the strength of the composite deteriorates due to the imperfections and also due to the inability of the matrix to hold the fibers well. Abrate reported that[127] the fibers did not break at all except when their loading was insufficient to restrain the matrix, in which cases large stresses could develop at low strain, Flink et al reported the mechanical properties of NR / allyl acrylate and allyl methacrylate grafted cellulose fiber composite.[128] Tensile properties of short sisal fiber reinforced LDPE composites were reported by Thomas et al.[129]

Both modulus and strength are affected by the orientation of the fibers. Theoretical aspect of orientation of an individual fiber on its strength and modulus has been studied.[130 -131] Modulus was found to be more dependent on the fiber orientation than the strength of the composite. The effect on Young's modulus (E) could be calculated from the equation

$$1/E_\delta = \cos^2\delta / E_L + \sin^2\delta / E_T \qquad 1.11$$

Hardness always increases in the presence of fibers and increases with fiber loading. Goettler[132] reported that a composite of EPDM with 65 phr of cellulose fiber showed a hardness increase of 16 shore A units.

Tear resistance of short fiber reinforced composites ~~are~~ is larger than that of any other rubber compounds. Kainradl and Kainradle[133] published an excellent treatise dealing solely with the tear strength measurement of vulcanised rubber, including the effects of shape, prenotching of the sample and the thickness of the test piece. Generally low fiber concentration can itself elevate the tear strength of the composite above that of the matrix.[134-135] De and coworkers found that tear strength increased with the increase of fibers.[18] Increase in tear resistance with increase in fiber content was also reported by many workers.[40,136] A tear resistant short fiber reinforced conveyor belt based on various fibers like polyamide, polyesters, aramids, glass with silicon rubbers and carboxylated polybutadiene rubbers has been published by Hasegwer et al.[137]

Heat build up usually increases with fiber content, [136,138-139] still it may be less than that produced by reinforcing carbon blacks. The heat generated due to the excess force needed to obtain the fixed compression cannot dissipate easily through the non- conductive matrix, resulting in extreme heat build up at higher fiber concentrations in tough elastomeric matrices. Heat build up property of short PET - NR composite was reported by Nando et al.[140]

1.7.3. STRESS RELAXATION

Stress relaxation is the gradual reduction of stress with time under a constant strain. Stress relaxation of filled and unfilled elastomers have been studied by many workers.[141-146] De et al studied the influence of short jute fibers on the stress relaxation pattern of the elastomer.[147] Nando and Kutty reported the stress relaxation characteristics of short Kevlar fiber reinforced thermoplastic polyurethane composite.[148] Recently Ibarra and coworkers explored the relaxation pattern of the short fiber reinforced composites with respect to the effect of fiber orientation, adhesion between the fiber and the matrix.[62]

1.7.4. THERMAL PROPERTIES

Thermal degradation of short fiber reinforced composites has been studied by many researchers. Thermal degradation of polyurethanes has also been investigated extensively. Degradation of urethane linkages due to the high shear and stress at elevated processing temperature was reported by Schollenberger et al.[149] Yang et al[150] studied the thermal degradation of urethanes based on 4,4' diphenylmethane-diisocyanate and 1,4 butanediol and reported that urethanes undergo degradation at elevated temperature producing isocyanates and alcohol. Grassie and Mendoza studied the degradation of polyurethanes formed from high and low molecular weight polyols.[151] Degradation characteristics of short Kevlar fiber reinforced thermoplastic polyurethane was determined by Nando et al.[152] Thermal stability of NR - polyester short fiber composites has been studied by Younan et al.[153] Ronald and coworkers [154] reported the influence of short fibers on the thermal resistance of the matrix, Tg and kinetic parameters of degradation reaction of thermoplastic polyurethane.

1.8. FRACTURE ANALYSIS BY SEM

Scanning electron microscope is an important tool for the determination of fiber orientation, fiber distribution, fiber matrix adhesion and fracture mechanism of fiber reinforced composites. Derringer used phase microscopy to investigate dispersion and the fiber breakage etc. of a glass fiber reinforced rubber composite.[13] He also made use of SEM to characterise the dispersion and fracture of various NR composites filled with Nylon, Rayon, polyester and acrylic fibers.[14] SEM studies on the distribution of fiber length due to buckling and crimping under large deformations during processing of aramid fiber in PU elastomer was reported by Moghe.[5] De and coworkers extended the SEM application to study the properties of short glass fiber filled rubber composites with and without silica. They also studied the effect of bonding agents on the fiber pull out on the fracture surface of the jute fiber filled composites.[155-156] With the help of SEM Boustany and Arnold studied the extent of breakage of the glass and Santoweb^r fibers in the elastomer matrices.[26] SEM has been used successfully to interpret different fracture surfaces of the short fiber elastomer composites.[32,157-159] With the help of SEM Kutty et al explained the tear and wear properties of short Kevlar fiber reinforced TPU composite and failure mode of the composite.[160]

1.9. FACTORS AFFECTING THE PROPERTIES OF THE COMPOSITES

The mechanical properties such as modulus, strength and ultimate elongation depend upon fiber orientation, aspect ratio, fiber dispersion and adhesion between fiber and the matrix compound.[126] Several researchers tried to find out the effect of these parameters on the mechanical properties of natural as well as synthetic rubber composites.[7-9]

1.9.1. TYPE AND ASPECT RATIO OF FIBER

A composite with high longitudinal modulus is obtained with the use of a short fiber with higher modulus. Aspect ratio of the fiber is a critical parameter for improving the composite properties.[5] Considerable fiber breakage occurred during mixing of fibers with high aspect ratio (as high as 500) resulting in a reduction in aspect ratio.[161] A high degree of breakage of short glass and Kevlar fibers at the time of mixing was reported by Czarnecki and White.[124] They also proposed a 'kinking mechanism' for fiber breakage based on buckling during rotation in shear flow. Rogers discussed the problems related to mixing of fiber loaded stocks.[162] Depending on the fiber type and the matrix used the proper aspect ratio should be around 100 - 200.[6] Chakraborty reported[32] that the aspect ratio of the short fiber was reduced from 130 to 10 after mixing in the case of short jute fiber rubber composites. For synthetic fibers an aspect ratio in the range of 100 - 500 is easily attained as they are available in diameter of 10 - 30 μm. An excellent treatise on the importance of aspect ratio especially with respect to the modulus of the matrix is given by Abrate.[127] Since fiber length is not uniform after mixing the effect of fiber length distribution was included in the micromechanics analysis. During processing fibers are buckled and crimped under large deformations resulting in a distribution of fiber lengths. A moderate breakage of short jute fibers during mixing with NR - PE thermoplastic - elastomer in a Brabender Plasticorder was reported by Akthar et al.[163] Kutty et al reported the [159] high reduction in the length of aramid fiber due to the high shear rate experienced during mixing in a Brabender Plasticorder. Chen et al showed that the PET fiber reinforced composites had good mechanical properties when the fiber content was 8 - 9 phr, the aspect ratio of the fiber was 643 and the fiber diameter was 14µm.[90] Roy et al reported that Brabender mixing followed by milling of short carbon fiber thermoplastic elastomer composite resulted in about 30 fold decrease in the fiber aspect ratio and a random fiber orientation.[51] The more mechanical steps the fiber sees and the more rigid and brittle the fiber is , the more likely that it will be broken up during processing.

1.9.2. FIBER DISPERSION

A good dispersion of fibers in the matrix is another important factor for getting a high performance composite. Good dispersion implies that there will be no clumps of fiber in the finished product, ie, the fiber will be separated from each other during the mixing operation and surrounded by the matrix. Dispersion of fibers depends on the nature of the fibers, especially its length and also is greatly influenced by the amount of the fiber.[164] According to Derringer, for getting a better dispersion, the commercially available fibers such as polyester, Nylon, Rayon and acrylic flock must be cut into small length of approximately 0.4 mm.[14] Foldi reported that [8] fibers (glass or wire) which break up during mixing process could be incorporated at much higher levels (up to 50 phr) with ease, but the resultant composite would be less effective. Several methods were found out to get better dispersion and they were : the coating of the fiber surface with other materials to prevent the fibers from sticking to each other, replacing the conventional slab as the source of the gum rubber with powdered elastomer. To predict the dispersion of short fibers from a given size internal mixer to another Shen and Rains developed a conversion parameter (NRs). They also suggested an upside down mixing for getting better dispersion of treated wood cellulose (Santoweb) in a wide range of elastomers and investigated the effect of fiber dispersion on modulus and strength.[52] For getting a better dispersion it is better to add fibers at first in the Banburry.

1.9.3. FIBER ORIENTATION

Among the parameters fiber orientation affect the composite properties most. It is very clear that the final orientation adopted by the fibers, at the conclusion of the molding cycle will have a major effect on the anisotropy of physical properties of the molded component.[165] The effect of fiber orientation in unidirectional discontinuous rubber composites has been studied by Coran et al.[126] They also suggested a mathematical formulation to find out the dependence of modulus on fiber orientation.` During processing such as milling, extrusion, calendering etc. of rubber composites the fibers tend to orient along the flow direction causing anisotropy in mechanical properties.[4] Thus optimum properties can be generated for a given product by changing or suitably controlling the flow direction. A simple and easy way to orient fibers in one direction is by sheeting using a two roll mill. A large shear flow during milling forces the fibers to orient along the mill direction. It was observed by Moghe that [5] all the fiber orientation which can be obtained for a given mill opening is achieved during the first pass itself. He also reported that smaller thickness of milled sheet is equivalent to greater fiber orientation along the mill direction. Foldi reported [8] that for Nylon and glass fibers the efficiency of orientation increases with the increase of fiber loading and this high degree of orientation increased the green strength and stress at low elongation in the direction of orientation. Blackley suggested that [166] a maximum level of fiber orientation included 80 - 90 % of fibers oriented within ± 10° to the mill direction. A detailed review of short fiber orientation was given by McNally.[167] Goettler described the fiber orientation under different types of flow, ie, convergent, divergent, shear and elongational [53] and reported that fibers aligned in the direction of flow when the flow was convergent type and fibers aligned perpendicular to flow direction in a divergent flow. In shear flow, depending on the shear rate the fiber alignment could vary from random to unidirectional while in the elongational type flow the fibers oriented themselves in the direction of applied stress. The rate of rotation and direction of alignment were controlled by the magnitude and velocity gradient. The velocity gradient is positive in a convergent flow, since the flow accelerates because of the reduction in the cross sectional area of the channel and hence the fibers align in the direction of flow making a small angle with the flow axis. Effect of fiber orientation on the thermoelastic properties of short fiber filled composites has been evaluated by Chou and Nomexa.[168] A detailed discussion on the design and application of extrusion dies for controlling the fiber orientation was given by Goettler.[169] Fukuda and Chow used a probabilistic approach based on Halpin - Tsai equation to suit composites containing a distribution of fiber orientation.[104] The effect of mixing on fiber breakage, dispersion and orientation has been the object of a number of studies.[6,170] Nando et al [136]reported that optimum properties of short PET fiber filled NR composites were obtained by passing the composite twice through tight nip.

1.9.4. FIBER MATRIX ADHESION

Physical properties of the composites consisting of an elastomeric matrix and short fiber depend on the existence and strength of the fiber matrix interface and it is very difficult to define the interface in a composite. Cola [171] considered the interface region as comprising of two surfaces one of the fiber and the other of the matrix and the region between them. The load transfer in short fiber composite mainly depend on fiber to matrix adhesion and the aspect ratio. He also suggested that the properties of the interface were controlled by the physical and mechanical properties of the polymer. Pukanszky studied the influence of the interface bonding on the ultimate tensile properties of the composite.[172] The effect of adhesion between fiber and matrix on the equilibrium swelling of short sisal fiber reinforced natural rubber composites has been studied by Kuriakose et al [42] and reported that the increase in adhesion reduced the swelling considerably. Influence of components and interface conditions on the mechanical properties of composites and blends were determined by Pegararo and Dilandro and suggested [173] that fiber - matrix adhesion in the case of TPU matrices was influenced by the presence of residual stresses due to the cooling of the material from the processing temperature to the final temperature. Effect of interface debonding on the various moduli of short fiber composites was reported by Ghosh et al.[174]

Interfacial bonding is known to play an important role in composites since this interface has a decisive impact on the end result and service properties of the composite.[17] Different techniques have been employed to achieve a strong interface or a good adhesion between fiber and matrix. These include conventional adhesive additive formulations, three component dry blends based on HRH (hexamethylenetetramine, resorcinol and hydrated silica) or RFL (resorcinol - formaldehyde latex), fiber grafting reaction, the incorporation of coupling agents or fiber treatment with such agents. The proper choice of bonding agents were the object of many investigations[7,32,39,176] and a review of bonding systems available was given by Goettler.[6] Kondo reviewed the selection of adhesives for bonding short fiber reinforcements in SBR and NR composites.[177]

Creasey et al studied the role of silica in promoting the adhesion between fiber and matrix.[178] Derringer evaluated the effect of HRH system with various fibers in nitrile and NR and found that HRH system was not so much effective with polyester fibers in many elastomeric matrices.[14] It has been shown by Das that carbon black can also promote adhesion in the absence of silica.[179] A special polymeric bonding agent for cellulose fibers was developed by Boustany et al.[25] Foldi tried to improve[8] the adhesion of Nylon fibers with NR - SBR matrix by using RFL dip and found that the reinforcing ability of these fiber was reduced. O'Connor found that HRH system and RH system did not work for glass fiber reinforced NR composites.[22] The relative effect of resorcinol and Hexa on the rate of resin formation has been reported by Morita.[180] Murty and De have tried to evaluate [39] the role of silica and carbon black in adhesion of jute fiber reinforced NR composites and reported that in the presence of carbon black the orientation and dispersion of fibers were better than those observed in the presence of clay. Many other researchers have evaluated the effect of HRH bonding agent on short fiber reinforced elastomer composite and found an improvement in the properties of the composites. [35,37,40]

It has been reported that a pretreatment of polyester and aramid fibers before RFL dipping improved the adhesion with the matrix.[181] Influence of adhesive system on the properties of composites of polyester fiber and SBR filled with magnesium silicate has been reported by Ibarra.[182] Janssen [183] modified the conventional RFL dip system to improve the adhesion.

Effect of fiber pretreatment with polyesteramide polyols and silane coupling agent on the dry and wet strength of jute fiber - polyester composites has been studied by Muckerjee and coworkers[184] and reported that the pretreatment improved the dry as well as wet strength of such composites. They also reported the role of fiber-polymer interface on some of the composite properties. Maldas and Kokta have studied the influence of maleic anhydride as a coupling agent on the performance of wood fiber polystyrene - composites.[185] Grafting of cellulose fibers with poly(allylacrylate) has been done to improve the adhesion between the fiber and the matrix.[186] Grafting of short polyester fiber has been done by Ibarra[82,96,187] et al for improving the adhesion with various elastomeric matrices and TPUs and has studied the influence of adhesion on various properties of the different composites. Acetylation was carried out by Thomas et al[42] or improving the adhesion of sisal fiber with NR and reported that a minimum of 12 % (v/v) loading of the acetylated fiber was necessary for proper reinforcement.

The interfacial adhesion between Nylon and vinylon short fiber reinforcements treated by different methods used in NBR and SBR matrices was studied by swelling measurements, SEM, dynamic viscoelastic spectrum and mechanical property measurement by Zhou et al.[188] Also, they proposed an effective interfacial thickness concept based on Halpin - Tsai equation to characterize the fiber rubber interface. Bonding of polyester and aramid cord in EPDM and HNBR was developed by Janssen et al.[189] Some

Japanese workers also reported the development of adhesion of polyester fibers to different matrices.[190] Various studies on the short fiber interfacial adhesion with different fibers and matrices were carried out by Zhou[191]et al.

1.10. APPLICATIONS

Now a days short fiber reinforced composites find wide applications in various fields and can even replace the continuous cord reinforcements in many applications, since they can simulate the continuous cord reinforcements by adjusting the parameters like aspect ratio, adhesion etc. Also, they can offer design flexibility, advantages in processing and can impart better properties. The main application areas for short fiber composites are hose, beltings, solid tyres and pneumatic tire components. Miscellaneous applications include roofings, dockfenderes, seals, diaphragms, cables etc.

Power transmission belts, more precisely V - belts, represent an extreme dynamic application for short fiber-rubber composites. When a V - belt is running over pulleys it is subjected to severe stresses when bent and flexed in the direction of rotation at a frequency of thousands of cycles per minute. At the same time, because of wedging in and out of each pulley, it is subjected to transverse forces on the side walls. Also, there are stresses resulting from the static torsioning and load transmission and these tension stresses are supported by the textile reinforcing member in the V - belt. The compressive side wall pressure is supported mainly by the base rubber. The V - belt must exhibit high modulus in the transverse direction and low modulus coupled with high flexibility in the axial direction. To obtain these properties V - belts from anisotropic composites of rubber reinforced with short fibers have been used. The desired transverse orientation of fibers in the base rubber can be achieved by constructing the raw V - belt from compounded sheet that was first calendered to orient the fibers and then rolling up in the 90° direction. Rogers studied[162] the reinforcing effects of flow of different fibers in a Neoprene matrix and found out that the treated cellulose fibers reinforced composites with a high level of anisotropy, in addition to the strong bond between the fiber and the matrix could act as a base rubber for V - belts. A Japanese work reported the use of CR rubber reinforced with aramid short fiber for transmission belts.[192]

An important application that utilizes the full reinforcing potential of short fibers in load bearing is as a replacement for knit or spiral wound cords in rubber hoses. The main advantage of using short fiber reinforced composites in hoses are process simplifications, lower cost and high production rate. It excludes the intermediate steps like braiding operation without sacrificing the physical properties. The major field of application for short fiber reinforced hose is in the automotive industry. The short fiber composite hose is equal or superior in burst strength and growth under pressure. Shinada and Hazelton[193] defined the service life of hose and belting products made of EPDM reinforced with various short fibers under typical operating conditions. Applications in radiator hose have also been demonstrated.[132] Schroden et al [194] developed a high - tech hose for a high tech car turbo engine.

The application areas of short fiber reinforced composites in tyre are the tread, belt over lay, inner liner, bead of filler - apex, bead wrap and chafer. The use of short fibers in tire treads to improve wear characteristics has received much attention. Beatty and Hamed [134] reported a reduction in crack propagation rate (improvement in the chipping and cutting resistance) when a small percentage of cellulose fiber was added to the tread compound. Improvement in modulus and crack resistance of urethane rubber was observed when chopped organic fibers such as Nylon, polyester and polyacrylonitrile were incorporated.[6] Goettler et al[169] in a study of extrusion of fiber reinforced rubber profiles with controlled fiber orientation and their use as tire components such as OTR treads, tire chafer, shoulder inserts and bead filler, suggested that a circumferential orientation of fiber was almost as good as that of radial orientation. Walker and Harber[195] have illustrated improved chipping / chunking resistance in retreaded OTR mining tires by the incorporation of treated cellulose fibers. Borowczak studied[196] the engineering properties of reinforced elastomer composites which are useful in tires. A review of the short fiber reinforced elastomer composites provides the prospects for short fiber reinforcements in tire and rubber industry.[47] Kikuchi[61] reported that the tire made from short Nylon fiber reinforced NR had got a better cut and rolling resistance.

Application of short graphite fiber reinforced elastomers in gaskets was evaluated by Hirari.[197] EPDM reinforced with various short fibers finds application in rubber sheetings, rock fenders etc. Due to the anisotropy resulting from the orientation and better modulus, these short fiber reinforced composites have got a variety of applications like piston cups, seals, diaphragms etc.

1.11. SCOPE AND OBJECTIVES OF THE PRESENT WORK

Polyurethanes are one of the highly versatile polymeric materials, with a number of advantages like high elasticity, flexibility over a range of temperatures, good weather resistance etc. in addition to high abrasion resistance and solvent resistance. Highly flexible urethane chemistry makes it possible to prepare polyurethanes with a wide range of properties to meet different service conditions. However, one draw back of polyurethane elastomer is its relatively poor modulus at low elongations and tensile strength at room temperature. Fillers can be used to improve the strength properties of the polymeric systems. Short fibers with their ability to impart anisotropic mechanical properties, design flexibility and their easy processability, are the ideal choice. Usage of short fibers as reinforcing agents in elastomers opens up a new avenue for the utilisation of waste fibers, available in plenty from fiber and textile industries.

However, short fiber - rubber composites fail to attain the performance exhibited by continuous cord reinforcements. The extent to which they can simulate the cord rubber composites is critically dependent on the fiber - rubber interfacial bonding in addition to the other factors like modulus ratio of the fiber to that of matrix, aspect ratio of the fibers, and fiber orientation and dispersion. A survey of the available literature showed that many methods have been used to improve the interfacial bonding and this includes usage of adhesive systems, external bonding agents, coupling agents, pretreatment of fibers and grafting of fibers. Most extensively used technique is the use of external bonding agents based on hexamethylenetetramine, resorcinol and hydrated silica (HRH) as interface modifier in short fiber - elastomer composites.

However, it has been reported that this system had a detrimental effect on the sulphur curing of polyurethane elastomer based composites. The objective of this work is to develop a new suitable bonding agent for polyurethane elastomer based short fiber composites and evaluate it with reference to the various technological properties of the composite.

Evaluation of cure characteristics of the composites with the new bonding agents gives an idea of the suitability of this bonding agents. The parameters like scorch time, $T_{max} - T_{min}$ and optimum cure time provide information on the curing and crosslinking of the polymer composites.

Since processing of a composite material involves flow under shear, studies on the rheological behaviour of the composites becomes important. An important parameter that influences the processability of the composite is shear viscosity which is dependent on the processing parameters like shear rate and temperature in addition to fiber loading and the presence of bonding agents. Thus a thorough knowledge of the influence of the shear rate, temperature, fiber loading and the new bonding agent on the flow properties are essential.

One of the criteria in selecting a composite for a particular service or application is their mechanical properties. Incorporation of short fibers in conventional rubber vulcanisates improve the mechanical properties. The main factors that affect the mechanical properties of the composite are the fiber concentration, fiber dispersion and orientation, aspect ratio of fiber and the last but the most important is the fiber - matrix adhesion. So a detailed study of the effect of these parameters on the mechanical properties of the composite will be highly useful. Scanning electron microscopic studies of the tensile fracture surfaces would reveal the various failure modes and fiber orientation in the matrix.

In many applications, decay of stress in a stretched sample decides the service life and performance. So far most of the work on the stress relaxation have been limited to the gum vulcanisates and only a few work has been reported about the stress relaxation of the filled vulcanisates. The stress relaxation pattern of PU elastomer is affected by the strain rate, strain level, fiber loading and the interfacial adhesion. Hence a thorough study of the stress relaxation behaviour of the composites with respect to these parameters will be very interesting.

Since the thermal stability of polyurethane elastomer may be influenced by the presence of short fibers and bonding agent, a detailed study of the composite with respect to these parameters will be critical in analysing the composite. Thermogravimetric Analysis will be useful in this study.

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CHAPTER II

EXPERIMENTAL TECHNIQUES

This chapter deals with the details of the formulation of the mixes, the method of sample preparation and experimental techniques adopted for the present investigation.

2.1. MATERIALS

Polyurethane rubber (Adiprene CM): Adiprene CM is an ether based sulphur curable millable polyurethane elastomer and was supplied by the Uniroyal Chemical Co., USA. The physical Properties are given below.

Specific gravity(g/cc)	1.06
Appearance	Amber Colour
Odour	Faint, characteristic
Viscosity	about 60 (Mooney, MS -10 at 100 °C)
Solubility	Soluble in THF, DMF & MEK
Storage stability	Excellent
Health hazard	None

Short polyester fiber: Polyester staple fiber of length 4 mm and diameter of 21 μm was provided by Madura Coats, India. Specification of Polyester cord is given below.

Construction in raw stage	100 Denier *3 * 3
Dip pickup	8 %
Breaking strength	627 N
Elongation at break	13 %
Chemical treatment for adhesion	Not supplied

2.2. CHEMICALS

Caytur 4: A zincchloride - MBTS complex, used as a catalyst for polyurethane vulcanisation, was obtained from Uniroyal Chemical. Co., USA.
2,2' Benzothiazyldisulphide (MBTS) and silica (Vulcasil S) of Analar grade were procured from Bayer India Ltd.

Mercaptobenzothiazole (MBT), hexamethylenetetramine and resorcinol were supplied by Merck India.

Polypropylene glycol with a molecular weight of 2000, an AG product, was obtained from Fluka Chemie, India.

Glycerol and propylene glycol were provided by BDH, Bombay, India.

Elemental sulphur was of chemical pure grade.

MDI and TDI were supplied by Manali Petrochemicals Ltd. The characteristics of TDI and MDI are:

Property	TDI 65/35	MDI
Appearance	Clear liquid	Brown coloured liquid
Viscosity, cps/25 °C	-	185 ± 35
NCO content, wt%	purity -99.5 %	31.0 ± 0.5
Hydrolyzable chlorides,%	0.010 - 0.013	0.1 - 0.3

Solvent : Tetrahydrofuran used was manufactured by E. Merck, India.

2.3. PROCESSING

2.3.1. MIXING

The mixing of urethane elastomer was done as per ASTM D 3184 (1980) and D 3182 - 74 on a laboratory size two roll open mixing mill (150 * 330 mm). Once a smooth band was formed on the roll, ingredients were added in the order: fibers, resin, activators, accelerators and finally sulphur. After complete mixing the stock was passed six times through the tight nip and finally sheeted out at a fixed nip gap so as to orient the fibers in one direction.

2.3.2. CURE TIME DETERMINATION

Optimum cure time and the other cure characteristics were determined by using Goettfert Elastograph Model 67.85 at 150 °C. The machine uses two directly heated, opposed biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. The specimen was kept in the lower die which was oscillating through a small deformation angle (± 0.2°) at a frequency of 50 oscillations per minute. The torque transducer on the upper die senses the force being transmitted through rubber. A typical cure curve is shown in the Figure 2.1.

Scorch time was taken as the time for 10 % rise in torque from the minimum torque. The optimum cure time (t_{90}) corresponds to the time to achieve 90% of the maximum cure which was calculated using the formula

Torque at optimum cure. = $0.9\,(T_{max} - T_{min}) + T_{min}$

where T_{max} and T_{min} are the maximum and minimum torques, respectively.

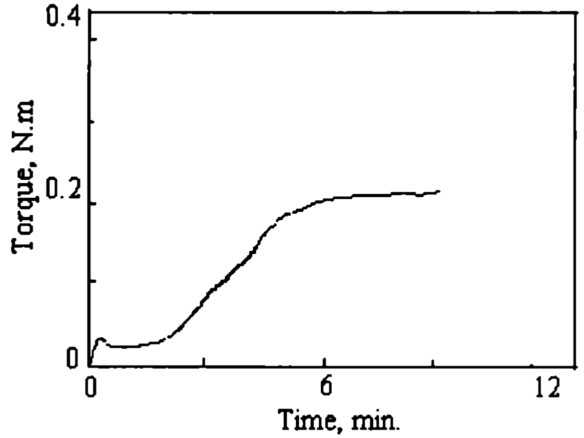

Figure 2.1. A Typical Cure Curve

2.3.3. VULCANISATION

Blanks cut from the unvulcanised sheets, marked with the direction of the mill grain were vulcanised at 150 ± 2 °C and at a pressure of 120 kg/cm^2 in an electrically heated 30 cm * 30 cm hydraulic press to their respective cure times. Sufficient extra cure time was given to the thicker samples so as to get the same extent of cure. Moldings were cooled quickly in water at the end of the curing cycle and stored in a cold dark place for 24 hrs and were used for subsequent property measurements.

2.4. FIBER LENGTH

The extent of fiber breakage during mixing of the urethane rubber in a Brabender Plasticorder was determined by dissolving the matrix in tetrahydrofuran, followed by extraction.

Examination of the length distribution of the fibers was done using an optical microscope.

2.5. SWELLING STUDIES

Samples of approximately 1 cm diameter and 0.25 mm thickness and 2 gm weight were punched out from the compression molded sheets, weighed accurately and allowed to swell in excess of solvent (Tetrahydrofuran) at room temperature for specific period (36 hours). Samples after swelling were taken out, dried quickly with a filter paper and weighed. The weight of the samples after complete drying was also found out. Volume fraction of rubber (V_r) was then calculated using the equation

$$V_r = \frac{(D - FT)\,\varrho_r^{-1}}{(D - FT)\,\varrho_r^{-1} + A_0\,\varrho_s^{-1}} \qquad (2.1)$$

where

T = Initial weight of the sample

D = Deswollen weight of the sample

F = Weight fraction of insoluble components

ϱ_r = Density of the rubber (For polyurethane $\varrho_r = 1.06$)

A_o = Weight of the solvent absorbed by the sample

ϱ_s = Density of the solvent (for Tetrahydrofuran = 0.88)

2.6. RHEOLOGY

The mixes were prepared in a Brabender Plasticorder / Haake Rheomix. The mixing temperature was maintained at 60°C and the speed at 30 rpm for 4.5 minutes. Mixing sequence is given below.

Time (min.)	Mixing Sequence
0	1/2 Rubber
1	1/2 Rubber
1.5	Fiber
3	Other ingredients
4.5	Dump the material

The rheological studies were carried out using a Monsanto Processability Tester (MPT) using dies of L/D ratios 20 and 30. The shear rates studied were between 0.106 s^{-1} and 0.244 s^{-1} and the temperature of study was 90 - 160 °C. The shear rate range studied was limited by the upper load limit of the machine. The test was conducted by loading the barrel of the machine with a definite amount of the composite sample and letting the piston traverse at pre-selected speeds corresponding to the selected shear rates. The machine automatically selected the shear stress values when the shear stress stabilized. The material was allowed to attain an equilibrium test temperature before being extruded out. The shear viscosity was then calculated from the shear stress and shear rate values.

The true shear stress was calculated as[1]

$$\Gamma_w = P.R/2L \tag{2.2}$$

where

Γ_w is the true shear stress at the wall,
P is the pressure drop inside the capillary,
L is the length, and
R is the radius of the capillary.

Apparent shear rate and shear rate at the wall were calculated using the equations:

$$\dot{\gamma}_a = 32\,Q / \pi\, d_c^{\;3} \qquad (2.3)$$

where

γ_a is the apparent shear rate (sec^{-1})
Q is the volume flow rate (mm^3/sec)
d_c is the capillary diameter (mm).

On applying the Rabinowitsch correction for the rate of shear at the wall (γ_w), equation becomes

$$\dot{\gamma}_w = \frac{(3n'+1)\,.\,\dot{\gamma}_a}{4n'} \qquad (2.4)$$

where

$$n' = \frac{d\,(\log F)}{d\,(\log Q)}$$

where F is the load on the plunger (N). n' was calculated by regression analysis of the log Γ_w and log $\dot{\gamma}_a$.

Shear viscosity was calculated as

$$\eta = \Gamma_w / \dot{\gamma}_w \qquad (2.5)$$

2.7. PHYSICAL TEST METHODS

Mechanical properties of the vulcanisates were tested according to the relevant ASTM standards. Properties, except hardness, resilience and compression set, were determined both along (longitudinally oriented fibers) and across (transversely oriented fibers) the grain direction. Schematic representation of fiber orientation in different samples is given in the Figure 2.2. For determining the aging resistance, samples were aged in an air oven for 48 hours at 70°C (ASTM D 573 - 88). The properties were measured 24 hours after the completion of aging.

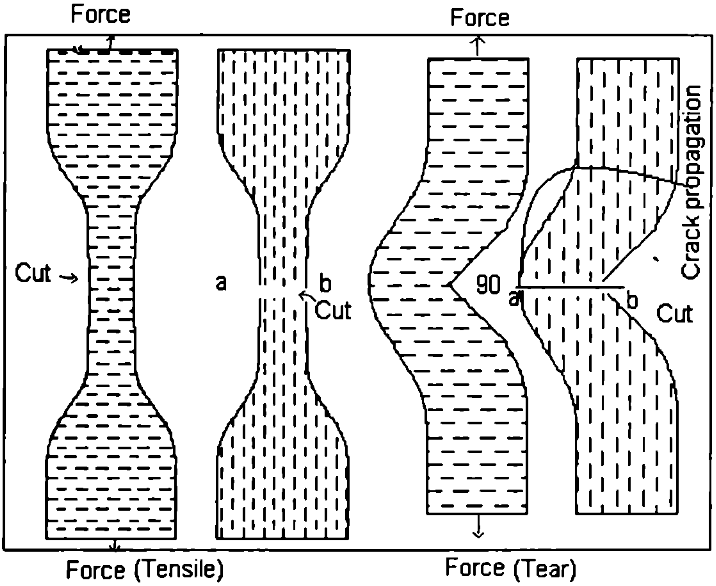

Figure 2.2 Schematic representation of fiber orientation (i) longitudinal (ii) transverse

2.7.1. *TENSILE PROPERTIES*

Tensile properties were measured using a Zwick Universal Testing Machine Model 1445 according to ASTM D 412. All the tests were carried out at 28 ± 2 °C. Test pieces were punched out from the molded sheets along and across the direction of the fiber orientation using a Dumbbell die (Die E). The thickness of the narrow portion was measured using a thickness gauge. The tests were carried out at a grip separation speed of 500 mm/ min.

2.7.2. *TEAR STRENGTH*

The test was done on a Zwick UTM as per ASTM D 624 - 54 using unnotched 90° angled tear test specimen (die C). The samples were punched out from the molded sheets along and across the direction of fiber orientation. The test speed was 500 mm/min.

2.7.3. *ABRASION RESISTANCE*

Abrasion resistance of the composites was measured using a DIN abrader based on DIN 53516, both in the longitudinal and transverse directions. Cylindrical samples having a diameter of 12 ± 0.2 mm and a thickness of 16 to 20 mm was placed on a rotating sample holder and a load of 10 N was applied. Initially a pre - run was given for conditioning the sample and the sample weight was taken. Weight after the test was also noted. The difference in weight is the weight loss of the test piece after its travel through 40 m on a standard abrasive surface. The results were expressed as volume loss per hour.

2.7.4. HARDNESS

The hardness (Shore A) of the samples was determined using Zwick 3114 hardness tester according to ASTM D 2240 - 86. Samples having dimensions of 12 mm diameter and minimum 6 mm thickness were used. A load of 12.5 N was applied and the readings were taken 10 seconds after the indentor had made a firm contact with the specimen.

2.7.5. REBOUND RESILIENCE

Resilience of the composites were measured using Dunlop Tripsometer (BS 903, Part A 8). The sample was placed in the sample holder and was conditioned by striking the sample with the indentor six times. Finally the angle of rebounce of the indentor was measured and the rebound resilience was calculated as follows:

$$\text{Rebound resilience } (\%) = \frac{1-\cos\phi_2}{1-\cos\phi_1} * 100 \qquad (2.6).$$

where ϕ_1 and ϕ_2 are the angle of incidence and the rebound angle respectively. ϕ_1 was kept constant at 45° for all the samples.

2.7.6. HEAT BUILD UP

Goodrich Flexometer was used to measure heat buildup of the composites. The test was carried out as per ASTM D 623-78, method A. The samples were 25mm in height and 19mm in diameter. The oven temperature was kept constant at 50 °C. The stroke was adjusted to 4.45 mm and the load to 10.05 kg/cm^2. The samples were preconditioned at the test temperature in the oven for 20 minutes prior to the test. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature rise (ΔT°C) at the end of the specified time interval (20 minutes) was taken as the heat build up. For the fiber reinforced samples, the failure occurred within 20 minutes. Heat build up in these cases was reported as the maximum temperature rise (ΔT_{max}, °C) at the time of the failure.

2.7.7. COMPRESSION SET

Compression set under constant strain was measured according to ASTM D 395 - 86, method B. Samples having dimensions of 6.5 mm thickness and 4 mm diameter were compressed to constant strain (25 %) and kept for 22 hours in an air oven at 70 °C. After the heating period, the samples were taken out and cooled to room temperature for half an hour and the thickness was measured. The result in percentage is expressed as

$$\text{Compression set } (\%) = \frac{T_i - T_f}{T_i - T_s} * 100 \qquad (2.7)$$

where T_i and T_f are the initial and final thickness of the specimen and T_s is the thickness of the spacer bar used.

2.7.8. DENSITY

Density of the samples was measured as per ISO 2781 (method A). Samples weighing about 2.5 g with smooth surface were used. Weight of the specimen in air and water was taken. Density of the sample was calculated as

$$\text{Density} = \frac{W_1}{W_2} * D \tag{2.8}$$

where

W_1 = weight of the sample in air
W_2 = loss of weight in water
D = density of water, (1 g/cm^3)

2.8. STRESS RELAXATION

Stress relaxation study was carried out using a Zwick UTM (Model 1445). The test specimens punched out from the molded sheets conforming to ASTM D 412 - 80 were used. The samples were pulled to desired strain levels at different strain rates (cross head speeds). The stress was recorded as a function of time for three hours, initially at higher speeds and then slowly towards the end of the test. The stress relaxation curves were plotted as the ratio of the stress to initial stress versus the logarithm of time. The rate of relaxation was calculated from the slopes of the straight line portion of the graph.

2.9. THERMOGRAVIMETRIC ANALYSIS

Thermal stability of the samples ~~were~~ was tested by a Dupont Thermal analyser. The heating rate was 10 °C/minute and the test was carried out under Nitrogen atmosphere. The order of the degradation reaction of the composites was calculated from TGA curves by using modified form of Freeman and Carroll equation as [2]

$$\frac{\Delta \log dw/dt}{\Delta \log W_r} = \frac{X_d - (\Delta E_d / 2.3\,R)\quad (\Delta 1/T)}{\Delta \log W_r} \qquad (2.8)$$

where

dw/dt is the rate of reaction

X_d is the order of the reaction

ΔE_d is the energy of activation

W_r is $(W_i - W)$ and is proportional to the amount of the reactant

W_i is the total weight loss associated with a given reaction

W is the weight loss at the point where the weight is taken

R is the gas constant

T is the absolute temperature.

The order of the reaction and the energy of activation were calculated by finding out the slopes and intercepts of the plots of

$$\frac{\Delta \log dw/dt}{\Delta \log W_r} \quad \text{Vs} \quad \frac{(\Delta 1/T)}{\Delta \log W_r}$$

2.10. SCANNING ELECTRON MICROSCOPY

The SEM basically consists of an electron beam (usually of tungsten filament thermionic emission type) which produces and accelerates electrons to an energy between 2 keV and 50 keV. These electrons are directed down to the centre of an electro - optical column consisting of two or three condensing lenses which cause a fine electron beam to be founded on to the specimen surface.[3] The fine beam of electron is scanned across the specimen by deflector coils while an electron detector counts the number of low energy secondary electrons given off from each point on the surface. At the same time the spot of a cathode ray tube (CRT) is scanned across its screen while the brightness of the spot is controlled by, for instance, the number of electrons counted by a secondary electron detector. The beam of electrons and CRT are scanned in a rectangular set of straight lines known as "raster". The raster scanned by the electron beam on a specimen is made smaller than the raster displayed on CRT. The linear magnification is the side length of the CRT divided by the side length of the raster on the specimen. In order to increase magnification it is only necessary to reduce the currents in SEM scanning coils. As a consequence, it is easy to obtain high magnifications in SEM. Besides its resolving power a great advantage of SEM is the enormous depth of field which is available when using a specimen. This arises from the small angular apertures used and is about 1000 times better than for a light microscope at a similar magnification.

To study the failure mode, the surfaces were carefully cut from the failed test specimens without touching the fracture surface and were sputter coated with gold. The SEM observations were made within one weak of gold coating. The orientation of the photographs was kept constant in a particular mode of failure.

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CHAPTER III.A
CURE CHARACTERISTICS - I*

Properties of short fiber – elastomer composites critically depend upon the interfacial bonding between the fiber and the matrix, in addition to other factors such as aspect ratio of fiber, orientation and dispersion of fiber and modulus of the fiber to that of the matrix. In a short fiber - rubber composite the load is transferred from the matrix to the fiber through the fiber matrix interface and this requires a strong bond between the fiber and matrix. Several methods have been used to improve the matrix - fiber adhesion [1-7] Kondo reviewed the selection of adhesives for bonding short fiber in styrene - butadiene rubber and natural rubber compounds[8]. Use of external bonding agents based on HRH has been found to improve the performance of the composite considerably[9-11]. However this system is not useful in polyurethane elastomer based composite. Also, in the presence of the HRH bonding agent the polyurethane matrix could not be sulphur cured[12]. This aspect has been investigated in detail by analysing the cure pattern of the composite and an alternative new bonding agent based on urethane resin has been suggested.

Formulation of the mixes are shown in the Table III.A.1. Sample preparation and the various test methods are detailed in Chapter II.

3.A.1. EFFECT OF FIBER LOADING

Figure 3.A.1 shows the cure pattern of mixes A-G, containing 0 - 30 phr of polyester short fibers. In the

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* Results of this chpter has been published in Plast.Rubb. Comp. Proces. Appl. 24(1995) 37 – 41.

presence of short fibers the cure behaviour of polyurethane elastomer is greatly altered.

Ingredients	Mix No.								
	A	A1	B	C	D	E	F	G	H
Polyester fiber	-	5	10	20	30	10	-	-	-
Tpresin	-	-	-	-	-	-	-	-	-
HMTA*	-	-	-	-	-	5	5	-	-
Resorcinol	-	-	-	-	-	2.5	2.5	-	-
Silica	-	-	-	-	-	1.6	1.6	-	-
$CuSO_4.5H_2O$	-	-	-	-	-	-	-	5	-
$CuSO_4$ (anhydrous)	-	-	-	-	-	-	-	-	5

(Continued)

Table III.A.1. Formulaton of the mixes

Ingredients	Mix No.								
	I	J	K	L	M	N	O	P	Q
Polyester fiber	-	-	10	10	10	-	5	20	30
Tpresin	-	-	2	5	8	5	5	5	5
HMTA*	5	5	-	-	-	-	-	-	-
Resorcinol	2.5	2.5	-	-	-	-	-	-	-
Silica	5	10	-	-	-	-	-	-	-
$CuSO_4.5H_2O$	-	-	-	-	-	-	-	-	-
$CuSO_4$ (anhydrous)	-	-	-	-	-	-	-	-	-

* HMTA - Hexamethylenetetramine. Adiprene 100 phr, Zinc Stearate 0.5 phr; Caytur -4 0.35 phr; MBTS 4 phr; MBT 1 phr and Sulphur 0.75 phr are common to all mixes. TP resin was prepared by mixing molar proportions of polymeric toluenediisocyanate and polypropyleneglycol in the ratio 1:2.

Table III.A.1. Formulaton of the mixes

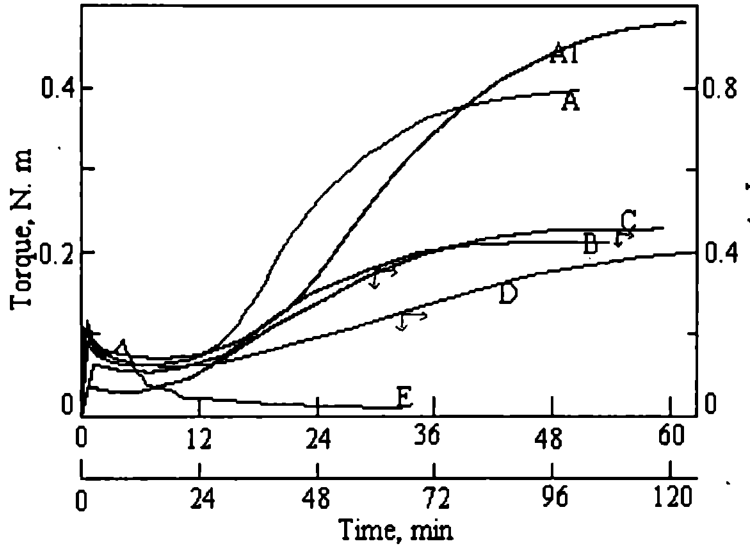

Figure 3.A.1. Rheographs of Mixes A-G.

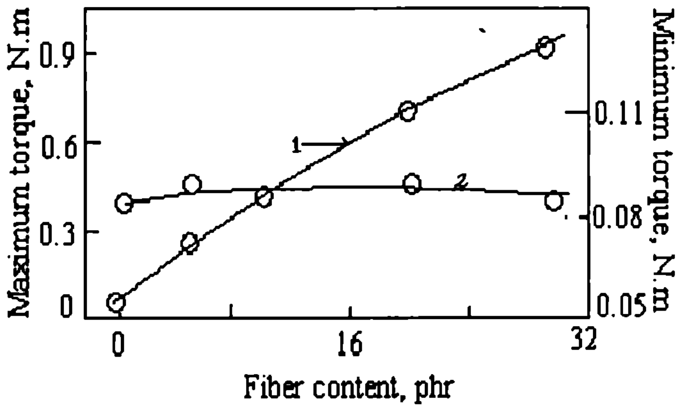

Figure 3.A.2. Variation of maximum and minimum torque with fiber loading (Series 1: Minimum torque, 2: Maximum torque)

The minimum torque shows a linear increase with increase in fiber loading, as shown in the Fig 3.A.2. However the maximum torque remains more or less constant. A similar result in the case of polyurethane - short Kevlar fiber composite has been reported earlier [12].

The scorch time and the cure time are found to increase with increase in fiber content (Figure. 3.A.3.). Scorch time is increased from 13.4 minute at 0 phr fiber loading to 32.8 minutes at 30 phr fiber loading. Correspondingly, the cure time is increased from 31.6 minutes to 90.8 minutes. This coupled with a constant maximum torque at all fiber loadings indicates a reversible adsorption of curatives [12].

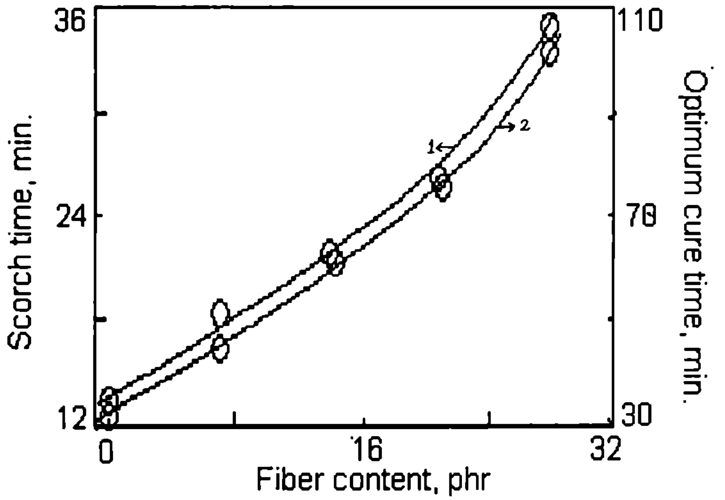

Figure 3.A.3. Variation of scorch and optimum cure time with fiber loading.(Series 1: Scorch time, 2: optimum cure time)

3.A.2. EFFECT OF BONDING AGENTS

3.A.2.1.HRH BONDING SYSTEM

The curing of 10 phr polyester fiber - filled polyurethane elastomer in the presence of HRH bonding system was studied and the cure curve (Figure 3.A.1.) shows that the system undergoes degradation instead of curing, after about 6 minutes. The cure behaviour was further studied in the absence of short fibers. Figure 3.A.4 gives the cure characteristics of mixes A and F. Mix A with normal curatives shows a good cure, where as mix F containing the HRH bonding agent fails to cure. The torque shows a distinct fall beyond the plastic flow region. At about 6 minutes of cure the torque drops from 0.021 Nm to 0.006 Nm and then shows only a marginal increase. The very low final torque indicates an extensive molecular chain breakage instead of crosslinking. The molecular breakdown in the presence of HRH dry bonding system may be attributed to the hydrolysis of urethane linkages of the elastomer. The resorcinol and hexamethylenetetramine at

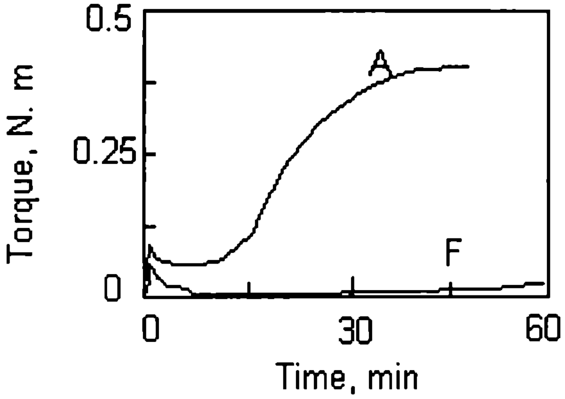

Figure 3.A.4.Rheographs of mixes A and F

the curing temperature react to form RF resin and the by product water molecules hydrolyse the urethane linkages.

This is further confirmed by studying the curing reaction with another water source that liberates water at elevated temperature. $CuSO_4$. 5 H_2O was selected as a water donor and was incorporated at a level of 5 phr (mix G). The cure behaviour is shown in Figure 3.A.5. This also shows a cure pattern similar to that of mix F. The torque is reduced from 0.042 Nm to 0.010 Nm at about 6 minute curing. The pro - oxidant effect of copper has been checked by studying another sample with anhydrous $CuSO_4$ (mix H) and the cure curve is shown in Figure 3.A.5. The torque shows a gradual and almost linear reduction with time. There is however no abrupt change in torque at 6 minutes. This indicates that the sudden change in viscosity of polyurethane in the presence of $CuSO_4.5H_2O$ is due to the hydrolysis of urethane by the water liberated by $CuSO_4$. This clearly confirms that the degradation of polyurethane

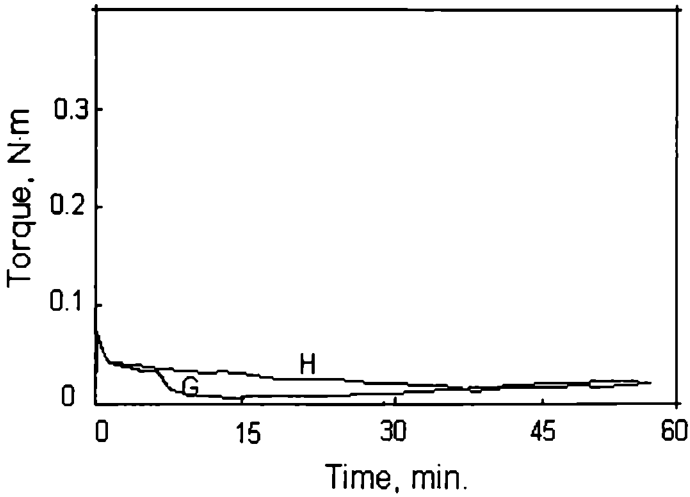

Figure 3.A.5.Rheographs of mixes G and H

in the presence of HRH dry bonding system is due to the water formed during resorcinol - formaldehyde resin formation.

Silica is incorporated as a modifier for resorcinol - formaldehyde resin formation.[12-13] The surface hydroxyl groups on silica may have an effect on the urethane curing reaction. This was studied by changing the silica concentration from 1.6 to 10 phr (mixes F,I,J). The cure behaviour of these mixes are shown in Figure 3.A.6. As expected, the final torque values decrease with increase in silica content. Increasing the acidic - OH concentration in the medium increases the chances of urethane breakage.

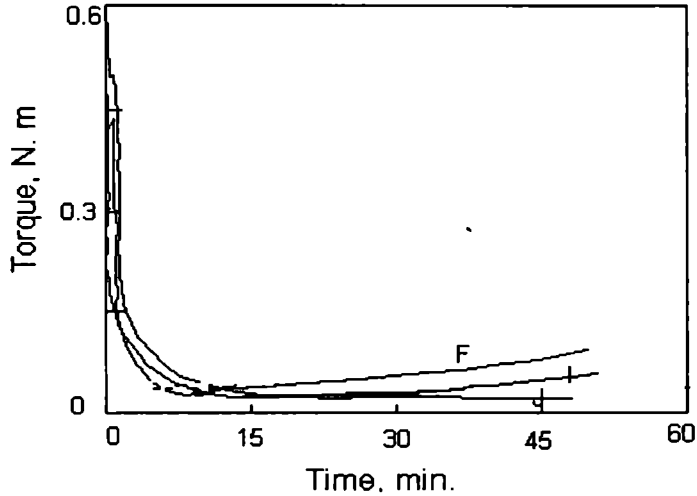

Figure 3.A.6. Rheographs of mixes F,I and J

3.A.2.2. URETHANE BASED BONDING SYSTEM

As an alternative a resin system (TP) based on polymeric toluenediisocyanate and polypropyleneglycol which does not form water as a byproduct was used as a bonding agent.

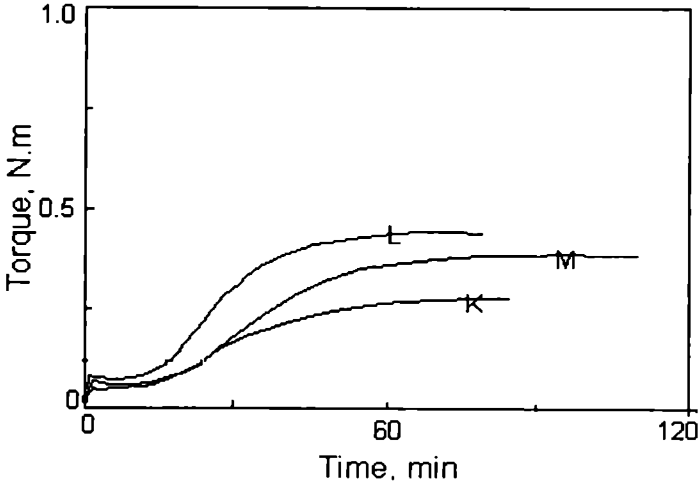

Figure 3.A.7 Rheohraphs of mixes K, L and M

Figure 3.A.7 shows the cure behaviour of polyurethane - polyester composite containing polymeric toluenediisocyanate and polypropyleneglycol corresponding to 2, 5 and 8 phr of TP resin (mixes K,L,M).

With increasing TP resin content the minimum torque and maximum torque values show a marginal increase with a maximum at 5 phr of TP resin (Fig. 3.A.8) indicating a more restrained matrix resulting from an improved fiber - matrix interfacial bonding. A 5phr loading of TP resin was selected for further studies. The scorch time and optimum cure time of these mixes are given in the Table III.A.2. .

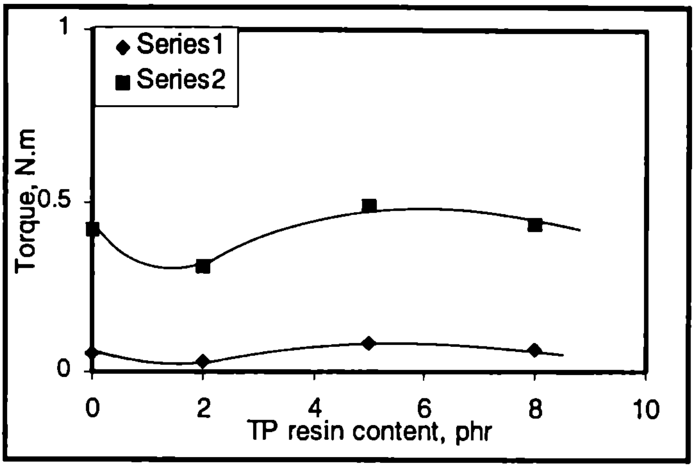

Figure 3.A.8.Variation of maximum and minimum torque with TP resin(Series 1: Minimum torque, 2: Maximum torque)

Mix No.	Scorch Time (min.)	Optimum Cure Time (min.)
B	21.6	62.4
K	14.0	58.8
L	16.8	40.8
M	21.2	58.0

Table III.A.2. Scorch time and optimum cure time of mixes K - M

Scorch time and optimum cure time decrease with the increase of resin content. However, mix containing a higher amount of resin shows a higher value of scorch time and optimum cure time. This may be due to the interference of the resin in the sulphur curing of the polyurethane elastomer.

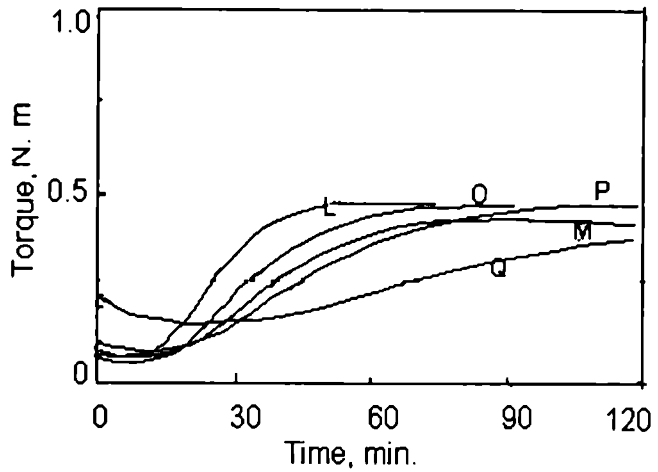

Figure 3.A.9.Rheographs of mixes L, N-Q

Figure 3.A.9 shows the cure behaviour of mixes containing 0 - 30 phr fiber with 5 phr TP resin (Mixes L, N - Q). Unlike in the case of HRH based compounds these mixes are found to give a perfect cure. A comparison of the T_{max} - T_{min} of the composites with and without TP resin (Figure 3.A.10) shows that the maximum torque developed is higher for the TP resin containing composite. This suggests that TP resin at a concentration of 5 phr is a good choice for improving the properties of polyurethane - polyester short fiber - composites. A comparison of scorch time and optimum cure time of the composites with and without TP resin is given in the Table III.A.3.

Scorch time and optimum cure time of the composites containing TP resin (mixes N, O, L, P, Q) increase in the presence of bonding agent and the effect becomes well pronounced as the fiber concentration increases. In the case of mixes containing bonding agents scorch time and optimum cure time decrease with increase of fiber concentration and further increase of fiber concentration

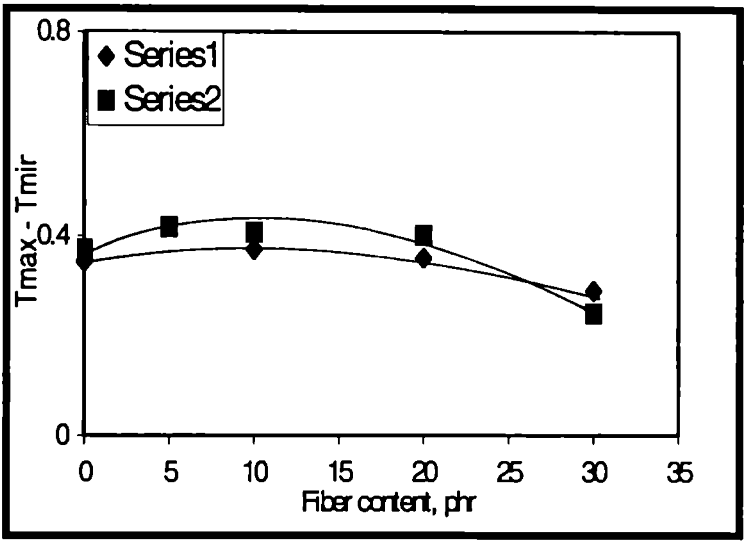

Figure 3.A.10. T_{max} - T_{min}. of composites with and without TP resin(Series 1: With resin, 2: Without resin)

Mix No	Scorch Time (min.)	Optimum Cure Time (min.)
A	13.4	31.6
A1	18.4	44.6
B	21.6	62.4
C	26.4	74.8
D	34.8	103.6
N	23.2	60.8
O	19.6	54.8
L	16.8	40.8
P	26.8	84.4
Q	40.4	103.6

Table III.A.3. Scorch time and optimum cure time of composites with and without TP resin

increases the scorch time and optimum cure time. This is because as the fiber concentration increases, the relative loading of bonding agent and hence its influence becomes less pronounced.

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CHAPTER III.B

CURE CHARACTERISTICS – II*

From the previous section it is evident that bonding agents based on urethane resins can improve the adhesion between the polyester fiber and polyurethane matrix. This section contains the results of optimisation of -isocyanate /- ol ratio in the urethane resins and the cure characteristics of the composites containing these resins.

Table III.B.1 shows the formulation of the mixes A - N. Except mix A, all the mixes contain MD resin based on different diols and polymeric MDI as the bonding agent. In mixes B- N the diol and isocyanate concentrations were so adjusted that the resin content was five parts per hundred rubber (phr) and the diol to isocyanate ratio varied from 1:0.67 to 1:2. Mixes B - E and F - I contain propyleneglycol and polypropyleneglycol, respectively as the diol. Mixes J - M contain a triol, glycerol as the -ol

Ingredients	**Mix No.**							
	A	B	C	D	E	F	G	H
PG	-	1.5	1.1	0.8	0.6	-	-	-
PPG	-	-	-	-	-	4.6	4.4	4.2
GL	-	-	-	-	-	-	-	-
MDI	-	3.5	3.9	4.2	4.4	0.4	0.6	0.8

(Continued)

Table III. B.1. Formulation of the mixes

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* Results of this section has been published in Int. J.Polym. Mater.38(1997) 205 – 218.

Ingredients	Mix No.					
	I	J	K	L	M	N
PG	-	-	-	-	-	-
PPG	3.9	-	-	-	-	2.2
GL	-	1.3	0.9	0.7	0.5	0.07
MDI	1.1	3.7	4.1	4.3	4.5	0.6

PG - Propyleneglycol, PPG - Polypropyleneglycol, GL - Glycerol and MDI - 4,4' diphenylmethane diisocyanate. Base Recipe: Adiprene 100, Short polyester fiber 20, Zincstearate 0.5, Caytur 4 0.35, MBTS 4, MBT 1 and Sulphur 0.75. All values are expressed as parts per hundred rubber (phr).

Table III. B.1. Formulation of the mixes

component. Mix N is a modified form of mix G , where 50 parts by equivalence of polypropyleneglycol was replaced by glycerol.

Preparation of mixes, determination of cure characteristics and V_r values are explained in Chapter 2.

3.B.1. MDI - PG RESIN

The cure curves of the mix A and mixes B - E containing MDI and propyleneglycol in the equivalence ratio of 0.67:1, 1:1, 1.5:1 and 2:1 are shown in Figure 3.B.1.

The cure characteristics of the mixes are shown in Table III.B.2. In mix B, the MD resin formed was -ol terminated whereas in mixes D & E the resin was isocyanate terminated. The presence of 5 phr of the MD resin in the matrix considerably alters the cure pattern of the polyurethane - short polyester fiber composite.

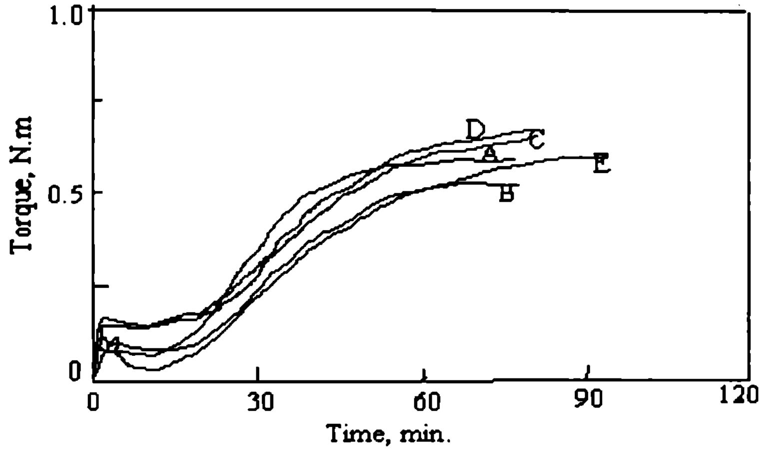

Figure 3.B.1.Rheographs of mixes A - E

Mix No.	Minimum Torque (N. m)	Maximum Torque (N. m)	Scorch Time (minutes)	Optimum Cure Time (minutes)
A	0.061	0.486	15.2	36.8
B	0.064	0.435	18.0	45.2
C	0.097	0.532	16.8	47.6
D	0.108	0.547	17.6	47.6
E	0.104	0.481	18.4	54.0

Table III. B.2 Cure characteristics of mixes A - E.

3.B.1.1.MINIMUM TORQUE AND (T_{max}. - T_{min}.)

Figure 3.B.2 shows the variation of minimum torque and the difference of maximum and minimum torque (T_{max}. - T_{min}.) with different MDI/ diol ratios. The minimum torque shows only a marginal increase with increasing isocyanate concentration. This indicates that the processability of the

composite is hardly affected by the incorporation of the urethane resin.

The (T_{max}. - T_{min}.) values show a major reduction when the MD resin formed is -ol terminated (mix B), whereas for mixes C and D torque values are higher than that of mix

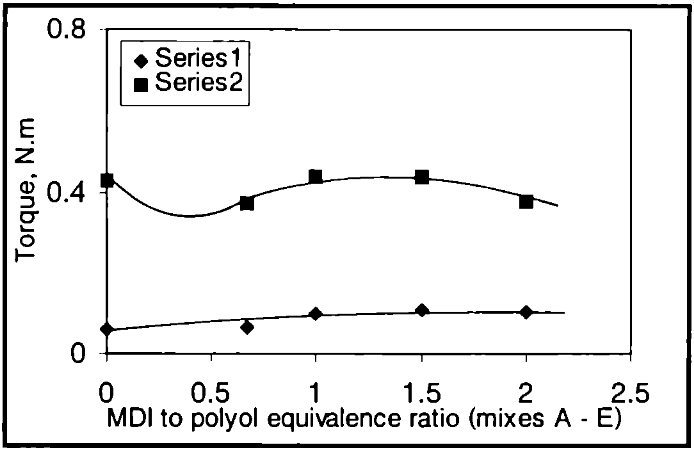

Figure3.B.2. Variation of maximum torque and '(T_{max} - T_{min})of mixes A-E (Series 1: Minimum torque, 2: T_{max} - T_{min})

A. At still higher MDI / diol ratio (mix E) torque is reduced significantly indicating that the optimum -NCO / -ol ratio is around one. Also, the V_r values of these mixes (Table III.B.3) do not show much variation.

The high values of (T_{max}. - T_{min}.) and almost constant V_r values of short fiber composite in the presence of MD resin point to a more restrained matrix resulting from a better fiber - matrix bonding.[1] The low values of (T_{max}. - T_{min}.) at very low and very high -NCO / -ol equivalence ratios are because of the less effective utilisation of the monomer functionalities. Since the MD resin components are adjusted to be 5 phr in all the mixes, at equivalence ratios other than one, the resin formation will not be optimum.

Mix No.	V_r
A	0.180
B	0.196
C	0.193
D	0.217
E	0.203
F	0.183
G	0.183
H	0.177
I	0.172
J	0.197
K	0.197
L	0.216
M	0.196
N	0.197

Table III.B.3 Volume fraction of the mixes A - N

3.B.1.2. SCORCH TIME AND OPTIMUM CURE TIME

Scorch time and optimum cure time increase as -NCO / -ol equivalence ratio increases (Figure 3.B.3). The optimum cure time registers an increase at an equivalence ratio of 2 (mix E) and there is a corresponding reduction in the cure rate.

Figure 3.B.4 shows the variation of cure rate of mixes A - E with the -NCO / - ol ratio in the composite. The cure rate of all the mixes containing MD resin is considerably lower than that of mix A, the minimum being shown by mix E. This suggests that the presence of MD resin, especially those containing excess isocyanate interferes with the

sulphur curing of polyurethane. This is in agreement with the low value of ($T_{max.}$ - $T_{min.}$) exhibited by mix E.

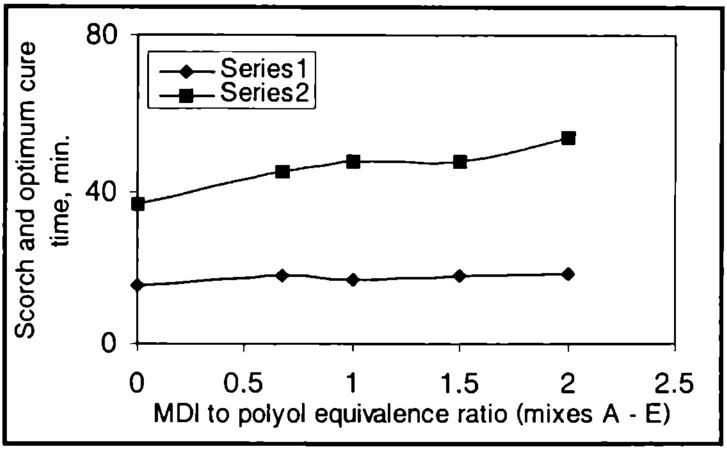

Figure 3.B.3. Variation of scorch time and optimum cure times of mixes A – E (Series 1: Scorch time, 2: Optimum cure time)

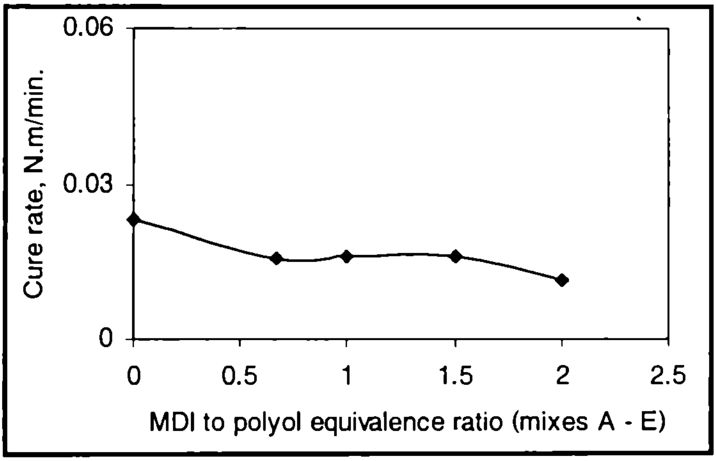

Figure3.B.4.Variation of cure rate of mixes A – E

3.B.2. MDI - PPG RESIN

Cure curves of the composites containing polypropyleneglycol based urethane resin (mixes F - I) are shown in Figure 3.B.5.

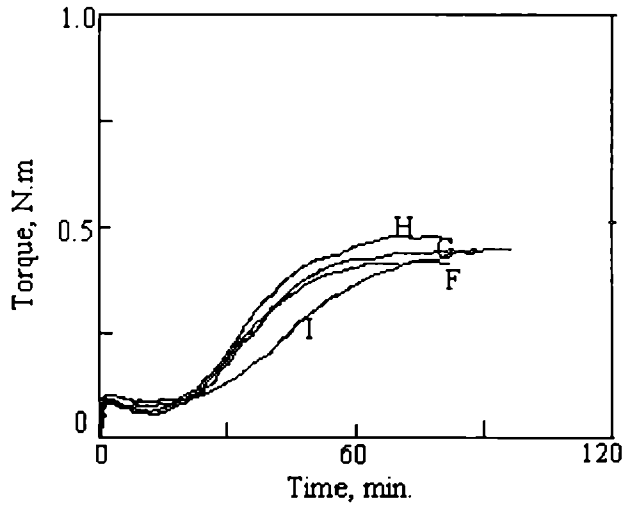

Figure3.B.5.Rheographs of mixes F – I

The variation of the minimum torque and the (T_{max}. - T_{min}.) with MDI / diol ratio is shown in Figure 3.B.6. The minimum torque values show a trend similar to that of MDI/ PG based composite. (T_{max}. - T_{min}.) shows a linear increase with increasing MDI / diol ratio upto 1.5 and thereafter remains more or less constant. Here also the V_r values show not much variation(Table III.B.3). The scorch time and cure time are increased in the presence of the MD resin(Figure 3.B.7).

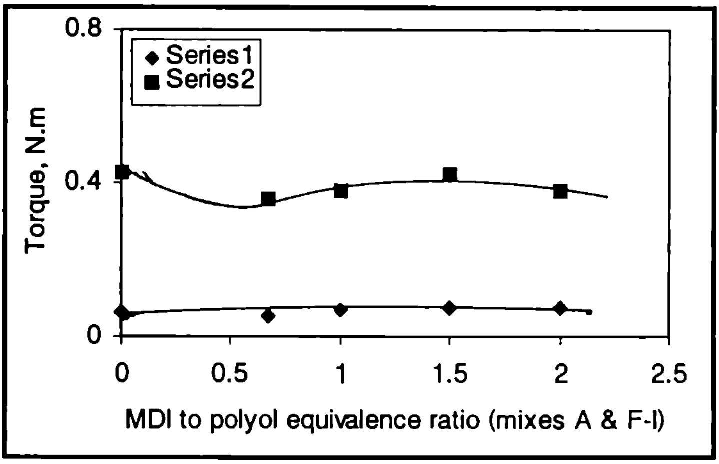

Figure3.B.6.Variation of minimum torque and (T_{max} - T_{min}.) of mixes A & F – I (Series 1: Minimum torque, 2: $T_{max} - T_{min}$)

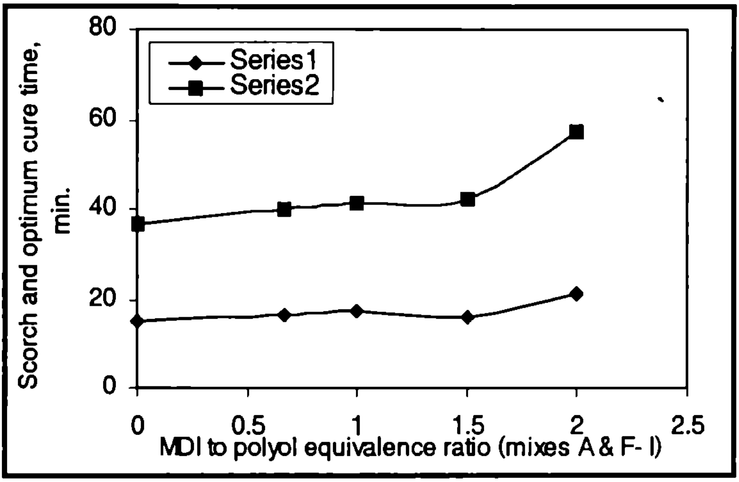

Figure3.B.7.Variation of scorch and optimum cure times of mixes A & F – I (Series 1: Scorch time, 2: Optimum cure time)

3.B.3. MDI - GLYCEROL RESIN

The cure characteristics of mixes J - M (Figure 3.B.8) show a trend similar to that of the propyleneglycol based mixes (mixes B - E). The minimum torque and ($T_{max.}$ - $T_{min.}$) at different MDI / -ol equivalence ratios are shown in Figure 3.B.9. The minimum torque shows a marginal increase with increasing MDI equivalence ratio. ($T_{max.}$ - $T_{min.}$) attains a maximum at an MDI equivalence ratio of 1.5, after which it drops drastically indicating that the resin formation is optimum when the MDI / -ol ratio is 1.5.

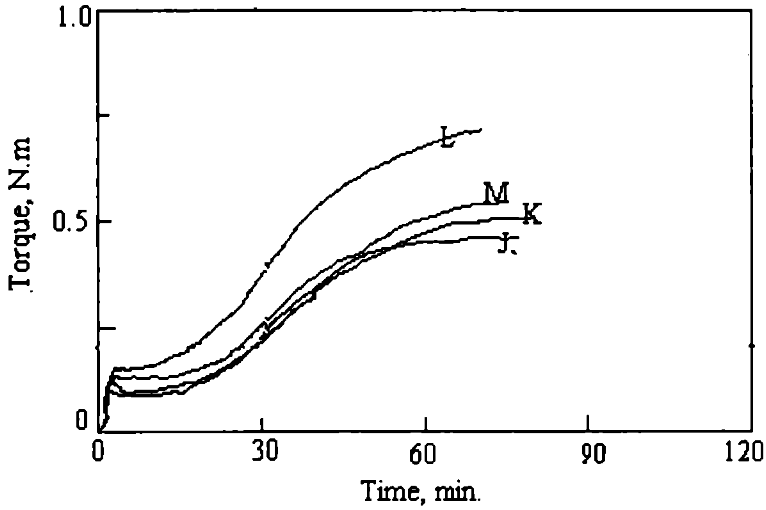

Figure 3.B.8. Rheographs of mixes J - M

Cure time and scorch time (Figure 3.B.10) show a trend as in the cases of MDI/PG and MDI/PPG based composites.

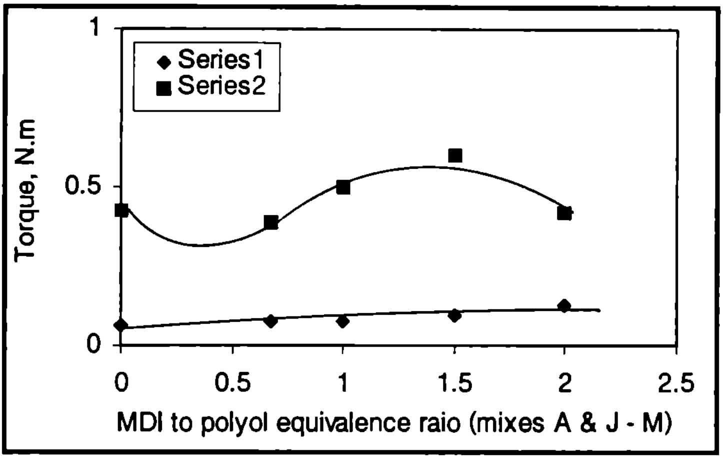

Figure3.B.9.Variation of minimum torque and (T_{max}-T_{min}.) of mixes A & J – M (Series 1: Minimum torque, 2: T_{max} – T_{min})

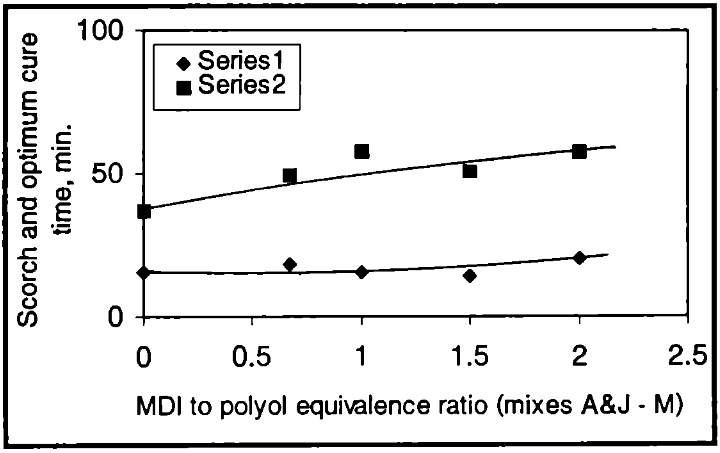

Figure3.B.10.Variation of scorch and optimum cure times of mixes A & J - M

3.B.4. MD RESIN BASED ON DIFFERENT DIOLS AND TRIOL

3.B.4.1.MINIMUM TORQUE AND (T_{max} - T_{min})

Figure 3.B.11 gives the minimum torque and the (T_{max} - T_{min}) of the composites containing MD resin with 1:1 equivalence of MDI and different -ols and also that of the composite containing no resin. The higher value of the (T_{max} - T_{min}) is exhibited by the composite containing glycerol based MD resin(mix K). This may be attributed to the trifunctionality of the glycerol. With MDI, the glycerol forms a three dimensional network structure leading to a more restrained matrix and improved fiber - matrix interaction. PPG/MDI resin based composite (mix G) exhibits the lowest (T_{max} - T_{min}) and minimum torque values, indicating a low level of crosslinking coupled with better processability. MDI / PG resin based composite

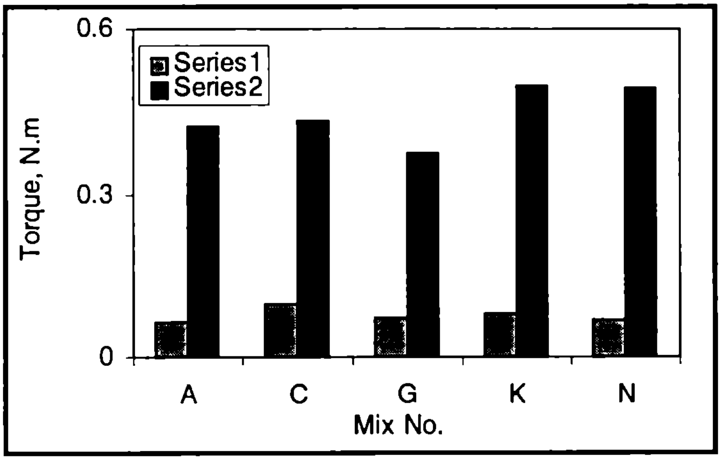

Figure3.B.11.Minimum torque and T_{max} - T_{min} of mixes A, C, G, K & N (Series 1: Minimum torque, 2: T_{max} – T_{min})

Mix No.	Scorch Time (minutes)	Optimum Cure Time,(minutes)	Cure Rate (Nm/min.)
A	15.2	36.8	0.023
C	16.8	47.6	0.016
G	17.2	41.6	0.017
K	15.2	57.6	0.014
N	13.6	34.8	0.027

Table III.B.4. Cure parameters of the mixes A, C, G,K&N

shows a ($T_{max.}$- $T_{min.}$) that is in between that of mixes G & K and the highest minimum torque. Substituting 50 parts by equivalence of the PPG by glycerol (mix N) has a favourable effect on the extent of crosslinking, as indicated by the higher ($T_{max.}$ - $T_{min.}$) values. At the same time, the minimum torque values show that processability is not hampered significantly.

3.B.4.2. SCORCH TIME, CURE TIME AND RATE OF CURE

Table III.B.4. gives the scorch time, optimum cure time and rate of cure of the composites containing MD resin with 1:1 equivalence of MDI and different -ols and that of composite without MD resin. Mixes C, G & K have higher cure time while mix N shows a low cure time compared to that of mix A. Also, Mix N shows a high rate of cure and a comparatively lower scorch time.

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CHAPTER IV.A

RHEOLOGICAL PROPERTIES – I*

Processing of a composite material involves flow under shear and is determined by the rheological study of the composite. White and Tokita[1-2] have established a correlation between rheology and processing. Crowson and Folkes[3] studied the rheology of short glass fiber reinforced thermoplastics and concluded that the fibers in the composite oriented along the flow direction during convergent flow, and that fiber alignment took place only at high shear rates. Several other studies have reported the rheological characteristics of short fiber reinforced polymer melts. [4-9] This section deals with the rheological characteristics of short polyester fiber - polyurethane elastomer composite with reference to the effect of shear rate, fiber concentration, temperature and the bonding agent on the shear viscosity.

The formulation of the mixes is given in the Table IV .A.1.

Ingredient	**Mix No.**			
	A	B	C	D
Adiprene	100	100	100	100
PET fiber	-	10	20	30

Base Recipe: Zinc stearate 0.5phr, Catur-4 0.35 phr MBTS 4phr and MBT 1 phr

Table IV. A.1. Formulation of the mixes

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* Results of this section has been published in Polym. Plast. Tech. Engg.36 (3) (1997) 399 - 409

The mixes were prepared using a Brabender Plasticorder and the details were given in Chapter 2.

Rheological studies were carried out using a Monsanto Processability Tester. The investigations were carried out in a shear rate range of 18 - 145 s^{-1} at different temperatures varying from 90 - 150 °C. A capillary of diameter 1.5 mm and L/D ratio of 20 was used for the study. Determination of fiber breakage after the Brabender mixing was given in Chapter 2.

4.A.1. FIBER BREAKAGE

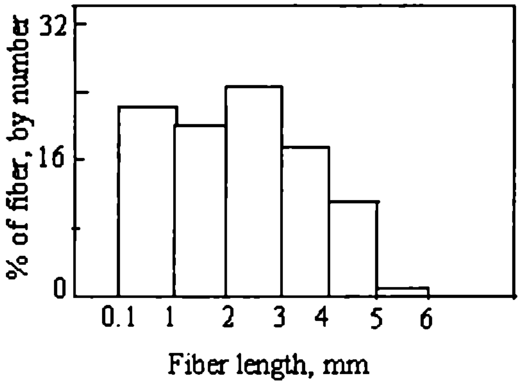

Figure 4.A.1.Fiber length distribution of mix B after mixing in a Brabender Plasticorder

The average length of fibers used for mixing was approximately 4 mm. Figure 4.A.1 shows the fiber length distribution of mix B after the Brabender mixing. It can be seen from the figure that during mixing the average fiber length is reduced and shows a broad distribution. The maximum is in the range of 1 - 3 mm indicating an extensive fiber breakage.

4.A.2. EFFECT OF SHEAR RATE

Figure 4.A.2. shows the effect of shear rate on the shear viscosity of mixes A - D at 90°C. Because of the instrument constraints the study was limited to a shear rate range of 18 - 145 s^{-1}. In all the cases the viscosity is found to decrease with increase in shear rate, indicating a pseudoplastic nature of the system.[6,9] Similar patterns are observed at 100,120 and 150 °C also (Figure 4.A.3 - 4.A.5.).

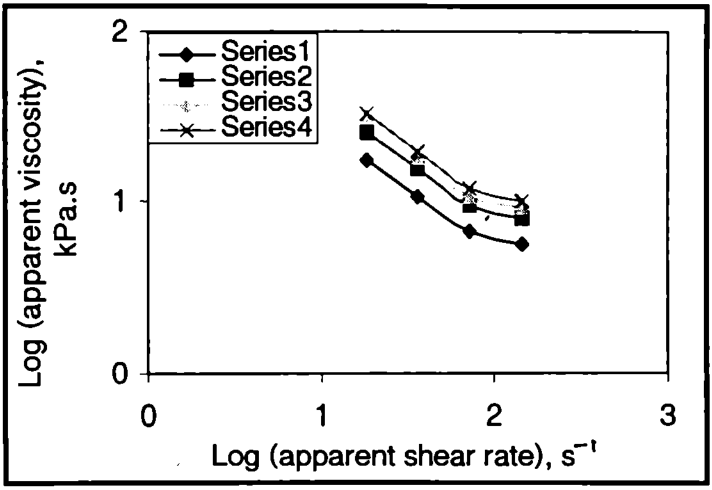

Figure 4.A.2.Variation of shear viscosity with shear rate of mixes A - D at 90°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

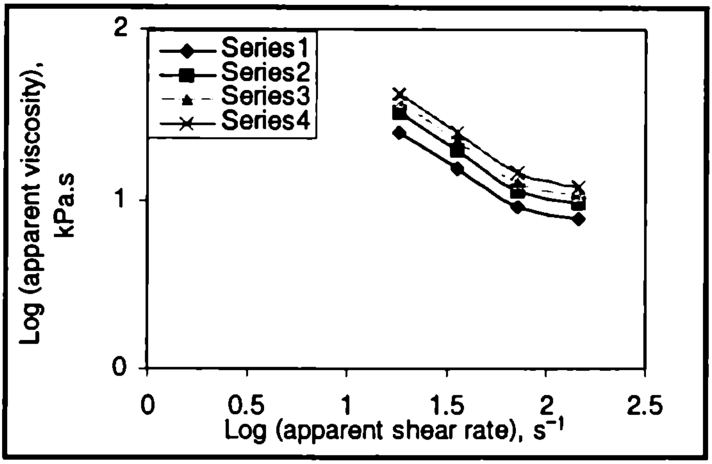

Figure 4.A.3. Variation of shear viscosity with shear rate of mixes A - D at 100°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

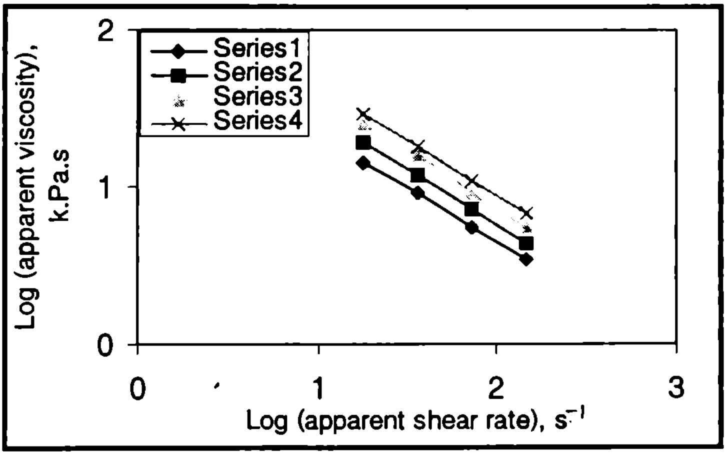

Figure 4.A.4. Variation of shear viscosity with shear rate of mixes A - D at 120°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

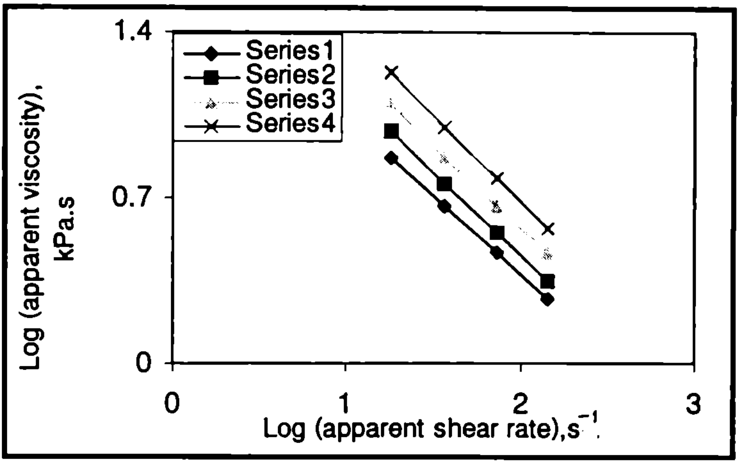

Figure 4.A.5. Variation of shear viscosity with shear rate of mixes A - D at 150°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

4.A.3. EFFECT OF SHEAR STRESS

A log - log plot of shear viscosity versus shear stress of mixes A - D at 120°C is given in Figure 4.A.6. The viscosity shows a linear reduction with shear stress . At 150°C the viscosity of the fiber filled samples registers a steeper reduction at a shear rate range of 18 - 36 s $^{-1}$ (Figure 4.A.7.). A relatively softer matrix at elevated temperature can facilitate orientation of fibers under shear deformation resulting in a lower shear viscosity.

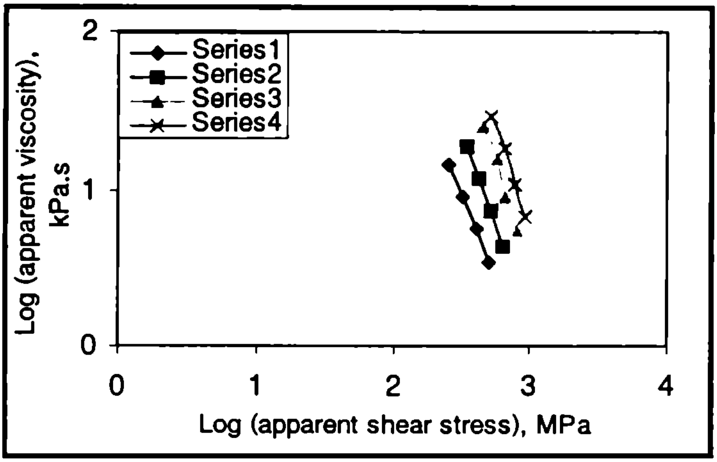

Figure 4.A.6. Variation of shear viscosity with shear stress of mixes A - D at 120°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

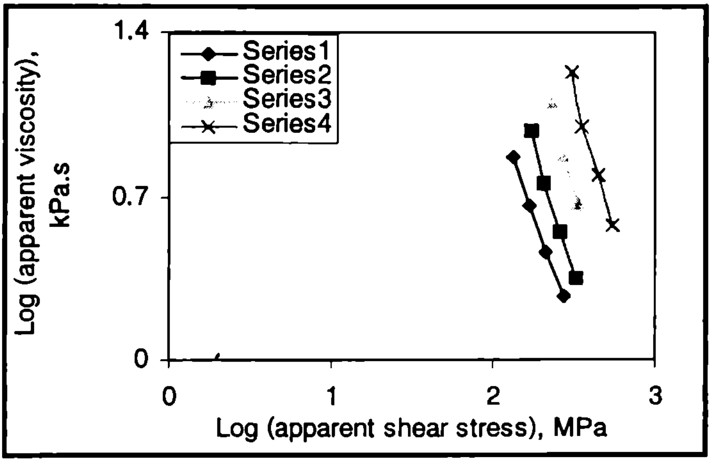

Figure 4.A.7.Shear stress versus shear viscosity at 150°C (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

4.A.4. EFFECT OF FIBER LOADING

In the shear rate range studied mix A exhibits the lowest viscosity. Progressive increase in the fiber content from 10 - 30 phr (mixes B - D) causes a rise in viscosity values at a given temperature (Figure 4.A.2). This effect is represented in Figure 4.A.8. as a plot of relative viscosity versus the volume fraction of fiber.

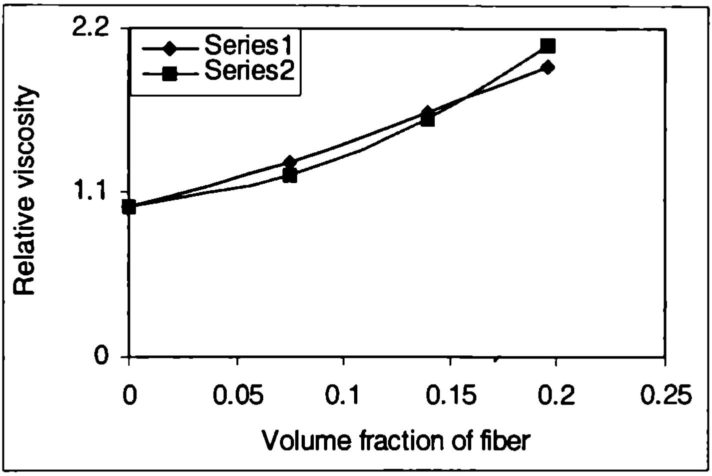

Figure 4.A.8.Variation of relative viscosity with volume fraction of fiber at a shear rate of 72.3 s^{-1} (Series 1: 120°C, 2: 150°C)

The relative viscosity is calculated as the ratio of the viscosity of the fiber filled compound to that of the unfilled one. The relative viscosity values of Figure 4.A.8. correspond to a shear rate of 72.30 s^{-1} at 120°C and 150°C. The two nonlinear plots in Figure 4.A.8. can be represented by the following equations:

$$3.8\,X^2 + 4.6\,X + 0.99 \qquad (4.A.1)$$

and

$$2\,3\,X^2 + 1.04\,X + 1 \qquad (4.A.2)$$

at 120 and 150°C, respectively. X is the volume fraction of fibers. It is observed that the relative viscosity is higher than one at all fiber loadings.

The relative viscosity at 150°C is lower than that at 120°C upto a fiber volume fraction of 0.140, after which the trend is reversed. This indicates that for a given melt viscosity a high melt temperature requires higher fiber loading upto the cross over point after which the reverse holds good. That is, for a given volume fraction of fiber the relative viscosity is higher at higher melt temperature. This is because of the lower melt viscosity of the matrix at higher temperature. The existence of such a cross over point indicates that a critical fiber loading is required for a

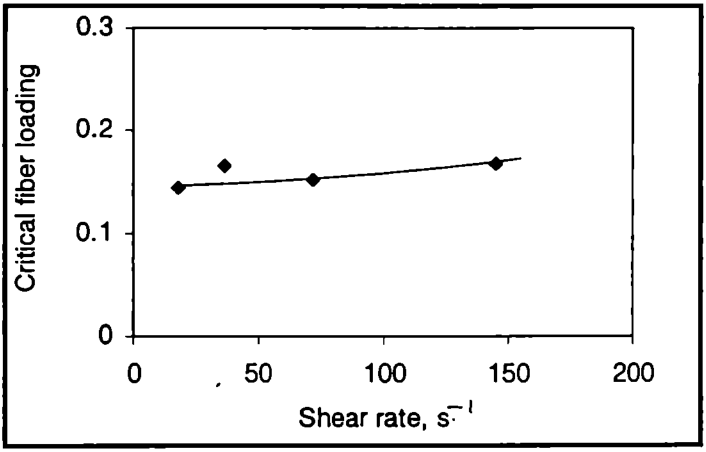

Figure 4.A.9. Variation of critical fiber loading with shear rate

better fiber - fiber interaction. At fiber loading lower than the critical value of the cross over point the fiber - fiber interaction is limited. When the fiber content is above the critical value the entanglement of the fibers occurs, leading to a more effective restraining of the matrix.

The critical fiber loading calculated from the plots of relative viscosity versus volume fraction of fiber at different shear rates is given in Figure 4.A.9. as a function of the corresponding shear rates. The critical fiber loading shows only a marginal increase at high shear rates.

4.A.5. ACTIVATION ENERGY

Activation energies of the composites calculated from the semi logarithmic Arrhenius plot of viscosity and temperature. In the Arrhenius equation, viscosity is related to absolute temperature by the following equation

$$\text{Apparent shear viscosity } (\eta) = A\,e^{-E/RT} \qquad (4.A.3)$$

where A is a constant characteristic of the polymer, E is the activation energy and R is the universal gas constant. From the slopes of the plots activation energies were calculated. Activation energy calculated at different shear rates are given in the Table IV.A.2.

In the shear rate and temperature range studied activation energy of the melt flow is not much affected by the presence of fibers, that is, the temperature sensitivity of the polyurethane elastomer is not much affected by the incorporation of fibers. Similarly the increase of shear rate also does not change the temperature sensitivity of the gum compound.

Mix No.	Activation Energy, kcal.		
	Shear rate s^{-1}		
	18.06	36.15	72.3
A	5.72	5.66	5.41
B	6.01	6.05	5.76
C	5.32	5.23	4.86
D	4.29	4.31	4.07

Table IV.A.2. Activation energies of the composites at different shear rates.

4.A.6. FLOW BEHAVIOUR INDEX

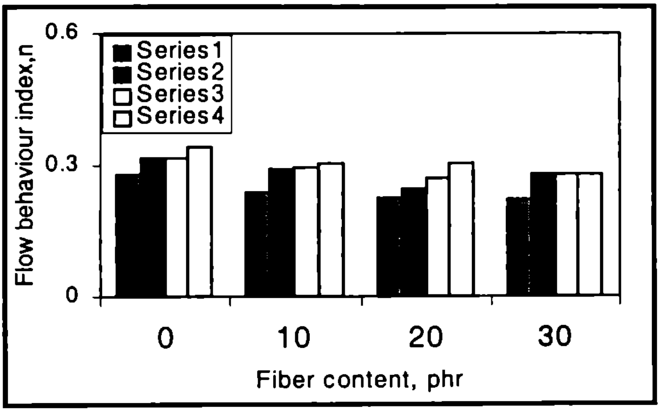

Figure 4.A.10.Flow behaviour indices of mixes at different temperatures (Series 1: 90°C, 2: 100°C, 3: 120°C, 4: 150°C)

Flow behaviour indices, n', of mixes A - D at different temperatures are shown in Figure 4.A.10. For mix A the n' increases as the temperature increases from 90°C to 150°C.

This indicates that the matrix becomes more Newtonian as the temperature increases. Mixes B - D show not much change with the increase of temperature. Flow behaviour indices of the fiber filled mixes are less than that of the gum compound. This may be due to the lower flowability of the fiber filled samples.[5,7]

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CHAPTER IV.B
RHEOLOGICAL PROPERTIES – II*

The rheological behaviour of polymer melts provides the choice of processing conditions and influences the morphology and mechanical properties of the final product. The effect of interfacial bond on the rheological characteristics ~~were~~ was studied by many workers.[1-3] In this section rheological characteristics of the composites with different bonding agents are evaluated in detail.

The formulation of the mixes is given in the Table IV.B.1. The mixes were prepared in a Haake Rheomix and the details were given in Chapter 2. Rheological studies were carried out using Monsanto Processability tester. A capillary of diameter 1.5 mm and L/D = 30 was used. The measurements were carried out at different shear rates ranging from 61 s^{-1} to 608 s^{-1} and at a temperature range of 100-160 °C.

4.B.1 EFFECT OF SHEAR RATE AND SHEAR STRESS

Figure 4.B.1 represents plot of log (viscosity) versus log (shear rate) at 120 °C of the composites with and without bonding agents. It is evident from the figure that for all the mixes viscosity decreases with the increase of shear rate indicating a pseudoplastic nature. Similar results have been reported earlier.[4]Over the whole shear rate range studied, the viscosity of the mix C1, containing bonding agent based on PPG and MDI shows a marginal decrease in viscosity than that of mix C, with no bonding agent.

Results of this chapter has been published in Polym. Plast. Tech. Engg. 37 (1) (1997) 57 - 70.

Ingredients	Mix No.			
	C	C1	C2	C3
Adiprene	100	100	100	100
PET fiber	20	20	20	20
Zinc stearate	0.5	0.5	0.5	0.5
Caytur-4	0.35	0.35	0.35	0.35
MBTS	4	4	4	4
MBT	1	1	1	1
PPG	-	4.44	-	2.22
GL	-	-	0.99	0.07
MDI	-	0.56	4.01	0.56

MBTS = Dibenzothiazyldisulphide; MBT = 2-mercaptobenzothiazole; PPG=polypropyleneglycol ; GL=glycerol; MDI= 4,4'-diphenylmethanediisocyanate.

Table IV.B.1. Formulation of the mixes

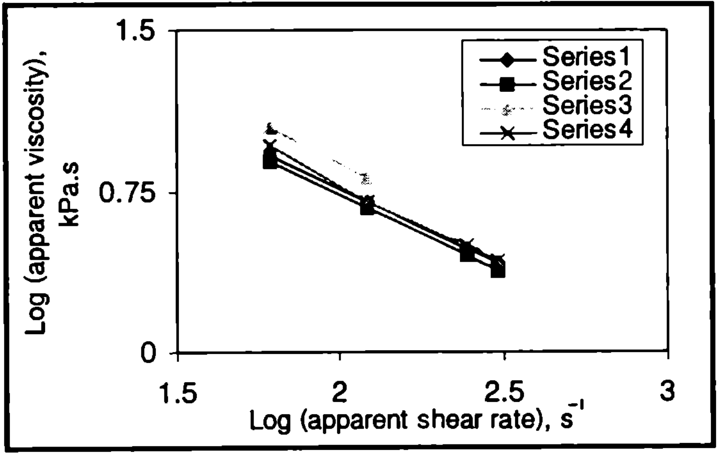

Figure 4.B.1.Variation of apparent viscosity with shear rate of mixes C - C3 at 120°C (Series 1: mix C, 2: mix C1, 3: mix C2, 4: mix C3)

The viscosity values of mix C2 suggest a more restrained matrix indicating a better fiber - matrix interaction in the presence of glycerol based bonding agent. With this bonding agent, the resin forms a three dimensional network structure in the matrix and the flow becomes more restricted and the molecular alignment in the flow direction under shear becomes less probable resulting in higher viscosity values. The observed mechanical properties also suggest a better fiber - matrix interaction in the presence of glycerol based bonding agent (Chapter V). As expected, the mix C3 containing both PPG and GL shows viscosity values in between that of mix C1 and C2. The presence of PPG seems to compensate for any restriction to flow due to glycerol and hence the mix C3 shows the viscosity values almost close to that of mix C.

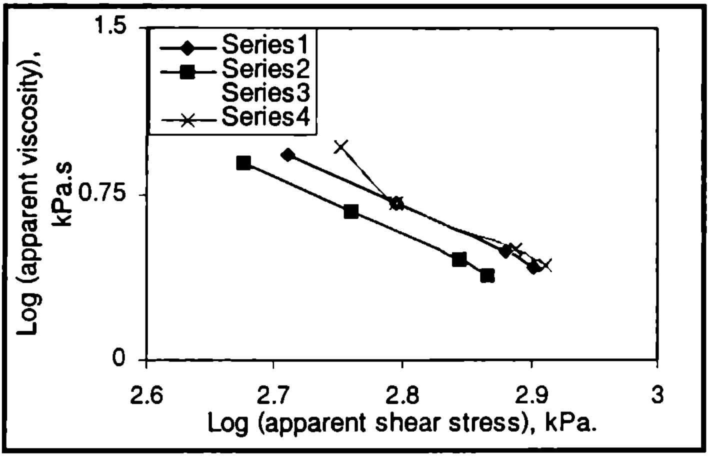

Figure 4.B.2.Variation of apparent viscosity with shear stress of mixes C - C3 at 120°C

A similar pattern of behaviour is observed in Figure 4.B.2 where log (viscosity) is plotted against log (shear stress), at 120°C. The difference between viscosity values of different mixes seems to be more significant in this figure. This suggests that the log - log plot of viscosity and shear stress will be a better tool to study the effect of interfacial bonding agents on the flow properties.

4.B.2 EFFECT OF TEMPERATURE

In the shear rate range studied, viscosity is found to decrease with increasing temperature (Figure 4.B.3). A similar trend is also observed in the case of composites containing different bonding agents (Figure 4.B.4 - 4.B.6). However, the variation in viscosity with temperature at a given shear rate is found to be different for different mixes.

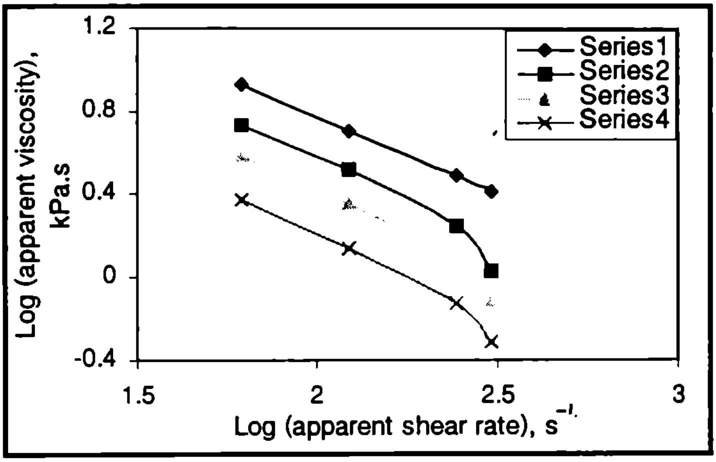

Figure 4.B.3.Effect of temperature on the variation of apparent viscosity with shear rate of mix C (Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)

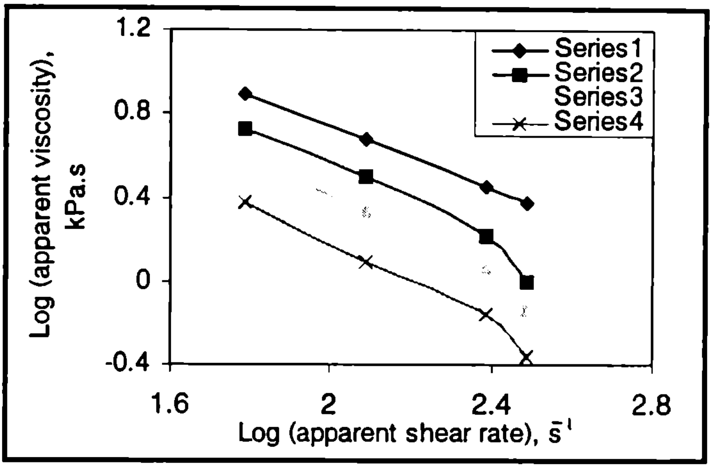

Figure 4.B.4. Effect of temperature on the variation of apparent viscosity with shear rate for mix C1(Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)

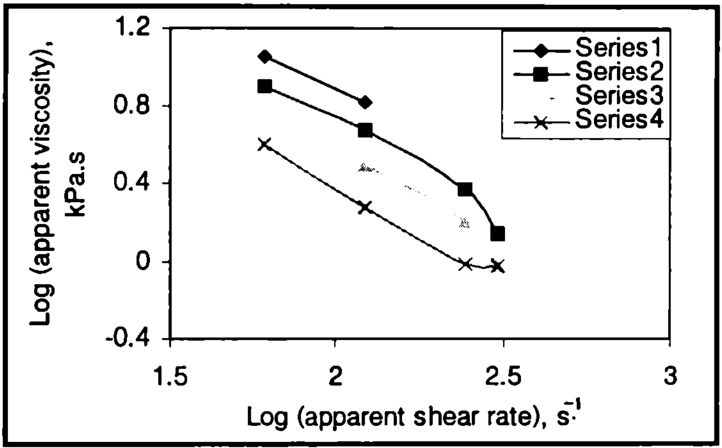

Figure 4.B.5. Effect of temperature on the variation of apparent viscosity with shear rate of mix C2(Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)

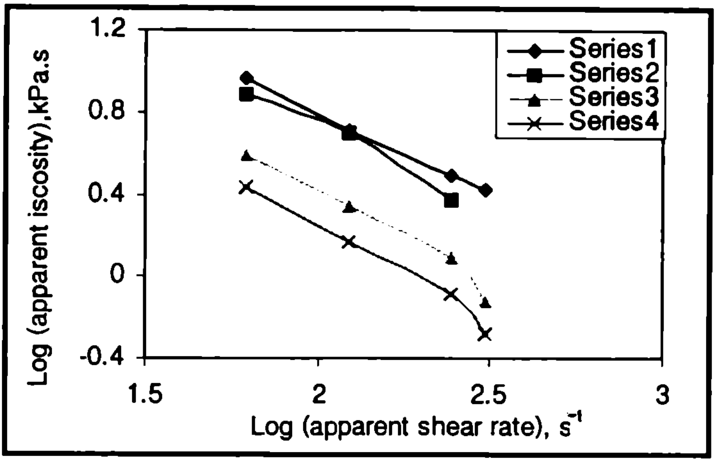

Figure 4.B.6. Effect of temperature on the variation of apparent viscosity with shear rate of mix C3 (Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)

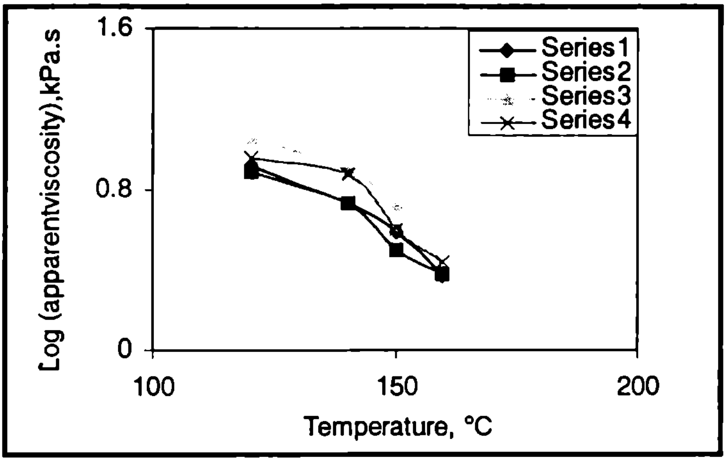

Figure 4.B.7.Variation of viscosity of mixes C -C3 with temperature at a shear rate of 61.3 s^{-1}(Series 1: mix C, 2: mix C1, 3: mix C2, 4: mix C3)

Figure 4.B.7 shows a plot of viscosity versus temperature at a shear rate of 61.3 s^{-1}, for different mixes. It shows that beyond a temperature of 140°C, the viscosity of different composites falls very sharply. The fall is less drastic in case of mix C2 containing glycerol based bonding agent when compared to mix C1 and C3. Between temperature 120 °C and 140°C the reduction in viscosity is less significant.

4.B.3 ACTIVATION ENERGY

Activation energies of the composites C and C1 - C3 are calculated from the plots of log (apparent viscosity) versus 1/T (Figure 4.B.8). Table IV.B.2. gives the value of activation energies at three different shear rates.

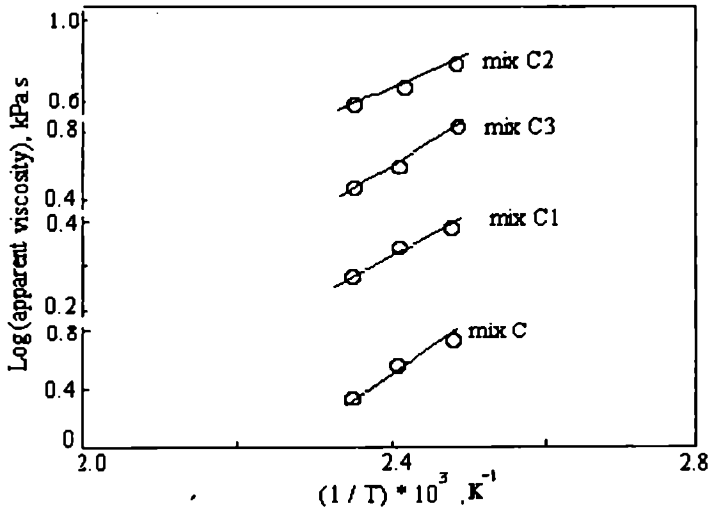

Figure 4.B.8.Variation of apparent viscosity with 1/T at a shear rate of 61.3 s^{-1}

The more or less same values of activation energies of the composites indicate that the temperature sensitivity of the composites remains unaffected with the rate of shear in the shear rate range studied. Similarly there is not much change in the activation energies of the composites containing different bonding agents. This again shows that the presence of bonding agents also does not alter the temperature sensitivity of the composite.

Mix No.	Activation energy (kcal)		
	Shear rate s^{-1}		
	61.3	122.6	306.5
C	15.39	15.56	15.81
C1	15.25	15.61	16.20
C2	17.43	17.73	15.25
C3	18.30	19.75	18.95

Table IV.B. 2. Activation energies of the mixes C and C1 - C3

4.B.4 FLOW BEHAVIOUR INDEX

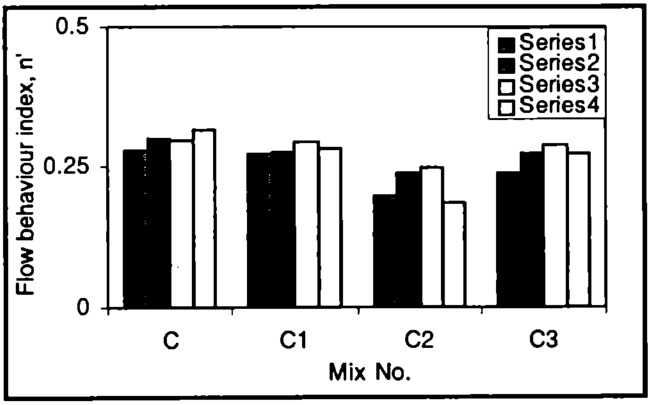

Figure 4.B.9.Variation of flow behaviour indices of mixes C - C3 with temperature (Series 1: 120°C, 2: 140°C, 3: 150°C, 4: 160°C)

Figure 4.B.9 shows the flow behaviour index, n', of the composites C and C1 - C3 , with and without bonding agents at different temperatures. The magnitude of n' indicates the extent of non - Newtonian behaviour of the composite. It is clear from the figure that for all the composites n' increases with the increase of temperature showing that as the temperature increases the melt becomes more Newtonian in nature. Composites with PPG based bonding agent show more or less the same values of n' as that of the composite without bonding agent where as composites with GL and PPG - GL mixture based bonding agents show lower values of n'. This indicate that the bonding agent formed from GL and PPG -GL with MDI increases the pseudoplasticity of the composite.

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CHAPTER V

MECHANICAL PROPERTIES*

Mechanical properties are the major criteria in selecting a composite for a particular application. The properties of short fiber composite mainly depend on the type and concentration of the fiber, aspect ratio of the fiber and the degree of adhesion between the fiber and the matrix. Many investigations on the properties of the composites based on both natural as well as synthetic rubbers and fibers have been reported.[1-4] This chapter includes the evaluation of the mechanical properties of composite with respect to fiber concentration, orientation and fiber - matrix interaction.

5.1. PREPARATION OF COMPOUNDS AND MOLDING

Formulation of the test mixes are given in the Table V.1. The details of molding, sample preparation and testing has been discussed in Chapter 2.

5.2. TESTING OF VULCANISATES

Mechanical properties of the vulcanisates were tested according to their respective ASTM standards. Properties such as tensile and tear strength and abrasion resistance were determined both in the longitudinal (L) and transverse (T) orientation of fibers. For determining the aging resistance of the composites, tensile and tear samples were aged for 48 hrs at 70°C. The tensile and tear properties of these samples were determined 24 hours after the completion of aging.

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*Results of this section ~~has~~ have been accepted for publication in Polym. Plast. Tech. Engg.

Ingredients	Mix No.					
	A	B	C	D	E	A1
PET fiber	-	10	20	30	40	-
PPG	-	-	-	-	-	4.44
GL	-	-	-	-	-	-
PG	-	-	-	-	-	-
MDI	-	-	-	-	-	0.56

(Continued..)

Table V.1. Formulation of the mixes

Ingredients	Mix No.					
	A2	A3	C1	C2	C3	C4
PET fiber	-	-	20	20	20	20
PPG	-	2.22	4.44	-	2.22	-
GL	0.99	0.07	-	0.99	0.07	-
PG	-	-	-	-	-	1.10
MDI	4.01	0.56	0.56	4.01	0.56	3.90

Base Recipe: Adiprene 100; Zinc stearrate 0.5; Caytur-4 0.35; MBTS 4; MBT 1 and Sulphur 0.75. All values are expressed as parts per hundred rubber (phr).MBTS = Dibenzothiazyldisulphide, MBT = 2-mercaptobenzothiazole, (PPG) = polypropyleneglycol, (GL) = Glycerol, (PG) = Propyleneglycol and (MDI) = 4,4'- diphenylmethanedi-isocyanate

Table V.1. Formulation of the mixes

5.3. CURE CHARACTERISTICS

Mix No.	Minimum Torque, N. m	Maximum Torque, N. m	Scorch Time minutes	Optimum Cure Time, minutes	Cure rate, N.m/ min.
A	0.022	0.218	9.40	23.00	0.019
B	0.046	0.514	13.20	32.40	0.029
C	0.061	0.399	18.00	44.40	0.015
D	0.080	0.383	20.00	54.80	0.010
E	0.084	0.299	22.00	60.80	0.006
A1	0.024	0.347	11.20	24.40	0.030
A2	0.045	0.433	12.00	29.80	0.025
A3	0.029	0.403	10.60	23.40	0.035
C1	0.061	0.426	18.00	46.80	0.014
C2	0.077	0.574	15.20	57.60	0.014
C3	0.065	0.412	18.00	45.60	0.014
C4	0.122	0.488	20.80	55.20	0.012

Table V.2. Cure characteristics

Cure characteristics of all the mixes are given in Table V.2. In the case of mixes A - E minimum torque increases linearly with fiber loading upto 30 phr and then remains more or less constant. The leveling out of maximum torque takes place at 20 phr of fiber loading itself. Scorch and optimum cure time increase with fiber loading. This may be because of the lack of sufficient concentration of curatives due to the adsorption of ingredients by the fiber.[5]

Cure rate also decreases with the increase of fiber loading. All the mixes containing MD resin as bonding agent show a higher minimum torque and maximum torque than the corresponding composite without MD resin.

Scorch time and optimum cure time also increase in the presence of bonding agent which indicates that bonding agent in the composite interferes and retards the sulphur curing of the polyurethane - short fiber composite.

5.4. EFFECT OF FIBER CONCENTRATION ON MECHANICAL PROPERTIES

Mechanical properties of the mixes A - E were determined. Figure 5.1. shows the variation of tensile strength with fiber loading. Tensile strength does not show much change at a fiber loading of 10 phr (mix B). This is because at 10 phr of fiber loading the dilution effect of the fibers in the elastomer matrix almost cancels the reinforcing effect

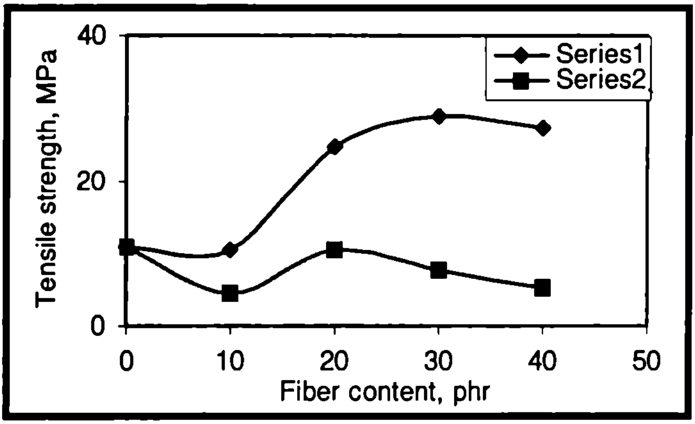


Figure 5.1.Variation of tensile strength with fiber loading (Series 1: longitudinal fiber orientation, 2: transverse fiber orientation)

brought by the fibers. With further increase in the fiber concentration, in longitudinal direction, the tensile strength increases. At higher concentration the fibers can more effectively hinder the fracture propagation and the stress is more evenly distributed and hence tensile strength increases. However beyond 30 phr loading the effect becomes less pronounced. Tensile strength in the transverse direction is less than that of the longitudinal direction at all fiber loading.

Variation of elongation at break with fiber loading is shown in Figure 5.2. Elongation at break in the L direction shows a drastic decrease at 10 phr of fiber loading and then remains more or less constant. A similar trend is observed in the T direction also.

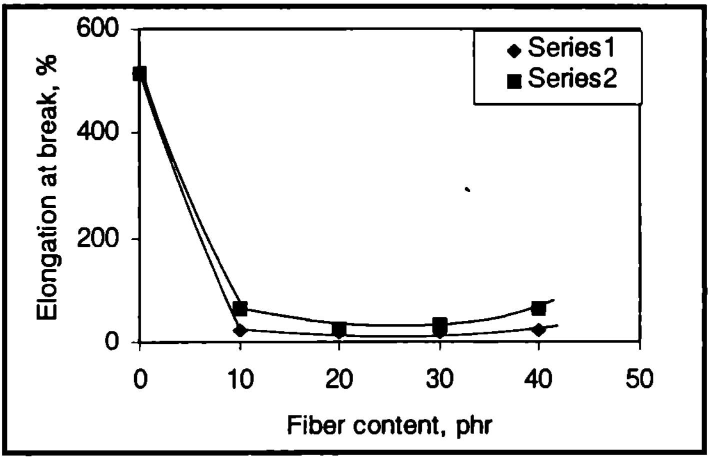


Figure 5.2 Variation of elongation at break with fiber loading (Series 1: longitudinal fiber orientation, 2: transverse fiber orientation)

Figure 5.3. shows the variation of modulus at 5 % elongation with fiber loading. Modulus in the L direction is higher than in the T orientation at all fiber loading. The

modulus is found to have a maximum at 20 phr fiber content. This is in agreement with the observed tensile strength.

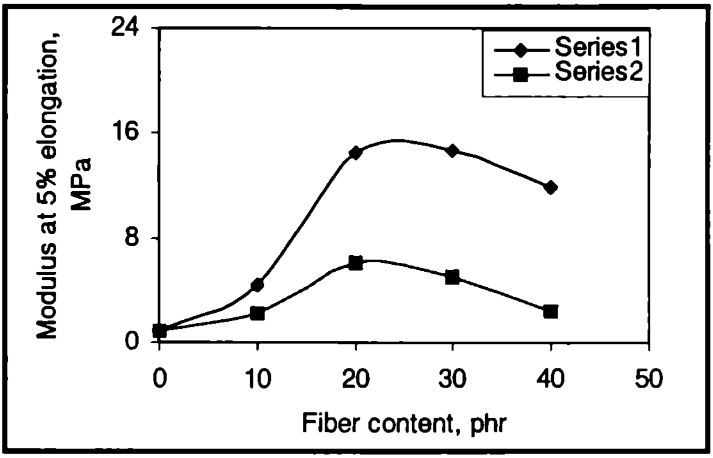


Figure 5.3. Variation of modulus at 5% elongation with fiber loading (Series 1: longitudinal fiber orientation, 2: transverse fiber orientation)

The variation of tear strength of the composites with fiber loading is shown in Figure 5.4. Tear strength in the L direction shows a linear increase with the increase of fiber concentration. This is because as the fiber concentration increases it can more effectively hinder the propagating tear path.[5-7] In the transverse direction however, the effect is less pronounced. The tear strength levels out at higher fiber loadings. The lower value of tear strength in T direction is due to the inability of fibers aligned parallel to the crack propagation to block the advancing crack front. When the fibers are oriented perpendicular to the crack propagation advancing crack path can be deflected or arrested by the fibers there by increasing the tear resistance. Some energy can be dissipated by fiber breakage and fiber pull out.[5] This also is not possible in the T orientation of fibers.

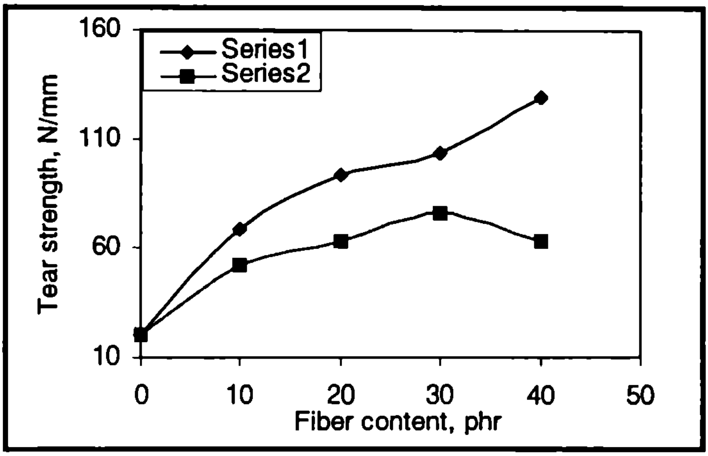


Figure 5.4. Variation of tear resistance with fiber loading (Series 1: longitudinal fiber orientation, 2: transverse fiber orientation)

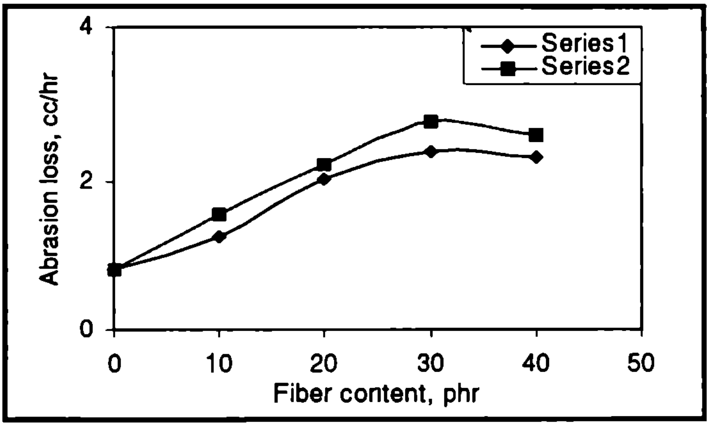


Figure 5.5. Variation of abrasion loss with fiber loading (Series 1: longitudinal fiber orientation, 2: transverse fiber orientation)

Abrasion loss of the composite increases with increase in the fiber loading (Figure 5.5.), but the rate of increase becomes less pronounced at higher fiber loadings. As the fiber loading increases resistance to wear increases due to the good mechanical properties of the fibers. The variation of abrasion loss in both the directions show a similar trend. But at all fiber loadings abrasion loss is higher for T direction than for L direction. Similar behaviour has been reported earlier.[3,5,8]

Hardness increases with the increase of fiber loading (Figure 5.6.). This is in agreement with the earlier report.[8,9] Resilience and compression set values decrease sharply at 10 phr of fiber content (Figure 5.6.) and then remains more or less constant.[5,8]

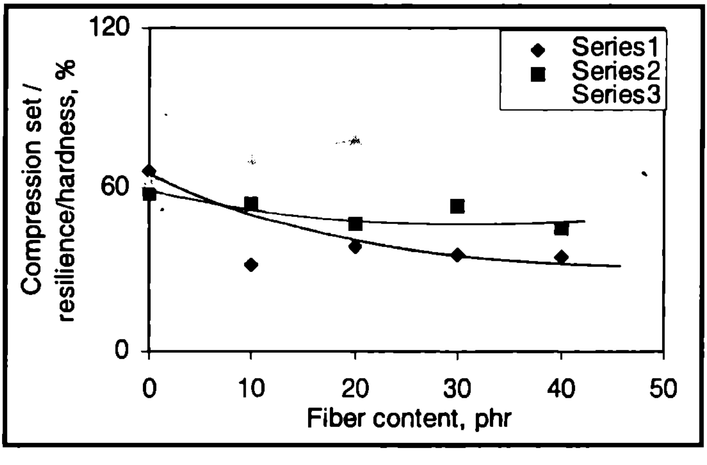


Figure 5.7. Variation of hardness, compression set and resilience with fiber loading (Series 1: Compression set, 2: Resilience, 3: Hardness)

Heat build up was so high that the test could not be completed even for the 10 phr fiber filled samples (Table V.3.). The samples developed cracks a few minutes after the start of the test and blew out immediately due to the large amount of heat generated inside the system. The same behaviour is reported in the case of short polyester fiber - natural rubber composites.[6,10] The blow time decreases with the increase of fiber loading. In all the cases the blow out time is less for samples having transverse orientation of fibers than the longitudinal orientation.

Property	Fiber orientation	Mix No.				
		A	B	C	D	E
Heat buildup	L	24	-	-	-	-
	T	24	-	-	-	-
$t_{m,\ min.}$	L	-	17.7	11.3	5.6	3.7
	T	-	13.1	8.9	3.7	3.2
ΔT_b,°C	L	-	52	74	58	68
	T	-	52	74	56	61

L – longitudinal, T – Transverse, t_m = the time for blow out of the sample, ΔT_b = Temperature at the blow out time

Table V.3.Heat build up values of mixes A - D.

5.5. EFFECT OF BONDING AGENTS

Effect of bonding agents based on different diols and triol was ~~were~~ also determined. The mechanical properties of the gum vulcanisate containing different bonding agents are given in the Table V.4.

Mix No.	Tensile strength MPa	Tear strength MPa	Abrasion loss cc/hr	Compression set,%	Resilience %
A	10.65	19.78	0.82	66	58
A1	2.97	22.55	0.89	16	61
A2	3.68	24.43	0.96	25	62
A3	3.92	22.24	0.55	19	65

Table V.4. Mechanical properties of mixes A - A3

It can be seen that tensile strength and tear strength of the gum vulcanisates containing different bonding agents (mixes A1 - A3) are less compared to that of the mix A. Abrasion loss remains more or less the same as that of mix A. Compression set decreases considerably in the presence of bonding agents. Resilience shows a marginal increase with the incorporation of bonding agents.

Mechanical properties of the composites (mixes A - D) with and without bonding agents are shown in the Table V.5. In the presence of bonding agents tensile strength, modulus and abrasion resistance improved marginally and the improvement is more prominent at 20 phr of fiber loading. This composite was selected for further studying the effect of various bonding agents on the mechanical properties.

The mechanical properties of composite with and without bonding agents are given in the Table V. 6. It is found that tensile strength is higher for composites with bonding agent than the composite without bonding agent. This indicates an efficient load transfer to the reinforcing member arising from a better fiber matrix interfacial bond. However mix C3 shows a tensile strength which is also less than that of mix C.

Mix No.	L/ T	Tensile strength, MPa	Modulus, MPa	E.B, %	Tear strength N/mm	Abrasion loss, cc/hr
A	L	10.7	0.9	616	19.8	0.82
	T	10.7	0.9	616	19.8	0.82
A1	L	3.0	0.2	220	22.6	0.89
	T	3.0	0.2	220	22.6	0.89
B	L	10.3	4.5	24	68.6	1.25
	T	4.5	2.3	68	51.8	1.55
B1	L	12.2	7.4	20	53.2	1.37
	T	4.9	2.7	70	43.5	1.68
C	L	24.8	14.5	21	93.2	2.01
	T	10.4	6.1	26	62.6	2.21
C1	L	28.8	15.1	19	107.0	1.32
	T	6.3	4.5	33	61.0	1.71
D	L	28.9	14.6	18	104.0	2.39
	T	7.6	5.0	36	75.5	2.77
D1	L	30.7	12.7	24	125.0	1.13
	T	5.1	5.0	34	57.1	1.89

(continued)

L- longitudinal orientation of fibers, T – transverse orientation of fibers, E.B – elongation at break

Table V.5. Mechanical properties of mixes A - D with and without bonding agents

Mix No.	L/ T	Resilience %	Compression set, %	Heat buidup		
				ΔT	t_m,min	ΔT_b,°C
A	L	58	66	24	-	-
	T			24	-	-
A1	L	61	16	20	-	-
	T			20	-	-
B	L	54	32	-	17.7	52
	T			-	13.1	52
B1	L	50	16	34	-	-
	T			43	-	-
C	L	46	38	-	11.3	74
	T			-	8.9	74
C1	L	51	44	-	17.4	52
	T			-	6.7	54
D	L	53	36	-	5.6	58
	T			-	3.7	56
D1	L	45	35	-	11.1	51
	T			-	5.4	41

t_m = Time for blow out of the sample, ΔT= Heat build up, ΔT_b = Temperature at the blow out time

Table V.5. Mechanical properties of mixes A - D with and without bonding agents

The highest improvement in tensile strength is exhibited by the mix C2 (≈19 %). It may be attributed to the more rigid, three dimensional net work of the bonding agent formed from glycerol and MDI, which produces a better bonding between the fiber and matrix. Mixes C1 and C4 show more or less same level of improvement in tensile strength (≈16%). The tensile strength of mixes C1 - C4 in the T direction is less than that of the mix C.

Elongation at break in L direction shows a marginal decrease for mixes C1 - C4 which also indicates an improved in the fiber - matrix bonding. Comparison of the

Property	L/T	Mix No.				
		C	C1	C2	C3	C4
Tensile strength, Mpa	L	24.8	28.8	29.6	22.2	28.9
	T	10.4	6.3	7.8	9.5	6.3
Modulus, Mpa	L	14.5	15.1	15.3	12.8	14.1
	T	6.1	4.5	3.6	6.0	3.8
Elongation at break %	L	21	19.0	18.0	16.0	18.0
	T	26	33.0	46.0	29.0	65.0
Tear resistance, N/mm	L	93.2	107.0	106.7	93.8	91.6
	T	62.6	61.0	55.6	63.5	60.7
Abrasion loss cc/hr	L	2.01	1.32	0.75	0.58	1.19
	T	2.21	1.71	1.60	0.97	1.30
Hardness, Shore A	-	62.0	77.0	77.0	83.0	83.0
Resilience %	-	46.0	51.0	48.0	53.0	47.0
Compression set , %	-	38.0	44.0	42.0	44.0	41.0
t_m,min.	L	11.3	17.5	11.6	8.4	16.0
	T	8.9	6.7	6.0	7.3	6.4
ΔT, °C	L	74.0	52.0	51.0	58.0	47.0
	T	74.0	54.0	65.0	53.0	77.0

L= Longitudinal, T= Transverse, t_m = time for blow out of the sample, ΔT_b = temperature at the blow out time

Table V. 6. Mechanical properties of composites with different bonding agents

modulus at 5 % elongation in the L direction shows that there is not much change in the modulus for composites containing bonding agent. A marginal increase is shown by mixes C1 & C2 (≈ 5 %). Modulus in the T direction is less than in the L direction. This is similar to the results described earlier.

Tear strength of the composites with bonding agents is higher than that of the composite without bonding agent. Mixes C1 and C2 show a 14 % improvement in tear strength compared to the mix C. This again indicates a better interfacial bonding in these composites. However, for mixes C3 and C4 the tear strength is not improved. In the transverse direction there is not much change in the tear strength of the composites with and without bonding agents.

Abrasion loss of the mixes is given in the Table V.5. Abrasion loss is considerably lower in the case of mixes containing bonding agents,C1 - C3, than that of mix C. The mix C3 shows the maximum improvement (≈ 70.%) and the minimum is shown by the mix C1 (≈ 34 %). In all the cases abrasion loss is higher in the transverse orientation than the longitudinal orientation. This is in agreement with the results reported earlier.

Other properties such as resilience and compression set show a marginal increase in the presence of bonding agent and the highest values are exhibited by the composite containing PPG as one of the component in the bonding agent. The increased elasticity of the composite may be attributed to the higher molecular weight of the PPG, a polymeric diol. Hardness is considerably improved in the presence of bonding agents. For mixes C1 and C2 there is a 24 % increase where as mixes C3 and C4 show 34 % increase in hardness.

The heat buildup test could not be completed because of the premature blow out of the samples. The time for blow out of the sample is slightly higher in the case of composites containing bonding agents. While mix C containing bonding agents blow out in 11.3 minutes, where as mix C1, containing PPG based bonding agent blow out at 17.5 minutes - an improvement of 55 %. Mix C4 also shows a blow out time of 16 minutes (an improvement of 52 %).

While mix C shows a blow out temperature of 74 °C at a blow out time of 11.3 minutes where as the mixes containing bonding agents (C1 - C4) show considerably lower blow out temperatures, despite of the higher blow out time.

In the transverse orientation of fibers the samples blow out at shorter periods generating more heat. The same results have been reported earlier.[10]

These results show that the urethane based bonding agents improve the fiber matrix interface bonding and is very effective in reducing the heat generation of the short polyester fiber polyurethane composite under dynamic conditions. The best results are obtained with the composite containing PPG / MDI based bonding agents.

5.6. AGING RESISTANCE OF THE COMPOSITES C,C1 - C4

Aging resistance of the mixes C & C1 - C4 were studied and the percentage retention of properties in L and T directions is shown in the Figures 5.7. and 5.8. respectively. Retention of tensile strength of composites containing bonding agents is better than the composite without bonding agent. This indicates that upon aging the fiber matrix interfacial bond is not deteriorated. However the mix containing bonding agent based on GL (mix C2) shows lower retention values. The maximum retention is exhibited by the mixes C1 and C3 which contain PPG and PPG - GL mixture based bonding agents. The percentage retention of elongation at break is comparatively higher in the case of composites containing bonding agents and is not much altered with the nature of the resin. The percentage retention of modulus and tear strength is highest for the mix C3 which is similar to the observed retention of tensile strength. The above results show that resins based on 1:1 combination of PPG and PPG - GL with MDI are better interfacial bonding agent for short fiber reinforced polyurethane composite than the one based on GL and PG with MDI.

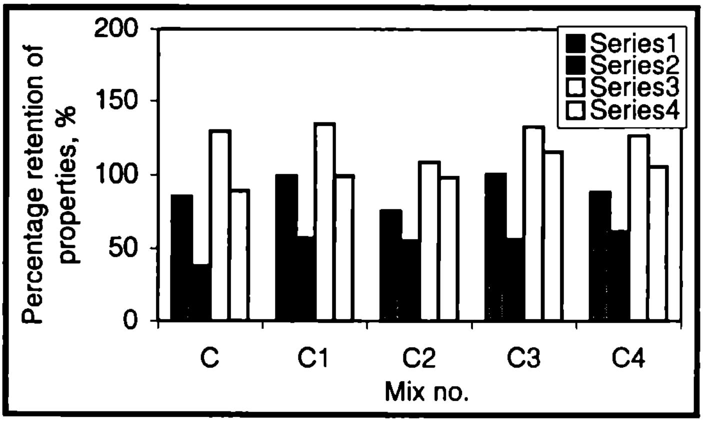


Figure 5.7. Percentage retention of mechanical properties in the longitudinal direction (Series 1: Tensile strength, 2: Elongation at break, 3: Modulus at 5% elongation, 4: Tear strength)

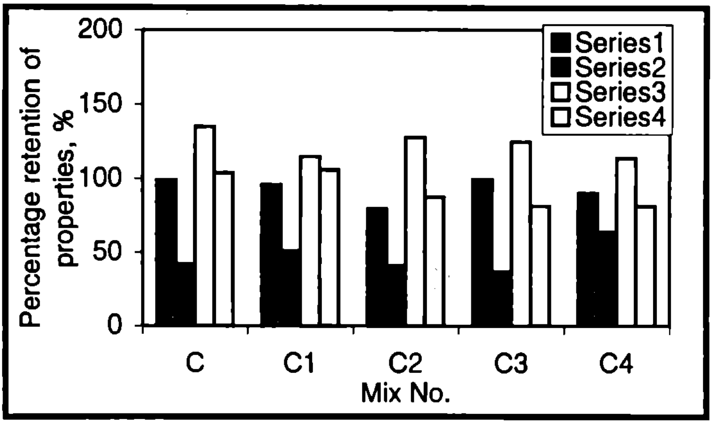
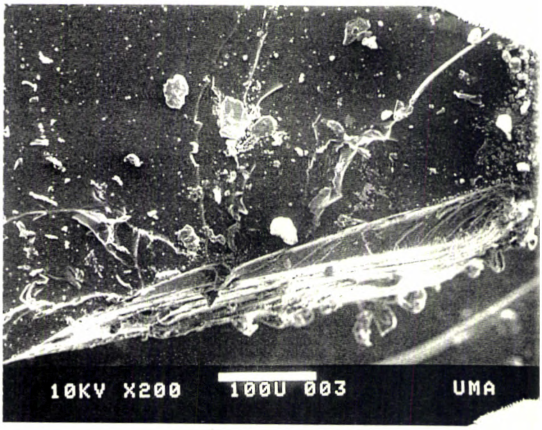


Figure 5.8. Percentage retention of mechanical properties in the transverse direction (Series 1: Tensile strength, 2: Elongation at break, 3: Modulus at 5% elongation, 4: Tear strength)

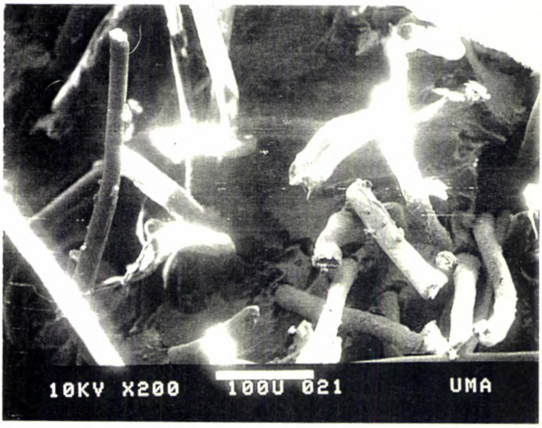
5.7. SEM STUDY

The SEM photomicrograph of the tensile fracture surface of the gum vulcanizate is shown in Figure. 5.9. The matrix mutilated due to the propagation of the fracture front and the resultant fracture path is clearly seen in the figure. The presence of a single major fracture path surrounded by a relatively smooth surface is in agreement with the very low tensile strength exhibited by the unfilled compound.

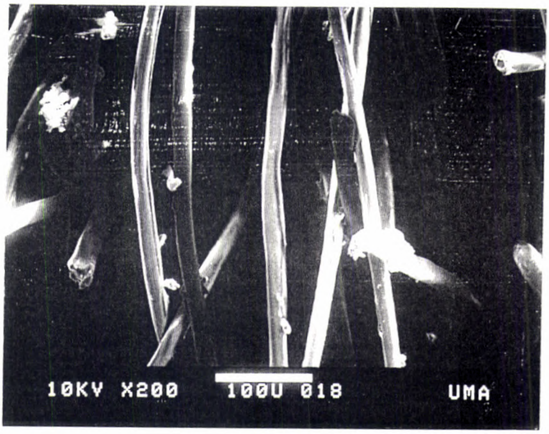
The SEM photomicrograph of the tensile fracture surface of the 20 phr fiber filled compound in L & T direction are shown in Figures 5.10 a & b. The fiber-ends protruding from the matrix and a few holes seen in the Figure 5.10.a suggest the fiber pull-out by breaking the fiber -matrix bond during the tensile failure. The presence of mutilated



5.9. SEM photomicrographs of tensile fracture surface of mix A

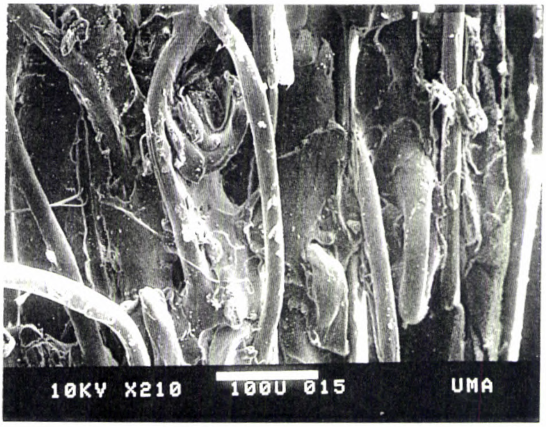


5.10.a. SEM photomicrographs of tensile fracture surface of mix C (Fibers in the longitudinal direction)



5.10.b. SEM photomicrographs of tensile fracture surface of mix C (Fibers in the transverse orientation)

5.11.a. SEM photomicrographs of tensile fracture surface of mix C4 (Fibers in the longitudinal direction)

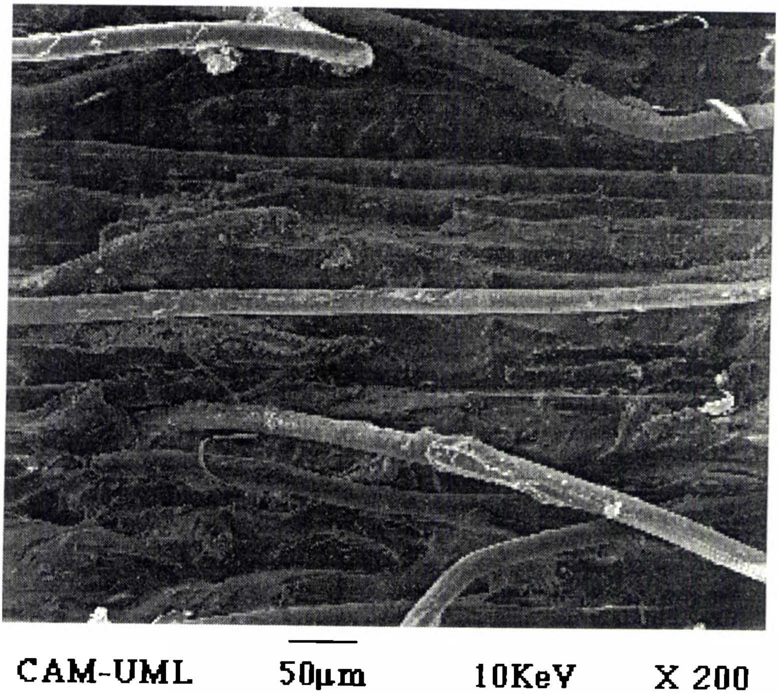


5.11.b. SEM photomicrographs of tensile fracture surface of mix C4 (Fibers in the transverse direction)

5.12.a. SEM photomicrographs of tensile fracture surface of mix C1 (Fibers in the longitudinal direction)

5.12.b. SEM photomicrographs of tensile fracture surface of mix C1 (Fibers in the transverse direction)

5.13.a. SEM photomicrographs of tensile fracture surface of mix C2 (Fibers in the longitudinal direction)



5.13.b. SEM photomicrographs of tensile fracture surface of mix C2 (Fibers in the transverse direction) fiber -ends indicates that some amount of fiber breakage also has taken place either during processing or during tensile failure. The tensile failure surface of the composite with fibers oriented in the transverse direction is shown in Figure 5.10.b. The preferential orientation of the fibers in the horizontal plane is clearly visible in the figure. The oriented fibers with smooth surface indicate a very easy debonding at the fiber -matrix interface. This is in agreement with the observed tensile strength of mix C in both the directions.

Figure. 5.11.a shows the SEM photomicrograph of the tensile fracture surface of the 20 phr fiber loaded sample in the L direction containing the PG based bonding agent. (mix C4). There are relatively fewer number of fiber-ends and the fiber pull-out holes seen in this figure which suggests a stronger fiber-matrix interfacial bond. This also supports the observed higher tensile strength of the mix C4 compared to mix C.

The tensile fracture surface of mix C4 with the fibers in the transverse direction is shown in Figure 5.11.b. The bare surface of the fibers oriented horizontally and the rubber matrix are clearly seen in the figure. Unlike in the case of the composite containing no bonding agent (Figure 5.10.b) here the fiber surface is not smooth. There seems to be some amount of the matrix material remaining bonded to the fiber surface owing to the presence of a bonding agent in the system.

Tensile fracture surface of the composite containing PPG based and GL based bonding agents (mixes C1 and C2) with the fibers oriented in the longitudinal direction is shown in Figures 5.12 , 5.13. a and b. They show patterns similar to that of Figure. 5.11.a, indicating similar strength properties for the composites mixes C1,C2 & C4 (Table V.5).

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CHAPTER VI
STRESS RELAXATION*

Because of the increasing use of short fiber reinforced composites in both dynamic and static applications under stress, for instance, hoses, V- belts, tubes and cables, studies on stress relaxation becomes important. Flink and Stenberg analysed the stress relaxation of short cellulose fiber - natural rubber composite.[1] The effect of strain level, pre-straining and bonding agent on the stress relaxation behaviour of short jute fiber - nitrile rubber has been studied by Bhagwan et al.[2] Kutty et al studied the stress relaxation behaviour of short kevlar fiber reinforced thermoplastic polyurethane composite.[3] Recently Ibarra and coworkers explored the relaxation pattern of the short fiber reinforced composite with respect to the effect of fiber orientation and adhesion between the fiber and the matrix.[4] In this chapter stress relaxation behaviour of short polyester fiber - polyurethane elastomer composite is included. The effects of strain rate, strain level, fiber loading, fiber orientation and bonding agent on the stress relaxation of the composites are discussed.

Formulation of the mixes is given in the Table VI.1. Mixes C1, C2 and C3 contain different bonding agents, MD resins, based on polypropylene glycol(PPG), glycerol(GL) and a mixture of PPG and GL with 4,4'-diphenylmethanedi-isocyanate (MDI). Sample preparation and the determination of the stress relaxation behaviour of the samples were given in Chapter 2. Stress relaxation was carried out at different strain levels (10 - 300 %) at different strain rates (0.021 - 0.104 s^{-1}).

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*The results of this chapter has been published in J. Elast. Plast. 30 (1998) 1 - 15.

Ingredients	Mix No.						
	A	B	C	D	C1	C2	C3
PET fiber	-	10	20	30	20	20	20
PPG	-	-	-	-	4.44	-	2.22
GL	-	-	-	-	-	0.99	0.07
MDI	-	-	-	-	0.56	4.01	0.56

Base recipe: Adiprene 100 phr, Zincstearate 0.5 phr, Caytur - 4 0.35 phr, MBTS 4 phr, MBT 1 phr and Sulphur 0.75 phr.

Table VI.1. Formulation of the mixes

6.1. STRESS RELAXATION OF THE GUM COMPOUND

Figure 6.1 shows a typical stress relaxation plot of the gum vulcanisate at 20% strain level strained at two different strain rates (0.042 s^{-1} and 0.104 s^{-1}). The figure consists of different straight lines with different ` slopes indicating a multistage relaxation mechanism. Slopes of these straight lines give the rate of relaxation of the compound. The point of intersection of these different straight lines indicates the cross over time of each relaxation process. The rate of relaxation and the cross over time of different stages of relaxation mechanism depend on the rate of straining and strain levels. It is clear from the figure that the relaxation takes place initially at a faster rate followed by a period of relatively low relaxation rate. However, beyond a time period of 240 seconds, the relaxation takes place again at a higher rate.

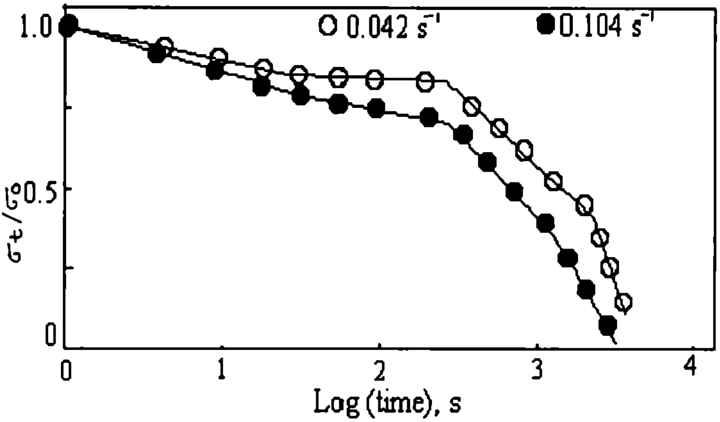

Figure 6.1. Stress relaxation plots of the gum vulcanisate at 20% strain level

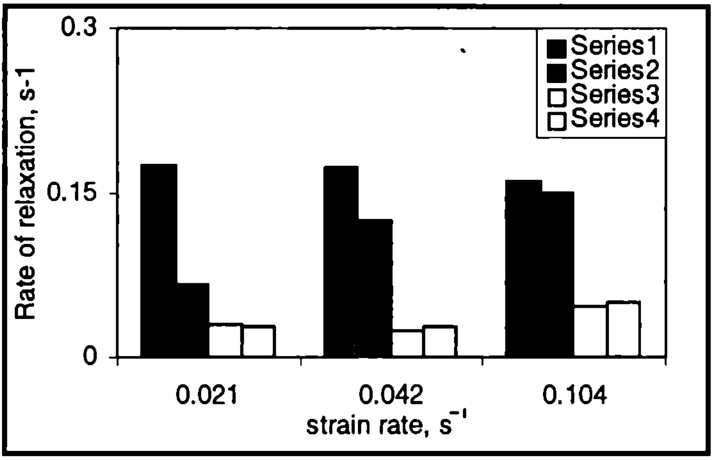

Figure 6.2.Variation of stage - I relaxation rate with strain rates at different strain levels (Series 1: 10 %, 2: 20 %, 3: 100 %, 4: 300 %)

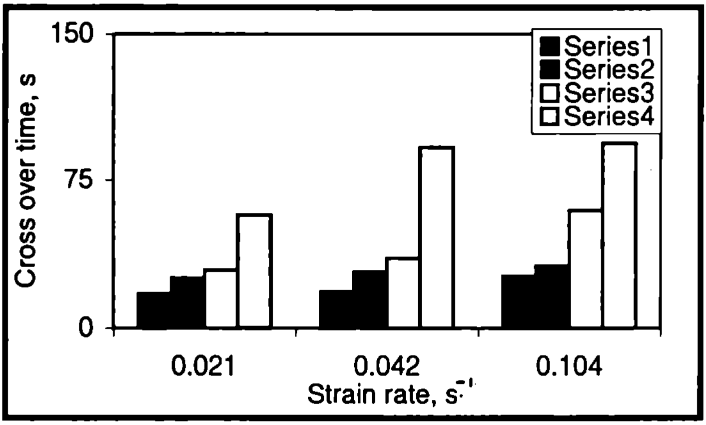

Figure 6.3.Variation of first cross over time with strain rates at different strain levels (Series 1: 10 %, 2: 20 %, 3: 100 %, 4: 300 %)

This behavior is reflected in the relaxation studies at different strain levels (10 - 300%) and strain rates (0.021 - 0.104 s^{-1}). The different rates of stage - I relaxation and the cross over times from these plots are given in Figures 6.2 and 6.3 respectively.

From the Figure 6.2 it is clear that at all strain rates, the stage -I relaxation rate decreases with strain level to more or less a constant value. Similar results have been reported in the case of a short Kevlar fiber reinforced composite.[3] At lower strain levels the rate of relaxation is more or less independent of the strain rate but for higher strain levels the rate is increasing with the strain rate. Figure 6.3 shows that the cross over time increases with increase of both strain level and strain rate.

Strain (%)	Strain rate s^{-1}	III rd slope, s^{-1}	Cross over time, s	
			II	III
10	0.021	0.456	368	2768
	0.042	0.492	258	1286
	0.104	0.153	190	1977
20	0.021	0.414	287	2950
	0.042	0.631	955	2689
	0.104	0.464	283	1562
100	0.021	0.051	219	1807
	0.042	0.039	453	2507
	0.104	0.062	244	2090
300	0.021	0.010	645	2494
	0.042	0.014	1000	2521
	0.104	0.052	502	-

Table VI.2. Slopes and cross over times of the gum vulcanisate at different strain rates and strain levels

6.2. EFFECT OF FIBER LOADING

The stress relaxation pattern of the fiber filled composite at a strain level of 10 % and at a strain rate of 0.042 s^{-1} is given in the Figure 6.4. The incorporation of fiber in the matrix alters the stress relaxation pattern of the gum vulcanisate. It can be seen from the figure that though the composite exhibits a similar pattern of relaxation there is no such a state where the rate of relaxation is very low.

The stage - I relaxation rate of the gum vulcanisate and the different composites at a strain level of 10 % and at different strain rates are shown in the Figure 6.5. All the composites show a lower rate of relaxation than that of the gum vulcanisate and at all strain rates the rate of relaxation decreases with the increase of fiber loading. This indicates

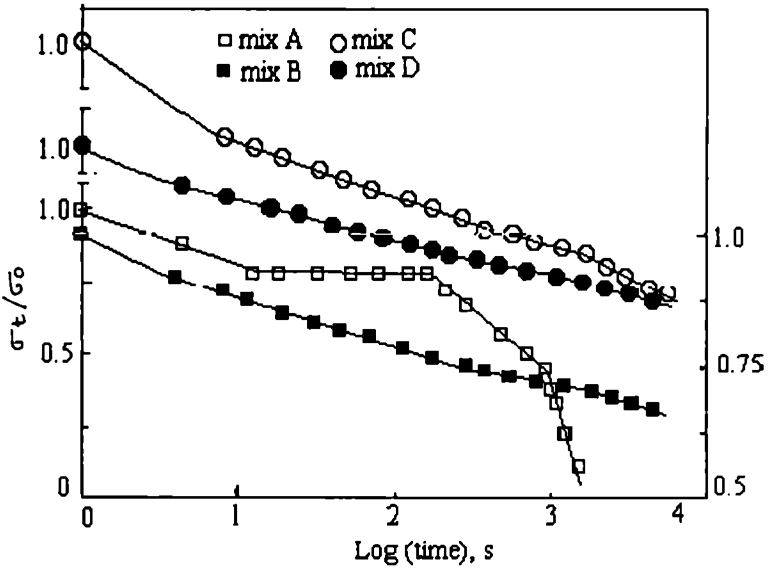

Figure 6.4. Stress relaxation plot of mixes A-D at 10% strain level and at a strain rate of 0.042 s^{-1}

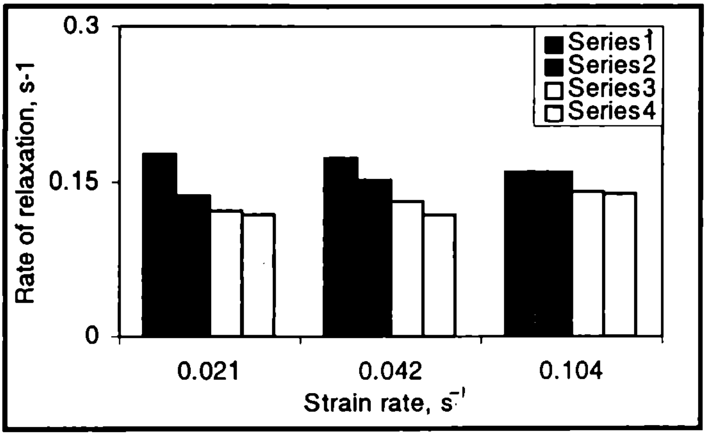

Figure 6.5.Variation of stage - I relaxation rate with strain rate, of mix A (strain = 10 %) (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

that the initial stage of relaxation process is greatly influenced by the incorporation of fibers. This is because the fiber matrix bond, being weaker in the absence of an added bonding agent, gets relaxed during the process of straining the sample to the test strain level during which time no stress is recorded. The stress is recorded only after the sample is brought to the desired strain level. Hence, the recorded portion reflects a lower relaxation rate. This method was adopted so as to carry out all the tests under identical conditions. Also, the composites show an increase in the rate of relaxation with strain rate as in the case of gum vulcanisate.

The cross over time of the first relaxation stage of the gum vulcanisate and different composites at a strain level of 10% is shown in the Figure 6.6. It is clear from the figure

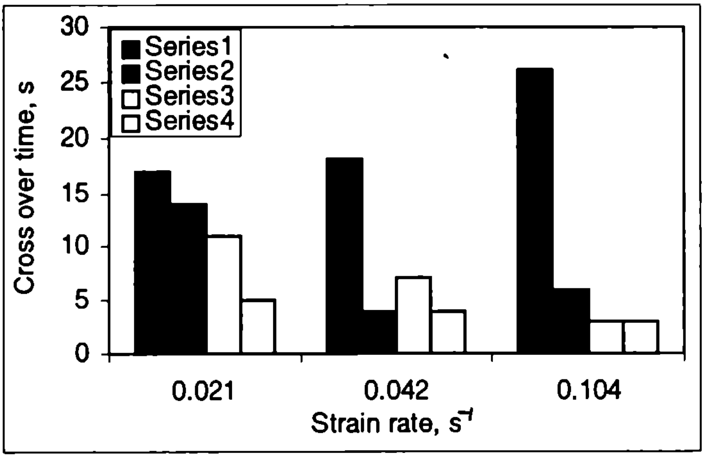

Figure 6.6.Variation of the first cross over time with shear rate of mix A (strain 10%)(Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

Strain rate, s^{-1}	Fiber loading (phr)	Slopes, s^{-1}		Cross over time, s	
		II	III	II	III
0.021	0	0.000	0.456	368	2768
	10	0.106	0.064	149	3727
	20	0.072	0.046	499	3104
	30	0.093	0.055	223	2493
0.042	0	0.000	0.492	258	1286
	10	0.087	0.048	401	2886
	20	0.070	0.055	499	2586
	30	0.074	0.047	303	1046
0.104	0	0.480	0.153	190	1977
	10	0.087	0.062	155	2317
	20	0.096	0.065	208	2493
	30	0.097	0.071	124	896

Table VI.3. Slopes and crossover times of mixes A - D at different strain rates (strain 10 %)

that the cross over time of the composites is less than that of the gum vulcanisate and the difference increases with the increase of shear rate. For the gum vulcanisate the cross over time increases with shear rate while it decreases in the case of composites.

The rates of relaxation of the other stages and the corresponding cross over times are given in Table VI. 3. The slope II is marginally higher for the fiber filled samples at lower strain rates. However at a strain rate of 0.104 s^{-1} the fiber filled samples exhibit a lower rate of second stage relaxation. The 3rd stage relaxation rates of the composite are significantly lower than that of the gum vulcanisate at all strain rates.

The second cross over times do not indicate any direct dependence on fiber loading and strain rate. The third cross over time decreases with increasing strain rate. With fiber loading, variation of 3 rd cross over time shows a peak at 10 - 20 phr.

6.3. EFFECT OF FIBER ORIENTATION

Figure 6.7 gives a typical stress relaxation plot of Mix C, with fibers oriented along and across the direction of strain. It shows that the relaxation mechanism in the transverse direction exhibits more stages than that of the relaxation in the longitudinal direction. Rates of relaxation of stage - I of the Mixes B, C and D in L and T directions, calculated from different plots, are shown in the Figure 6.8. The rate of relaxation is higher for the samples with longitudinally oriented fibers than that of the samples with transverse orientated fibers. At higher fiber loading (30 phr), however, the transverse fiber oriented samples show higher rate of relaxation.

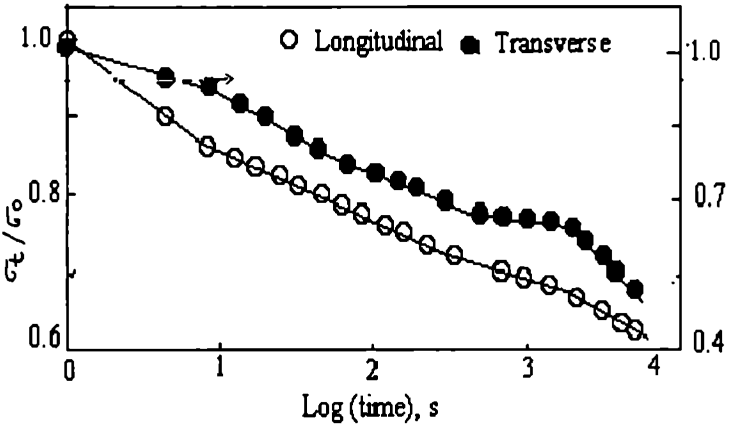

Figure 6.7. Stress relaxation plot of composite with different fiber orientation

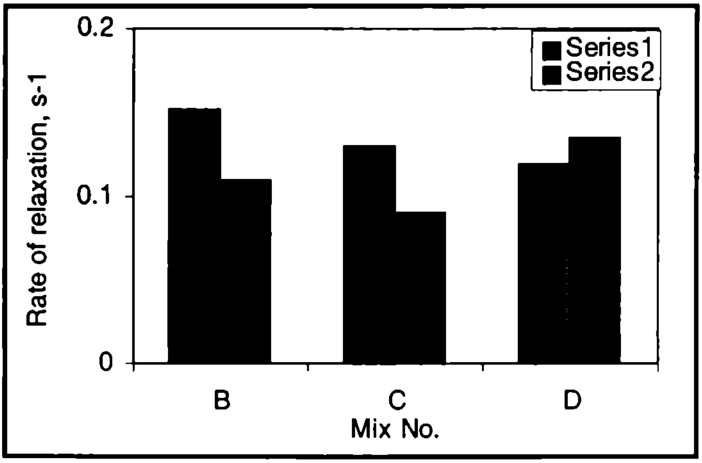

Figure 6.8.Rate of stage - I relaxation of mixes B - D with fibers in L and T orientation (Series 1: Longitudinal, 2: Transverse)

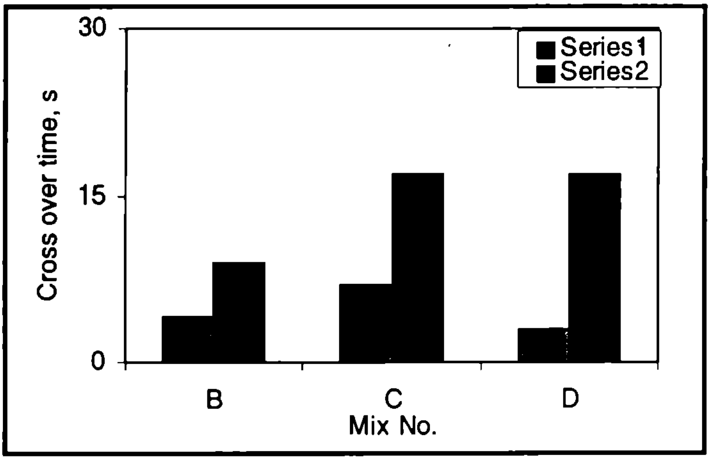

Figure 6.9. The first cross over time of mixes B - D with fibers in L and T orientation (Series 1: Longitudinal, 2: Transverse)

The third slope is higher in the T direction at all fiber loadings. The fourth slope is higher for L orientation of fibers except at 30 phr. For mixes B and C cross over time for the longitudinally oriented sample is higher than that of the transverse oriented samples, while the mix D shows a higher value for the transverse orientation.

At higher fiber loadings, in the transverse direction, the contribution of the matrix to the composite stiffness becomes very limited, and the relaxation mainly occur at the fiber - matrix interface which is reflected more in the transverse orientation of fibers (Table VI.4).. First cross over time of the mixes in the longitudinal (L) and transverse (T) directions (Figure 6. 9) shows that relaxation in the T direction exhausts only after a longer period than in the L direction.

Table VI.5. shows the rate of relaxation of the subsequent stages and the corresponding cross over times at a strain level of 10 % and at a strain rate of 0.042 s^{-1}. The rate of second stage of relaxation is only marginally affected by fiber loading. Except at a fiber loading of 10 phr, the rate of second stage relaxation is higher for T oriented samples.

Mix No.	Strain rate, s^{-1}	Fiber orientation	I st slope, s^{-1}	I st cross over time, s
B	0.021	L	0.138	15
		T	0.073	26
	0.042	L	0.144	4
		T	0.110	8
	0.104	L	0.160	6
		T	0.108	8
C	0.021	L	0.123	8
		T	0.081	10
	0.042	L	0.143	8
		T	0.099	17
	0.104	L	0.141	3
		T	0.134	4
D	0.021	L	0.120	5
		T	0.157	5
	0.042	L	0.121	3
		T	0.138	17
	0.104	L	0.139	7
		T	0.178	4

L - Longitudinal, T - transverse

Table VI.4. Slopes (I) and first over times of the mixes B, C and D at different strain rates in L and T fiber orientations (strain 10 %)

Mix No.	Fiber orient-ation	Slopes, s^{-1}			Cross over time, s	
		II	III	IV	II	III
B	L	0.087	0.048	0.085	401	2886
	T	0.069	0.152	0.030	75	518
C	L	0.070	0.055	0.108	499	2586
	T	0.090	0.174	0.027	54	622
D	L	0.074	0.047	0.077	303	1046
	T	0.085	0.046	0.138	1000	2725

L - Longitudinal, T - Transverse

Table VI.5. Slopes and cross over times of mixes B - D at a strain rate of 0.042 s^{-1} and at a strain level of 10 % in L and T fiber orientations

6.4. EFFECT OF THE BONDING AGENTS

Figure 6.10 shows the stress relaxation curves of the Mixes C, C1, C2 and C3 at a strain level of 10% and at a strain rate of 0.021 s^{-1}. The curves of the composites with and without bonding agents show a similar behaviour showing that the presence of bonding agents does not alter the relaxation pattern. However the rate of relaxation is found to be higher for the composite containing bonding agents (Figure 6.11).

This is because, compared to the composites containing no bonding agents, here the fiber matrix bond is stronger and does not get relaxed during the straining process; rather the relaxation takes place at a later stage which is reflected as a higher rate in the plot. This is also supported by the fact that a higher relaxation rate is observed when the strain

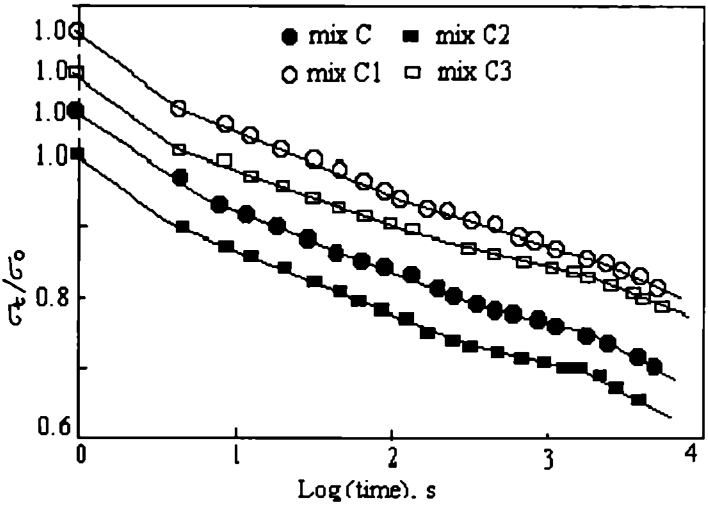

Figure 6.10. Stress relaxation curves of mixes C - C3 at 10% strain level and at a strain rate of 0.021 s^{-1}

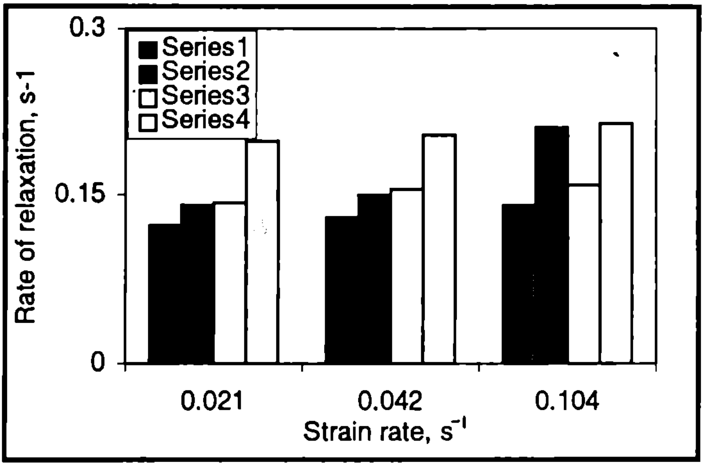

Figure 6.11. The stage - I relaxation rate of the mixes C - C3 (Series 1: mix C, 2: mix C1, 3: mix C2, 4: mix C3)

rate is high (Figures 6.2 & 6.5). Rate of relaxation is maximum in the case of composites with a bonding agent based on PPG - GL mixture with MDI, indicating a better interfacial bond in these case. Again, as in the case of composites without bonding agents, mixes C1, C2 and C3 show an increase in the rate with the increase of strain rate.

Strain rate, s^{-1}	**Mix No.**	**Slopes, s^{-1}**			**Cross over time, s**	
		II	**III**	**IV**	**II**	**III**
0.021	C	0.072	0.046	0.092	499	3104
	C1	0.076	0.058	0.089	167	4010
	C2	0.089	0.036	0.110	464	2586
	C3	0.101	0.069	0.110	167	3104
0.042	C	0.070	0.055	0.108	499	2586
	C1	0.076	0.043	0.070	373	3593
	C2	0.085	0.031	0.011	268	2994
	C3	0.110	0.071	0.117	346	3104
0.104	C	0.096	0.065	0.010	208	2493
	C1	0.062	0.023	0.069	122	2493
	C2	0.093	0.021	0.012	208	2886
	C3	0.097	0.058	0.087	136	2331

Table VI.6. Slopes and cross over times of mixes C - C3 at different shear rates (strain 10 %)

The second stage of relaxation also shows a similar trend but the rates of final stages (III and IV) of relaxation are found to be different (Table VI.6). In both the cases the rates of relaxation are minimum at intermediate fiber loading.

At lower strain rates the first cross over time is less for composites containing bonding agents and it is higher at higher rate of straining (Figure 6.12). Second and third cross over times do not show any linear dependence on the shear rates, as is the case with composite without bonding agents (Table VI.6).

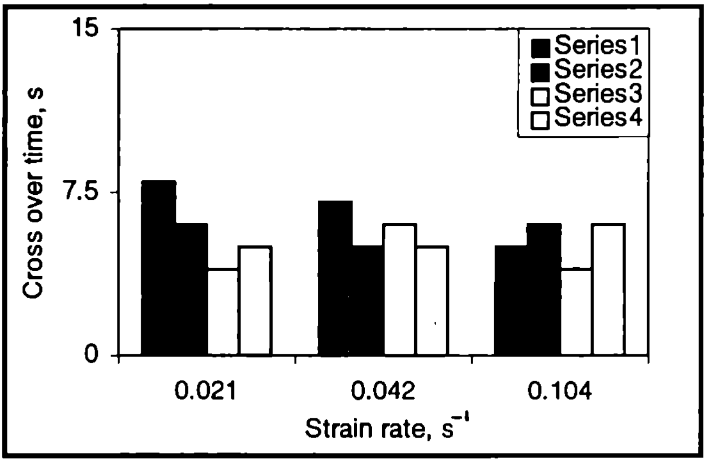

Figure 6.12.The variation of first cross over times with shear rate of the mixes C - C3 (Series 1: mix C, 2: mix C1, 3: mix C2, 4: mix C3)

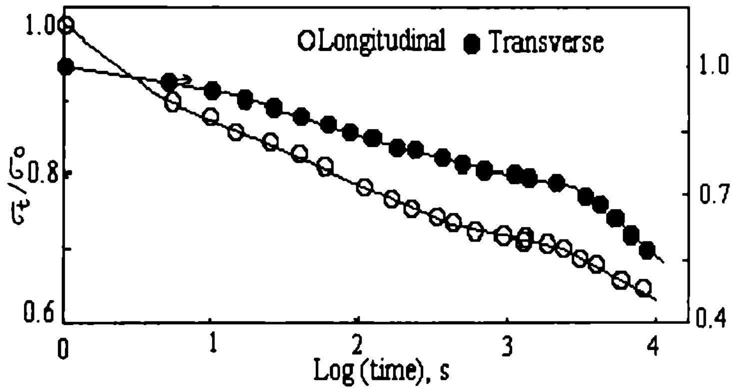

Figure 6.13.Stress relaxation plot of mix C3 in longitudinal and transverse orientation

Mix No.	L/T	Slopes, s^{-1}				Cross over times, s		
		I	II	III	IV	I	II	III
C	L	0.143	0.070	0.055	0.108	8	499	2586
	T	0.099	0.090	0.174	0.027	17	54	622
C1	L	0.151	0.076	0.043	0.070	5	373	3593
	T	0.095	0.050	0.145	0.032	7	203	474
C2	L	0.156	0.085	0.031	0.011	6	268	2994
	T	0.077	0.129	0.212	0.097	12	192	464
C3	L	0.204	0.110	0.071	0.117	5	346	3104
	T	0.115	0.060	0.076	0.214	15	386	649

Table VI.7.Rates of relaxation and cross over times of the mixes C - C3 at a strain rate of 0.042 s^{-1} and at a strain level of 10 %

Relaxation plot of composites containing bonding agents (mixes C1 - C3)with fibers oriented along and across the direction of strain is shown in the Figure 6.13. The relaxation behaviour is similar to that of composites without bonding agents (Figure 6.7). Different rates of relaxation and cross over times of these composites at a strain rate of 0.042 s^{-1} and at 10 % strain level are given in the Table VI.7.

It is observed that in all the mixes the rate of relaxation of the first stage is higher in the case of longitudinally oriented samples and the first cross over point is higher for the T orientation of fibers. This is similar to that of the composites without bonding agents. The other rates of relaxation do not show much dependence on the orientation. The other cross over times are less in the case of composites with transverse orientation of fibers.

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CHAPTER VII
THERMAL DEGRADATION*

A knowledge of the degradation characteristics of the composites at different fiber loading is important in many applications. Thermal degradation of urethanes has been investigated extensively.[1,2] Yang et al. have reported that the thermal degradation of the urethanes based on 4,4' diphenylmethane diisocyanate and 1,4 butane diol produced isocyanates and alcohols.[3] Influence of short fibers on the thermal degradation reaction of the thermoplastic polyurethane were also reported.[4,5] This chapter explores the thermal degradation of the short polyester fiber - polyurethane elastomer composite.

Formulation of the mixes is given in the Table VII.1. Mixes A1 - A3 and mixes C1 - C3 contain 5 phr of bonding agents (MD resins) based on polypropyleneglycol (PPG) and glycerol (GL) with 4,4'-diphenylmethanediisocyanate (MDI). The preparation of the samples and the experimental details were explained in Chapter 2.

Ingredients	Mix No.			
	A	B	C	D
PET Fiber	-	10	20	30
PPG	-	-	-	-
GL	-	-	-	-
MDI	-	-	-	-

(Continued)

Table V11.1. Formulation of the mixes

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*The results of this chapter has been published in the Journal of Polym. Degr. Stab.

Ingredients	Mix No.					
	A1	A2	A3	C1	C2	C3
PET fiber	-	-	-	20	20	20
PPG	4.44	-	2.22	4.44	-	2.22
GL	-	0.99	0.07	-	0.99	0.07
MDI	0.56	4.01	0.56	0.56	4.01	0.56

Base recipe: Adiprene 100 phr, Zincstearate 0.5 phr,Caytur-4 0.35 phr, MBTS 4 phr, MBT 1 phr and Sulphur 0.75 phr

Table V11.1. Formulation of the mixes

The derivative TGA curves of mixes A- D are shown in Figure 7.1. The peak degradation rates and the correspo-

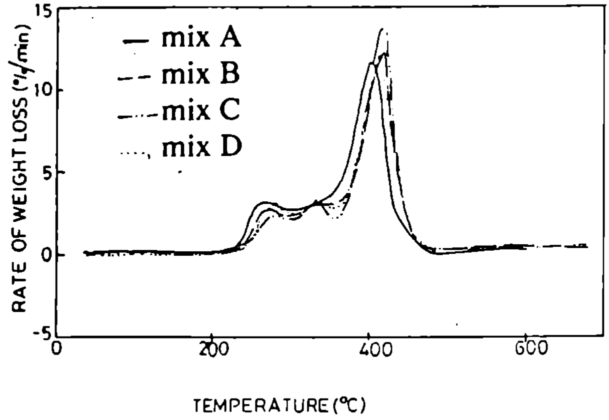

Figure 7.1.TGA traces of mixes A - D

nding temperatures (T_{1max}, T_{2max} and T_{mmax}) are given in the Table VII.2. It is clear from the figure that the degradation of the virgin polyurethane occurs in two steps as indicated by the two maxima at 257°C and 401°C. The onset of degradation is at 230°C. The peak rates of degradation at two maxima are 3.01 and 10.92 %/ min. respectively. The second degradation occurring at around 400°C is due to the decomposition of the primary degradation products. The plots also show that the fiber containing samples (mixes B- D) undergo a three - step degradation. The major degradation occurs at around 400°C, similar to that of the gum vulcanisate. The peak degradation rate at around 330°C is more prominent at higher fiber loadings. This indicates that the incorporation of polyester fiber affect the degradation stages of the matrix.

Mix No.	T_i, °C	T_{1max}, °C	R_{1max}, %/min	T_{2max}, °C	R_{2max}, %/min
A	230.1	257.5	3.01	-	-
B	238.1	266.7	2.65	328.6	2.98
C	239.3	275.0	2.98	333.3	3.00
D	238.3	274.0	2.37	330.1	2.75

(continued)

Table VII.2 Degradation characteristics of mixes A - D

Mix No.	T_{mmax}, °C	R_{mmax}, %/min.	Weights of residue after 600°C, %
A	401.4	10.92	3.88
B	414.3	11.45	5.56
C	411.9	11.98	5.87
D	417.8	13.48	4.88

T_i = Initiation temperature of degradation, R_{1max}, R_{2max} and R_{mmax} are the peak degradation rates and T_{1max}, T_{2max} and T_{mmax} are the corresponding temperatures.

Table VII.2 Degradation characteristics of mixes A - D

The onset of degradation is shifted from 230 to 238°C with the addition of 30phr of fiber, indicating improved thermal stability of the composite. Similar results have been reported earlier.[4] The degradation temperatures T_{1max} and T_{mmax} are increased from 257°C to 274°C and 401°C to 417°C respectively, at a fiber loading of 30phr. The variation of temperatures at which the two degradation rate maxima occur (T_{1max} and T_{mmax}) with fiber loading is shown in Figure 7.2. The initial degradation temperature (T_{1max}) increases linearly up to 20 phr of fiber loading and then levels to a constant value and the major degradation temperature (T_{mmax}) increases with the increase of fiber content.

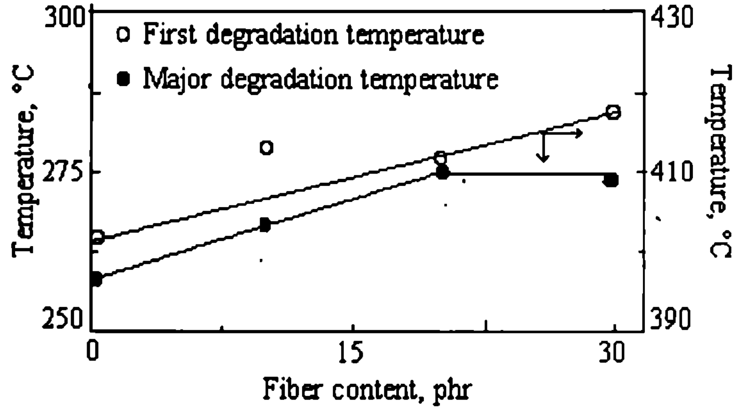

Figure 7.2.Variation of degradation temperature with fiber loading

The increase of the two temperature maxima indicate a lower rate of diffusion of the degraded products out of the matrix as indicated by the lower peak degradation rates exhibited at these temperatures (Table VII.2). Thus it is evident that the fiber incorporation restricts the diffusion of the degradation products from the matrix. The second peak degradation rate and the corresponding temperature (T_{2max}) are not changed considerably by the increase of fiber content.

The weights of residues after 600°C in various mixes (mixes A-D) are given in the Table VII.2. The weights of residue increases with the increase of fiber content.

7.1. KINETICS

The order of degradation was calculated using the Freeman - Carroll method. The relevant equation and the procedure are described in the Chapter II. Figure 7.3. shows an intercept value of one which indicates that the degradation of polyester fiber - polyurethane composite follows a first order reaction kinetics.

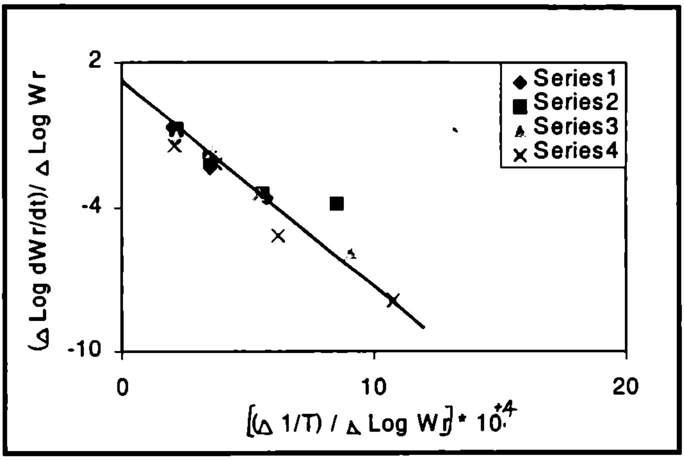

Figure 7.3. Freeman - Carroll plot of mixes A – D (Series 1: mix A, 2: mix B, 3: mix C, 4: mix D)

Similar results have been reported in the case of polyurethane elastomer and short Kevlar fiber reinforced thermoplastic polyurethane.[3,4]

7.2. BONDING AGENTS

7.2.1. GUM COMPOUND

The degradation of virgin elastomer and composites with different bonding agents were also studied. Figure 7.4. shows the degradation curves of the mixes A, A1, A2 and A3 and shows that the mixes containing bonding agents also show two - step degradation similar to that of mix A. The temperature of onset of degradation is higher for the mixes containing bonding agents and is highest for the mixes containing glycerol based bonding agent (mix A2). This indicate that the bonding agents improve thermal stability.

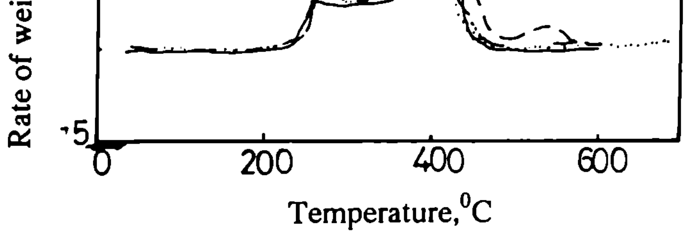

Figure 7.4. TGA traces of mixes A - A3

The peak degradation rates and the corresponding temperatures (T_{Imax} and T_{IImax}) are given in Table VII.3.

T_{1max} is higher for the mix containing bonding agent based on glycerol and MDI. The degradation rates are more or less same for the gum compound with and without bonding agents. The major degradation occurs at around 400 °C and is higher for the mixes containing bonding agents.

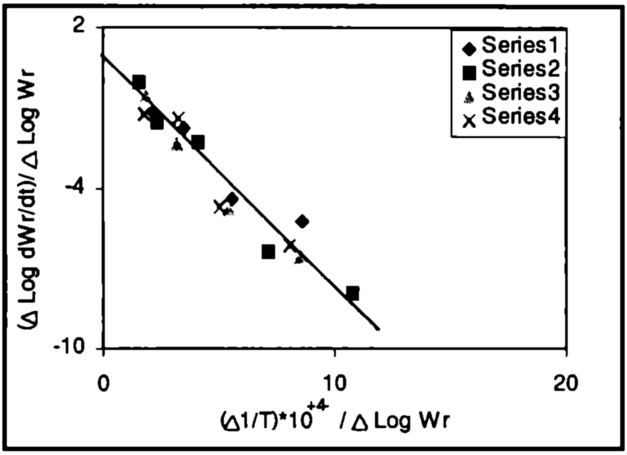

Figure 7.5.Freeman - Carroll plot of mixes A - A3 (Series 1: mix A, 2: mix A, 3: mix A2, 4: mix A3)

Mix No.	T_i °C	T_{1max} °C	R_{1max} %/min	T_{mmx} °C	R_{mmax} %/min	Weights of residue after 600°C, %
A	230.1	257.5	3.01	401.4	10.92	3.88
A1	233.1	257.1	3.10	407.1	11.9	4.56
A2	239.3	263.1	3.31	407.1	11.0	-
A3	235.6	257.5	3.02	405.5	12.1	3.55

T_i = Initiation temperature of degradation, R_{1max} and R_{mmax} are the first and major peak degradation rates and T_{1max} and T_{mmax} are the corresponding temperatures.

Table VII.3. Degradation characteristics of mixes A - A3

The major degradation temperature of mixes A1 - A3 remains more or less same and the degradation rates are marginally higher than the gum without bonding agents. The weight of residue remaining after 600°C of the mixes A - A3 are given in the Table VII.3. All the mixes show similar weights of residue. The plot of Freeman - Carroll method shows that all mixes show a first order degradation kinetics (Figure 7.5).

7.2.2. COMPOSITES

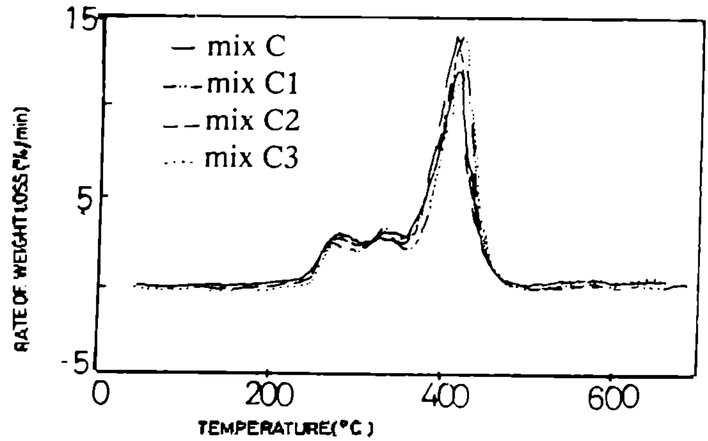

Figure 7.6. TGA traces of mixes C - C3

Figure 7.6 shows the derivative TGA traces of the composites containing bonding agents (mixes C, C1,C2 and C3). All these composites show a three step thermal degradation with maxima at around 270, 330 and 410 °C. The peak degradation rates and the corres-ponding temperatures of the composites are given in the Table VII.4.

For the composites with bonding agents initiation of degradation occurs at higher temperature than that of composites without bonding agents. The enhanced thermal stability may be due to the formation of the more constrained matrix in the presence of bonding agents. The initial degradation temperature is lower for mixes C1 and C3 while it is higher for mix C2 when compared to mix C. The T_{2max} and the corresponding peak degradation rates are not considerably influenced by the presence of bonding agents. The major degradation temperature is higher for composites with bonding agents and the rate of degradation is marginally higher than that of the composites without bonding agents.

Mix No.	**T_i °C**	**T_{1max} °C**	**R_{1max} %/min**	**T_{2max} °C**	**R_{2max} %/min**
C	239.3	275.0	2.98	333.3	3.00
C1	239.3	266.7	2.36	330.9	3.29
C2	245.4	279.4	3.01	335.9	2.65
C3	242.5	269.9	2.49	335.6	2.87

(Continued)

Table VII.4. Degradation characteristics of mixes C - C3

Mix No.	**T_{mmax} °C**	**R_{mmax} %/min.**	**Weights of residue after 600°C, %**
C	411.9	11.98	5.87
C1	414.3	13.27	4.14
C2	419.2	11.86	9.58
C3	420.5	13.80	6.17

T_i = Initiation temperature of degradation, R_{1max}, R_{2max} and R_{mmax} are the first, second and major peak degradation rates and T_{1max}, T_{2max} and T_{mmax} are the corresponding temperatures.

Table VII.4. Degradation characteristics of mixes C - C3

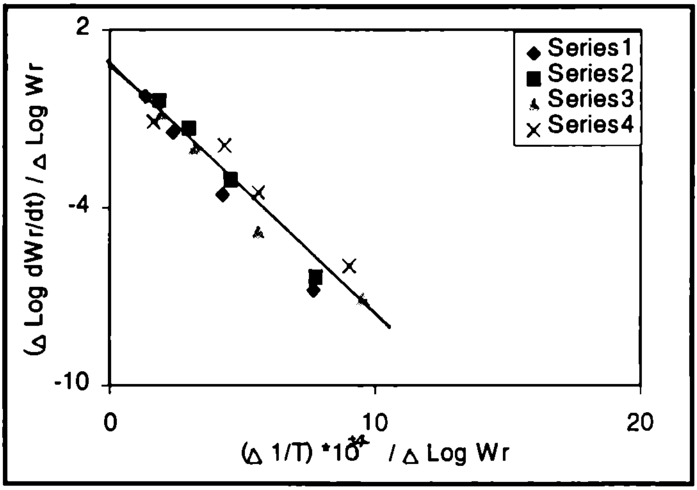

Figure 7.7. Freeman - Carroll plot of mixes C - C3 (Series 1: mix C, 2: mix C1, 3: mix C2, 4: mix C3)

The same behaviour is observed in the case of gum vulcanisates with bonding agents. The weight of residue remaining after 600°C of these composites (Table VII.4) shows that the residue is higher for mixes C2 and C3. The Freeman - Carroll plots of the mixes (Figure 7.7) shows that the presence of bonding agents does not alter the degradation kinetics of the composite.

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CHAPTER VIII

CONCLUSIONS

The inference from the different chapters can be summerised as follows:

1. In the presence of HRH bonding system the water liberated during the resin formation causes hydrolysis of the urethane linkages and hence HRH cannot be used as interfacial bonding agent for urethane based short fiber composite.

2. Resins based on a diisocyanate (TDI and MDI) and a diol or a triol (1:1 equivalence of MDI and -ol) can be used as interfacial bonding agents without lo~~o~~sing the curability.

The optimum resin loading with respect to the cure characteristics is 5 phr. MDI / Glycerol based resin imparts a higher rate of cure and lower processability than the MDI / PPG resin. MDI / PPG /GL based resin gives optimum combination of cure rate and processability.

3. Short polyester fiber reinforced polyurethane elastomer composites with and without bonding agents exhibit pseudoplasticity which decreases with temperature and increases with fiber loading.

Composites with PPG / MDI based bonding agent show lower viscosity at a particular shear rate than that of the composite without bonding agent, where as composite with GL /MDI based bonding agent shows the highest viscosity.

The presence of bonding agent and increase of shear rate does not change the activation energy of flow of the composites.

4. The mechanical properties of the composites are fiber - loading and fiber - orientation dependent and are altered by the bonding agent.

While the tensile strength, modulus, tear resistance and abrasion resistance are improved by the bonding agent, properties such as elongation at break and compression set are adversely affected. The optimum property improvements at room temperature is observed in the case of composites containing MDI / glycerol based bonding agent. For better aging resistance MDI / PPG combination and MDI / PPG - GL combination are better. SEM analysis of the tensile fracture surface indicated improved fiber - matrix bond in the presence of bonding agents.

5. The polyurethane elastomer and short polyester fiber filled elastomer composites exhibit a multistage relaxation mechanism. The rate of relaxation and cross over time of different relaxation stages depend on the strain level and strain rate in addition to fiber loading, fiber orientation and presence of bonding agent.

The initial rate of relaxation of the gum vulcanisate is decreased with the incorporation of fibers. Relaxation rate of the specimens with longitudinal fiber orientation is greater than that with the transverse orientation and the relaxation along the longitudinal direction exhausts easily compared to that of transverse direction.

At the strain level studied, the initial rate of relaxation is higher and cross over time is less for composites containing different bonding agents than the composite without bonding agents.

6. Polyurethane elastomer shows a two - step thermal degradation while the short polyester fiber reinforced composite shows a three - step thermal degradation.

Polyester fiber increases the thermal stability of polyurethane, the optimum being 20 phr fiber loading. The presence of bonding agents improves the thermal stability of the composite and the maximum improvement is shown by the bonding agent based on glycerol with 4,4' - diphenylmethanediisocyanate.

The thermal degradation of the polyurethane elastomer and the composites with and without bonding agents follows a first order reaction kinetics.

LIST OF PUBLICATIONS

1. Studies on the curing of short polyester fiber – polyurethane composite with different interfacial bonding agents., Plastics Rubber Composites Processing and Applications., 24 (1995) 37 – 41.

2. Cure characteristics of polyester fiber - polyurethane elastomer composite with bonding agents based on 4,4' diphenylmethanediisocyanate., International Journal of Polymeric materials., 38 (1997) 205 – 218.

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4. Rheological properties of short polyester fiber-polyurethane elastomer composite with different interfacial bonding agents., Polymer – Plastics Technology and Engineering., 37 (1997) 57 – 70.

5. Mechanical properties of short polyester fiber-polyurethane elastomer composite with different interfacial bonding agents., (Accepted for publication in Polymer – Plastics Technology and Engineering)

6. Stress relaxation of polyester fiber - polyurethane elastomer composite with different interfacial bonding agents., Journal of Elastomers and Plastics., 30 (1998) 1 – 15.

7. Thermal degradation of short polyester fiber-polyurethane elastomer composite., Polymer Degradation and Stability

LIST OF ABBREVIATIONS

γ_a	Apparent shear rate
μm	Micrometer
γ_w	Shear rate at wall
Γ_w	Shear stress at wall
-NCO	Isocyanate
-OH	Hydroxyl
ASTM	American society for testing and materials
CR	Chloroprene rubber
CRT	Cathode ray tube
DMF	Dimethylformamide
E_L	Composite modulus in the longitudinal direction
E_m	Modulus of the matrix
EPDM	Ethylene propylene diene monomer elastomer
E_T	Composite modulus in the transverse direction
GL	Glycerol
HDPE	High density polyethylene
HMTA	Hexamethylenetetramine
HNBR	Hydrogenated nitrile rubber
HRH	Hexamethylenetetramine - resorcinol -hydrated silica
kPas	Kilo-Pascal .second
L	Longitudinal
L/D	Length -to -diameter ratio
LDPE	Low density polyethylene
MBT	Mercaptobenzothiazole
MBTS	2,2'- benzothiazyldisulphide
M_c	Number average molecular weight of rubber between crosslinks
MD resin	Resin based on MDI and different glycols and triol

MDI	4,4'- diphenylmethane diisocyanate
MEK	Methylethylketone
MPT	Monsanto processability tester
MS -10 at 100°C	Mooney viscosity determined using small rotor at 100°C
N	Newton
n'	Flow behaviour index
NDI	1,5-Naphthalene diisocyante
N. m	Newton meter
NR	Natural rubber
OTR	Off the road
PET	Polyethylene terephthalate
PG	Propyleneglycol
PP	Polypropylene
PPG	Polypropyleneglycol
PU	Polyurethane rubber
Q	Volume flow rate
RFL	Resorcinol formaldehyde latex
RH	Resorcinol hexamethylenetetramine
rpm	revolution per minute
SBR	Styrene butadiene rubber
SEM	Scanning electron microscopy
T	Transverse
$\tan \delta$	Loss tangent
TD resin	Resins based on TDI and polypropyleneglycol
TDI	Toluenediisocyanate
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
$T_{max} - T_{min}$	Difference between the maximum and minimum torque
TPU	Thermoplastic polyurethane
UTM	Universal testing machine
V_r	Volume fraction of rubber