SHORT ISORA FIBRE REINFORCED NATURAL RUBBER COMPOSITES

Thesis submitted to the

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

In the partial fulfillment
of the requirements for the award of the degree of

DOCTOR OF PHILOSOPY

in Polymer Science
Under the Faculty of Technology

By

LOVELY MATHEW P

Department of Polymer Science and Rubber Technology

Cochin University of Science and Technology

Kochi 22, Kerala, India

JULY 2006

Department of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Kochi 22, Kerala, India

Dr. Rani Joseph
Professor and Head

Phone: 0484-2575723(Off)
0484-2577850(Res)
E mail: rani@cusat.ac.in

Certificate

This is to certify that the thesis entitled ***"Short isora fibre reinforced natural rubber composites"*** *which is being submitted by Mrs. Lovely Mathew P in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy, to the Cochin University of Science and Technology, Kochi - 22 is a record of the bonafide research work carried out by her under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Kochi - 22 and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.*

Rani Joseph
Dr. RANI JOSEPH
(Supervising Teacher)

The Head
Dept. of Polymer Science and Rubber Technology
Cochin University of Science and Technology
Cochin - 22

6th July 2006
Kochi 22

TABLE OF CONTENTS*

Chapter 1 General Introduction 01

Chapter 2 Materials and Experimental Techniques 65

Chapter 3 Isora fibres: Characterization 82

Chapter 4 Cure characteristics and mechanical properties of short isora fibre reinforced natural rubber composites 112

Chapter 5 Ageing behaviour of short isora fibre reinforced natural rubber composites 150

Chapter 6 Equilibrium swelling studies of short isora fibre reinforced natural rubber composites isora/NR composites 165

Chapter 7 Dynamic mechanical analysis of short isora fibre reinforced natural rubber composites 187

Chapter 8 Summary and Conclusions 209

List of abbreviations

List of scientific publications

Detailed contents are given at the beginning of each chapter

CHAPTER 1

INTRODUCTION

1 General Introduction
- 1.1 Classification of Composites
- 1.2 Fibre Reinforced Composites
  - 1.2.1 Fibres
  - 1.2.2 Chemical structure of Natural fibres
  - 1.2.3 Advantages of Natural fibres as reinforcement in composites
  - 1.2.4 Major drawbacks of Natural fibres
  - 1.2.5 Matrix materials
  - 1.2.6 Fibre matrix interface and interfacial modifications
- 1.3 Classification of fibre reinforced composites
- 1.4 Short fibre reinforced rubber composites
- 1.5 Factors affecting the properties of short fibre rubber composites
  - 1.5.1 Mixing of rubber compounds
  - 1.5.2 Fibre dispersion
  - 1.5.3 Fibre breakage
  - 1.5.4 Critical fibre length and aspect ratio of fibre
  - 1.5.5 Fibre orientation
  - 1.5.6 Fibre concentration
  - 1.5.7 Fibre matrix adhesion
- 1.6 Hybrid composites
- 1.7 Cellulose micro fibrils reinforced composites
- 1.8 Green Composites
- 1.9 Applications of short fibre reinforced rubber composites
- 1.10 Isora Fibre
- 1.11 Scope and objectives of the present work

2 References

CHAPTER 1

1. GENERAL INTRODUCTION

Progresses in the field of materials science and technology have given birth to fascinating and wonderful materials known as 'composites'. A composite material can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them. Composites are made up of continuous and discontinuous medium. The discontinuous medium that is stiffer and stronger than the continuous phase is called the reinforcement and the so called continuous phase is referred to as the matrix. The properties of a composite are dependent on the properties of the constituent materials, and their distribution and interaction. Composite materials are developed because no single, homogeneous structured material can be found that has all of the desired properties for a given application [1]. A composite material can provide superior and unique mechanical and physical properties because it combines the most desirable properties of its constituents while suppressing their least desirable properties. At present composite materials play a key role in aerospace industry, automobile industry and in other engineering applications as they exhibit outstanding strength to weight and modulus to weight ratio.

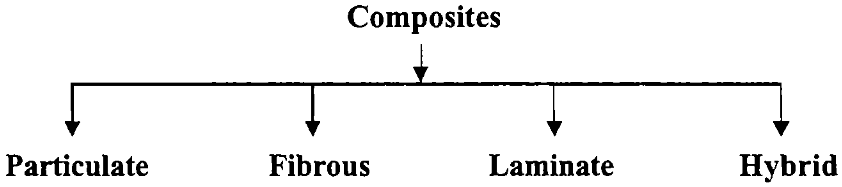
Based on the matrix material which forms the continuous phase, the composites are broadly classified into metal matrix (MMC), ceramic matrix (CMC) and polymer matrix (PMC) composites. Of these, polymer matrix composites are much easier to fabricate than MMC and CMC. This is due to relatively low processing temperature required for fabricating polymer matrix composite. PMC's generally consist of synthetic fibres like carbon or glass embedded in a plastic matrix, which surrounds and tightly binds the fibres. Typically, the fibres make up about 60 % of a polymer matrix composite by volume. The structure, properties and applications of various composites are being investigated world wide by several researchers [2-10].

The fibrous reinforcing constituent of composites may consist of thin continuous fibres or relatively short fibre segments. When using short fibre segments, fibres with high aspect ratio (length to diameter ratio) are used. Continuous fibre reinforced composites are generally required for high performance structural applications. The specific strength (strength to density ratio) and specific stiffness (modulus to density ratio) of continuous carbon fibre reinforced composites can be superior to conventional metal alloys. Also depending upon how fibres are oriented within the matrix, composites can be fabricated into products that have structural properties specifically tailored for a particular use. Polymer concretes are increasingly being used in buildings and other structures. They represent a new type of structural material capable of withstanding highly corrosive environments. The high strength to weight ratio and non-corrosive characteristics of these materials like fibre-reinforced plastics can be utilized to build innovative structures, which are desirable, and economical [11].

Although composite materials have certain advantages over conventional materials, they have some disadvantages also. PMC's and other composite materials tend to be highly anisotropic; that is, properties like strength, stiffness etc. are different in different directions depending on the orientation of composite constituent materials. These anisotropic properties pose a significant challenge for the designer who uses composite materials in structures that place multidirectional forces on structural members. Also formation of a strong connection between the components of the composite material is difficult. The broader use of advanced composites is inhibited by high manufacturing costs. However as improved manufacturing techniques are developed it will become possible to produce composite materials at lower cost than that is now possible, accelerating the wider exploitation of these materials.

1.1 Classification of Composites

According to the nature of the reinforcement used, composites are classified into particulate, fibrous, laminate and hybrid composites.



a. Particulate reinforcement

Particulate fillers are employed to improve high temperature performance, reduce friction, increase wear resistance and to reduce shrinkage [12]. In many cases particulate fillers are used to reduce the cost, under these conditions the additive is filler, whereas when a considerable change in the properties of the composite occurs, the additive is reinforcement. The particles will also share the load with the matrix, but to a lesser extent than a fibre. A particulate reinforcement will therefore improve stiffness but will not generally strengthen. Hard particles in a brittle matrix will cause localized stress concentrations in the matrix, which will reduce the overall impact strength.

b. Fibrous reinforcement

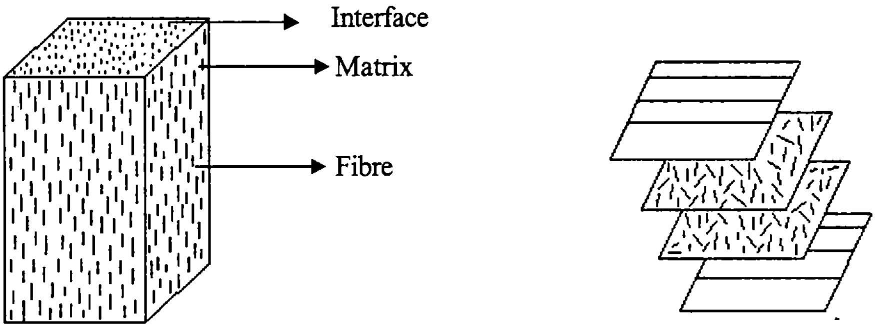
Fibrous reinforcement represents physical rather than a chemical means of changing a material to suit various engineering applications [13]. The measured strength of most materials is much less than that predicted by theory because flaws in the form of cracks perpendicular to the applied load are present in bulk materials. Fibres of non polymeric materials have much higher longitudinal strengths in this form because the larger flaws are not generally present in such small cross sectional areas. In the case of fibres from polymeric materials such as Kevlar, the orientation of the polymeric molecules along the long dimension produces strength in that direction. The fibres dispersed in the matrix may be continuous or discontinuous. In continuous fibre reinforcement, the transference of the load from matrix to the fibres will be easy and very effective whereas in discontinuous (or short) fibre reinforcement, the fibres must be of sufficient length to have load transference effectively. In short fibre composites, the properties of the composite vary with fibre length. Most continuous (long) fibre composites in fact contain fibres that are comparable in length to the overall dimensions of the composite part.

c. Hybrid composites

Composite materials incorporated with two or more different types of fillers especially fibres in a single matrix are commonly known as hybrid composites. Hybridisation is commonly used for improving the properties and for lowering the cost of conventional composites. There are different types of hybrid composites classified according to the way in which the component materials are incorporated. Hybrids are designated as i) sandwich type ii) interply iii) intraply and iv) intimately mixed [14]. In sandwich hybrids, one material is sandwiched between layers of another, whereas in interply, alternate layers of two or more materials are stacked in regular manner. Rows of two or more constituents are arranged in a regular or random manner in intraply hybrids while in intimately mixed type, these constituents are mixed as much as possible so that no concentration of either type is present in the composite material.

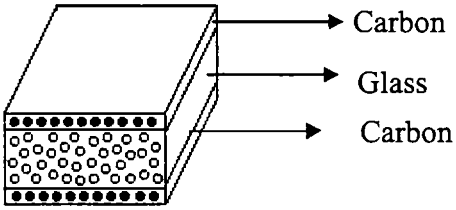
d. Laminates

A laminate is fabricated by stacking a number of laminas in the thickness direction. Generally three layers are arranged alternatively for better bonding between reinforcement and the polymer matrix, for example plywood and paper. These laminates can have unidirectional or bi-directional orientation of the fibre reinforcement according to the end use of the composite. A hybrid laminate can also be fabricated by the use of different constituent materials or of the same material with different reinforcing pattern. In most of the applications of laminate composite, man made fibres are used due to their good combination of physical, mechanical and thermal behaviour.



a) Short fibre composite

b) Laminate composite



c) Hybrid laminates composite

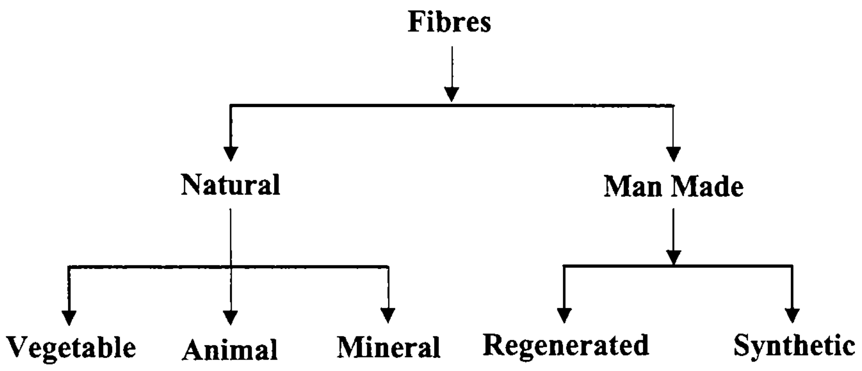
Figure-1.1 Schematic model of different composites

1.2 Fibre Reinforced Composites

The component materials of fibre reinforced composites are fibres and matrix. Fibres are the load carrying members while the surrounding matrix keeps them in the desired location and orientation. Further the matrix acts as a load transfer medium and protects the fibres from environmental damages due to elevated temperature and humidity. The nature of the interface between them is important as far as the properties of the composites are concerned. Fibre reinforced composites exhibit anisotropy in properties. The high strength and moduli of these composites can be tailored to the high load directions. They exhibit better dimensional stability over a wide range of temperature due to their lower coefficient of thermal expansion than those of metals. Also these composites exhibit high internal damping. This leads to better vibration energy absorption within the material and results in reduced transmission of noise and vibration to neighboring structures.

1.2.1 Fibres

'Fibre' is defined as any single unit of matter characterised by flexibility, fineness and high aspect ratio [15]. It is a slender filament that is longer than 100 μm or the aspect ratio greater than 10. Fibres have a fine hair like structure and they are of animal, vegetable, mineral or synthetic origin [16]. Fibres are broadly classified into types as natural and manmade or synthetic. The two categories are further classified as below.

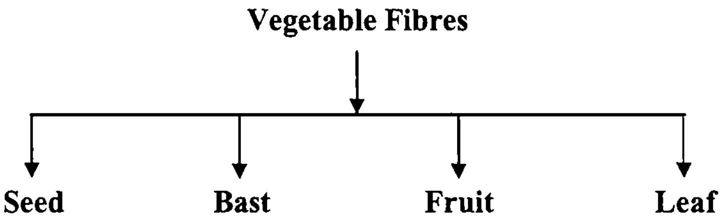


a. Natural Fibres

These are one of the major renewable resource materials throughout the world. There are about 2000 species of useful fibre plants in various parts of the world and these are used for many applications. Now a days industrialist utilize the locally grown fibres as substitute for expensive synthetic fibres.

Natural fibres are classified into three major types as animal fibres, vegetable fibres and mineral fibres. All animal fibres such as silk, wool and mohair are complex proteins. They are resistant to most organic acids and to certain powerful mineral acids. They constitute the fur or hair that serves as the protective epidermal covering of animals. Silk is an exception to this, which is extruded by the larvae of moths and insects and is used to spin their cocoons. It is the only filament that commonly reaches a length of more than 1000 m. Several silk filaments can be gathered to produce textile yarn and staple form is used to manufacture spin yarns. Naturally crimped wool fibres produce air trapping yarns that are used for insulating materials. An important class of naturally occurring mineral fibre is asbestos. Glass fibre is the inorganic mineral fibre made from silica sand, which is used for commercial applications.

Vegetable fibres can be divided into smaller groups based on their origin within the plant as given below.



Normally bast fibers are found in the inner bark of certain plant stems; for example, hemp, jute, flax, ramine, kenaf, etc. They are made up of overlapping cells of bundle in which fibres are bonded together by pectin. Older bundles are larger, more lignified and so stiffer. Banana, sisal, pineapple, abaca etc. are fibres of leaf origin. These fibres are occurring as a part of the fibro vascular system of leaves. Bast and leaf fibres are generally used in composite applications. The fibres found in fruits and seeds like that of cotton, kapok, oil palm, coir etc. are not assembled as bundles. These fibres originate as hairs born on the seeds or inner walls of the fruit, where each fibre consists of a single, long, narrow cell. All vegetable fibres predominantly contain cellulose, along with varying amounts of substances like hemicellulose, lignin, pectins and waxes. Cellulose resists alkalies and most of the organic acids but can be destroyed by strong mineral acids. The single fibre has a diameter of around 10-20 µm. From the living cell, cellulose is produced as microfibrils of 5 nm diameters; each composed of 30 to 100 cellulose molecules in extended chain conformation and provides mechanical strength to the fibre. A good orientation of microfibrils along with high cellulose content is essential for obtaining a fibre with good mechanical properties. The micro structure of natural fibres comprises of different hierarchical structures and so it is extremely complicated. Each fibre cell is constituted by four concentric layers. i.e., primary wall, outer secondary wall, middle secondary wall and inner secondary wall. Primary wall is porous and these pores act as diffusion paths of water through the wall. It is initially cellulosic but become lignified on growth. It also consists of pectin and other non carbohydrates.

The secondary wall is developed on to the inner surface of the primary wall which comprises of a number of cylindrical and anisotropic cellulose micro fibrils. These are surrounded and joined by a loose and complicated macro molecular network of lignin-hemicellulose matrix. The micro fibrils present in the inner secondary wall are spirally arranged about the fibre axis at an angle called the microfibrillar angle which varies from fibre to fibre. The lumen in the centre of the fibre contributes to the water uptake properties of the fibre [16]. Basic properties of some vegetable fibres are given in Table 1.1

b. Synthetic fibres

Synthetic fibres developed from natural cellulose are known are rayons. Rayons come under the category of regenerated fibres. Synthetic fibers such as acetates and triacetates are developed from cellulose acetate like rayon process. Fibres that are derived from organic polymers are termed as organic synthetic fibres, e.g. Nylon, Terylene, Polyester etc. Most of them are thermoplastics; i.e. they are softened by heat. The properties of these fibres depend on the base polymer, the spinning process and the post spinning treatment of the fibre. Carbon and graphite fibres are high strength materials that are used as reinforcing agents in composites. Carbon fibres are produced from rayon or acrylic fibres by thermal heating. Carbon fibres are converted to graphite fibres at temperatures above 2500°C. They can also be made from pitch, a residual petroleum product. The properties of some of the synthetic and mineral fibres are given in Table 1.2.

Table 1.1 Physical and Mechanical properties of some vegetable fibres

Properties	Coir	Jute	Oil palm	Sisal	Banana
Diameter(μm)	100-400	12-25	50-500	100-300	80-250
Density(g/cm^3)	1.15	1.45	1.5	1.45	1.35
Cellulose (%)	43	61	65	78	65
Lignin (%)	45	12	19	12	5
Moisture (%)	10-12	12	16	11	16
Modulus(GPa)	4-6	10-30	2-4	9-20	8-20
Tenacity(MN/m^2)	130-175	450-650	240-500	400-700	500-700
Micro fibrillar angle	4-5	-	42	10-22	11
Elongation (%)	15-40	1-2	10-14	3-7	1-4
Cost(Rs/Kg)	9	20	20	15	30

Ref: J.G.Cook, Hand book of textile fibre and Natural fibres, 4th Edn; Morrow publishing, England (1968)

During composite preparation, fibers are dispersed throughout the polymeric matrix to increase its rigidity and strength further and especially to add impact strength, which often lack in rigid materials [17]. Fibre is the major load bearing component in the composite [18]. Wide range of natural fibres and synthetic fibres like Kevlar, PET etc. which are crystalline in nature and amorphous fibres like glass, boron, silica etc. are used in composite preparation [19]. While glass and steel fibres are superior, it is found that many organic fibres offer very good properties making them materials of choice in many high performance composites.

Table 1.2 Mechanical properties of some mineral and synthetic fibres.

Fibre	Sp. Gravity	Tensile strength(GPa)	Tensile Modulus(GPa)	Strain to Failure (%)
Nylon 66	1.14	1.10	5.52	18
Kevlar 49	1.45	3.62	131	2.8
E-Glass	2.54	3.45	72.4	4.8
Carbon	1.76	3.20	86.9	1.4
Al_2O_3	3.95	1.90	379.3	0.4

1.2.2 Chemical structure of Natural fibres

The chemical composition and cell structure of natural fibres are quite complex. Each fibre is essentially a composite, in which rigid cellulose microfibrils are immersed in a soft lignin and hemicellulose matrix. The chemical composition of natural fibres varies depending on the type of the fibre. Primarily, fibres contain cellulose, hemicellulose and lignin [Figure 1.2]. The properties of each constituent contribute to the overall properties of the fibre. Hemicellulose is responsible for the biodegradation, moisture absorption and thermal degradation of the fibre and it shows least resistance where as lignin is thermally stable but is responsible for the u-v degradation.

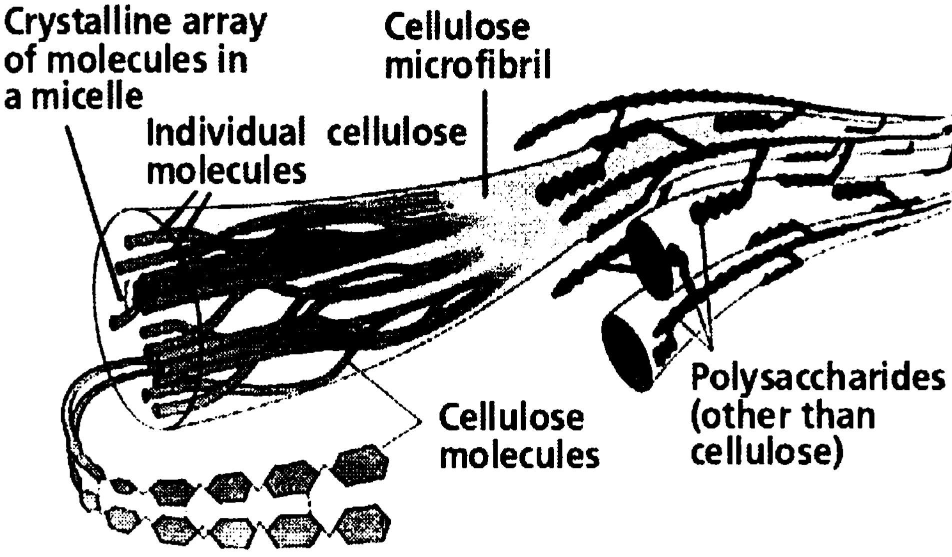


Fig 1.2 Diagramatic representation of the chemical components present in a cellulosic fibre

The term cellulose was first used by Payen [21] in 1838. Since then it has been generally accepted that cellulose is a linear condensation polymer consisting of d-anhydro glucopyranose units joined together by β-1-4 glycosidic bonds. The Haworth projection formula for cellulose is given in figure 1.3.

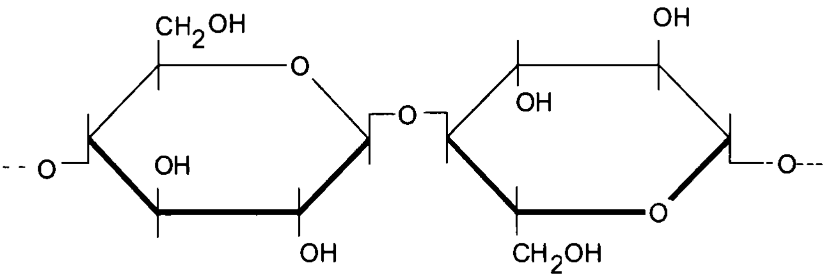
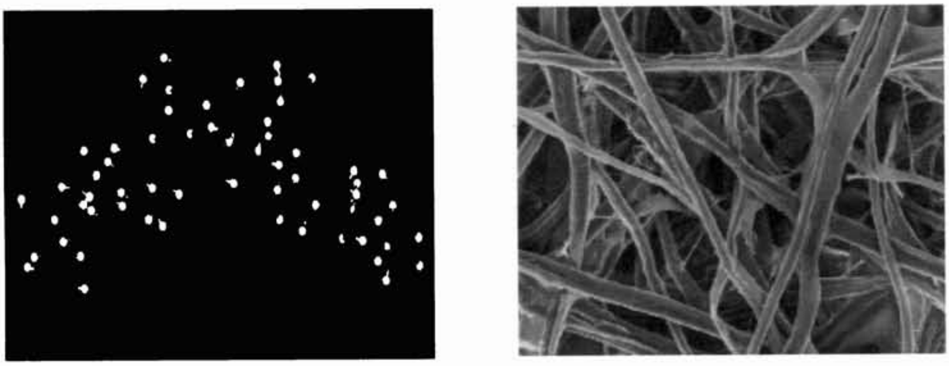


Figure 1.3 Haworth projection formula for cellulose

Each unit is rotated through 180° with respect to its neighbours so that structure repeats itself every two units. The pair of units is called cellobiose and since cellulose is made up of cellobiose units, cellulose is technically a polymer of cellobiose rather than α-D glucose. The chemical character of cellulose molecule is determined by the sensitivity of β-glucosidic linkages, between the glucose repeating units to hydrolytic attack and by the presence of three hydroxyl groups, one primary and two secondary in each of the base units. These reactive hydroxyl groups are able to undergo esterification and etherification reactions. The main cause of the relative stiffness and rigidity of the cellulose molecule is the intra molecular hydrogen bonding, which is reflected in its high viscosity in solution, its high tendency to crystallize and the ability to form fibrillar strands. The β-glycosidic linkages further favour the chain stiffness. The molecular structure of cellulose is responsible for its supramolecular structure and this in turn determines many of the physical and chemical properties of the fibre.



(a) **(b)**

Figure 1.4 (a) Three dimensional representation of cellulose molecule (b) SEM photograph of cellulose micro fibril

The mechanical properties of natural fibres also depend on the cellulose type, because each type of cellulose has its own cell geometry and the geometrical constitution determines the mechanical properties.The three dimensional representation of cellulose molecule is given in figure 1.4(a) and SEM photograph of cellulose microfibril is given in figure 1.4 (b)

The crystal structure of natural and regenerated cellulose is known as cellulose-I and cellulose-II respectively. In cellulose-I the chains within the unit cell are in parallel configuration [22] while they have antiparallel configuration [23] in cellulose-II. In addition to cellulose component, natural fibres contain hemicellulose, which consists of a group of polysaccharides that remain associated with the cellulose after lignin has been removed. The hemicellulose differs from cellulose in that they contain several sugar units whereas cellulose contains only glucopyranose units. Hemicellulose also exhibits considerable chain branching whereas cellulose is strictly linear. The degree of polymerization of native cellulose is also hundred times higher than that of hemicellulose. Unlike cellulose, the constituents of hemicelluloses differ from plant to plant [24]. Lignins, complex hydrocarbon with aliphatic and aromatic components are another important constituent of plant fibres. Lignin is an aromatic biopolymer, an integral cell constituent in all vascular plants including the herbaceous varieties. The schematic representation of the structure of fibre is given in figure 1.5.

The major inter unit linkage is an aryl-aryl ether type. Besides twenty types of bonds present in the lignin itself, lignin seems to be particularly associated with hemicellulose polysaccharides [25]. Lignin forms the matrix sheet around the fibres that hold the natural structure together. The mechanical properties of lignin however are lower than that of cellulose [26]. In addition to these, pectin and waxes make up parts of the fibre [27].

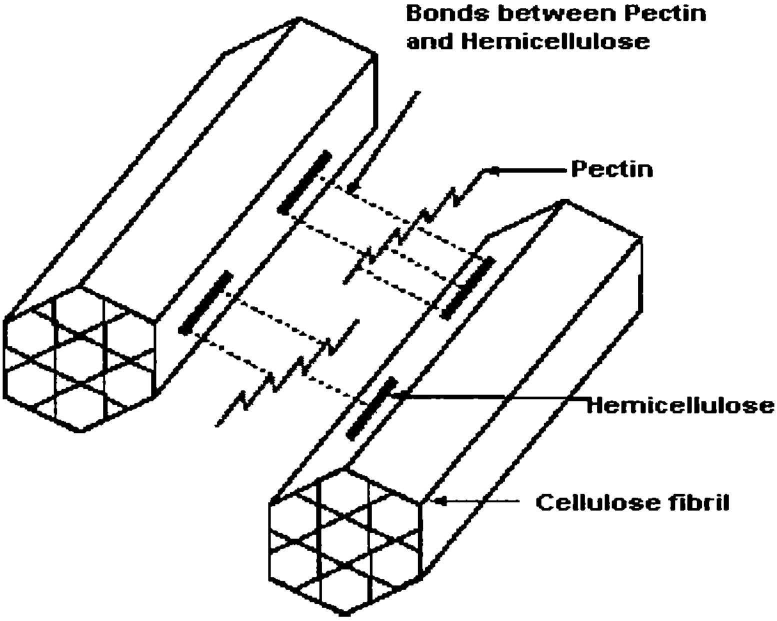


Figure 1.5 Schematic representation of the structure of fibre

1.2.3 Advantages of Natural fibres as reinforcement in composites

Natural fibres, as a substitute for glass components, have gained interest in the last decade, especially in the housing sector. The moderate mechanical properties of natural fibres prevent them from being used in high performance applications where carbon fibre reinforced composites would be utilized, but for many reasons they can compete with glass fibre. The low specific weight, which results in a higher specific strength and stiffness than those of glass, is a benefit. The use of renewable natural fibres contributes to sustainable development. Now a days natural fibre reinforced polymer composites come prior to synthetic fibre reinforced composites in properties such as biodegradability, combustibility, light weight, non toxicity, decreased environmental pollution, low cost, ease of recyclability etc. These advantages place the natural fibre composites among the high performance composites having economical and environmental advantages. The versatile high performance applications of natural fibre composites, which can replace glass and carbon fibres, were listed in an article by Hill [28]. The vegetable fibre have density of about half that of glass fibre. During the processing of natural fibre composites, there will be no abrasion of the processing machines. These fibres can withstand processing temperatures up to 250°C. Reinforcement of polymers with vegetable fibres glues good opportunities for the effective utilization of agricultural products. Physical, chemical and mechanical properties of some important natural fibres are given in Table 1.1 [16, 29, and 30]. They are cent percent combustible without the production of either toxic gases or solid residues. Wright and Mathias succeeded in preparing lightweight materials from balsawood and polymer [31]. Investigations have been carried out by Hedenberg and Gatenholm in recycling the plastic and cellulose waste into composite [32]. Systematic investigations on wood flour reinforced polystyrene composites have been carried out by Maldas and Kokta [33]. The effects of hybridization of saw dust with glass and mica and of the surface treatment of the reinforcing filler on the mechanical properties were studied [34]. Natural fibres like sisal, coir, oil palm, bamboo etc. have been proved to be a better reinforcement in rubber matrix [35-38]. Incorporation of natural fibres resulted in better long term mechanical performance of elastomers. The poor reinforcing effect of these cellulosic fibres in elastomers were overcome by giving specific modifications. The range of products in the automobile industry based on natural fibres is based on polymers like plastics and elastomers and fibres like flax, hemp, sisal etc. The use of natural fibres in automobile industry has grown rapidly over the last five years. Recently value added composite materials were developed from neisan jute fabric and polypropylene having enhanced mechanical properties and reduced hydrophilicity [39]. Yamini et al [40] investigated the effect of board density on the properties of particle board from oil palm fibre and urea formaldehyde resin.

Natural fibres enjoy the right potential for utilization in composites due to their adequate tensile strength and good specific modulus, thus ensuring a value added application avenue. Plant based composites have been widely used in construction; the ancient Egyptians used to reinforce clay walls. To eliminate problems resulting from the incorporation of synthetic fibres such as high abrasiveness, health hazards, disposal problems etc. incorporation of natural fibres is proposed. They are abundant, renewable, and cheap and are having low density. Material scientists all over the world focus their attention on natural composites reinforced with fibres like jute, sisal, coir, pineapple, banana etc. primarily to cut down the cost of raw materials.

1.2.4 Major drawbacks of Natural fibres

a. Moisture absorption of fibres

The lignocellulosic natural fibres are hydrophilic and absorb moisture. The swelling behaviour of natural fibres is generally affected by its morphology as well as physical and chemical structures. Biofibres change their dimensions with varying moisture content because the cell wall polymers contain hydroxyl and other oxygen containing groups, which attract moisture through hydrogen bonding [41]. The hemicelluloses are mainly responsible for moisture absorption. Water penetration through natural fibres can be explained by capillary action [42]. The waxy materials present on the surface help to retain the water molecules on the fibre. The porous nature of the natural fibre accounts for the large initial uptake at the capillary region. The hydroxyl group (-OH) in the cellulose, hemicellulose and lignin build a large amount of hydrogen bonds between the macromolecules in the plant fibre cell wall. Subjecting the plant fibres to humidity causes the bonds to break. The hydroxyl group then forms new hydrogen bond with water molecules, which induce swelling [43]. The schematic representation of swelling process in cellulose is given in figure 1.6

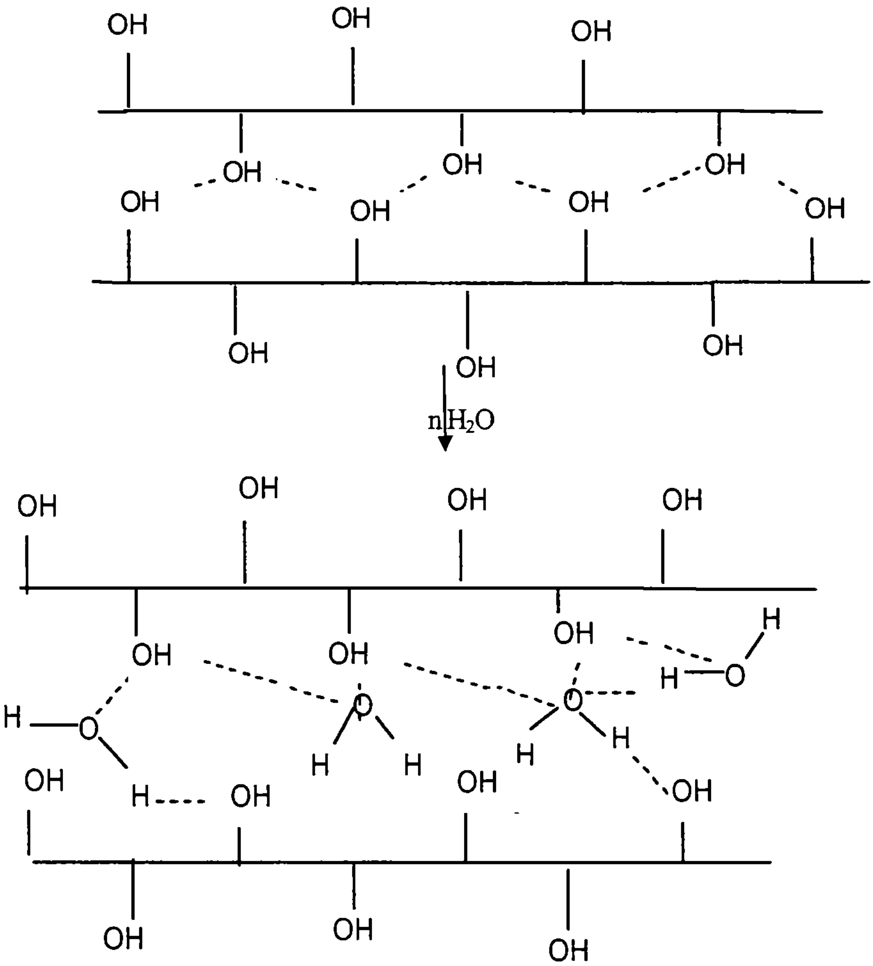


Figure 1.6 Schematic representation of the water absorption of cellulosic fibres

[Ref: Mwaikambo L.Y., Ansell M.P., J Appl Polym Sci (2002) 84: 2222.]

Generally moisture content in natural fibres varies between 5-10%. This can lead to dimensional variations in composites and also affect the mechanical properties of composites. Therefore the removal of moisture from fibres is very essential before the preparation of the composites. The moisture absorption of natural fibres can be reduced by proper surface modifications.

b. Thermal stability of natural fibres

Natural fibres are complex mixtures of organic materials and as a result, thermal treatment leads to a variety of physical and chemical changes. The limited thermal stability of natural fibre is one of their drawbacks. The thermal stability of natural fibres can be studied by Thermo Gravimetric Analysis (TGA). As mentioned above, natural fibre is composed of mainly cellulose, hemicellulose and lignin. Each of the three major components has its own characteristic properties with respect to thermal degradation which are based in polymer composites. However the microstructure and the three dimensional nature of natural fibre are variables, that also play important roles in terms of their effects on combustion behaviour. Thus the individual chemical components of the fibre behave differently if they are isolated or if they are intimately combined within each single cell of the fibre structure [44].

Lignin, specifically the low molecular weight protolignin, degrades first and at a slower rate than the other constituents. This is shown in figure 1.7(a). The TGA curve indicates that the beginning of the natural fibre degradation occurs at around 180°C but the rate of degradation is always lower than that of the cellulose, Figure 1.7(b).

This process has been described by Shurky and Girgis [45] who also presented an analysis of the products of degradation. From figure 1.7(b) it is observed that the weight loss in the cellulose sample is negligible below 300°C. However above that temperature the cellulose begins to degrade fast and at about 400°C only the residual char is found. Beall [46] has described this process as the loss of hydroxyl groups and depolymerization of the cellulose to anhydroglucose units. The thermal degradation of cellulose based fibres is greatly influenced by their structure and chemical composition. The natural fibre starts degrading at about 240°C. The thermal degradation of lignocellulosic materials has been reviewed by Tinh *et al* in detail for modified and unmodified materials [47-48]. Thermal degradation of natural fibres is a two stage process, one in the temperature range 80-180°C and other in the range 280-380°C.

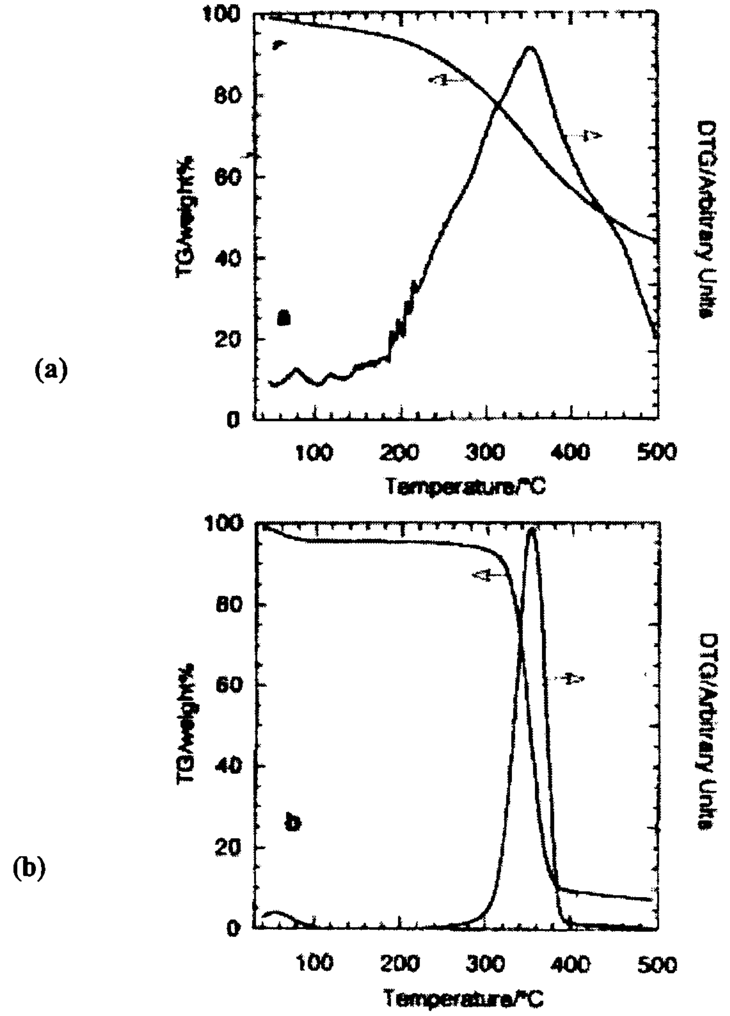


Figure 1.7 TG / DTG Vs Temperature curves of (a) Lignin (b) Cellulose

[Ref: Marcovich N.E., Reboredo M.M., Aranguren M.I., Thermochemica Acta, (2001)372:45

Gossan and Bledzki [49] studied the thermal degradation pattern of jute and flax and found that at temperatures below 170°C fibre properties were affected only slightly while at temperatures above 170°C significant drop in tenacity and degree of polymerization were observed. Because of chain sessions, a slight increase in the degree of crystallinity was observed. Thermal degradation pattern of other cellulosic fibres like oil palm, sisal, banana, coir, hemp, jute etc. was also reported [50-55]. It was reported that the chemical modification improved the thermal stability of their composites. Chemically modified fibres showed a satisfactory thermal stability at processing temperatures for potential composites. Thermal degradation of natural fibres is a two stage process. The low temperature degradation [80-180°C] process is associated with degradation of lignin, whereas the high temperature degradation [280-380°C] process is due to cellulose. The degradation of natural fibres is a crucial aspect in the development of natural fibre composites and thus has a bearing on the curing temperature in the case of elastomers and thermosets and extrusion temperature in thermoplastic composites [56-57].

c. Biodegradation and Photo degradation of Natural fibre

The lignocellulosic natural fibres are degraded biologically by very specific enzymes capable of hydrolyzing the cellulose especially hemicellulose present in the cell wall into digestible units [58]. Lignocellulosic exposed outdoors undergo photochemical degradation caused by ultraviolet light. Resistance to biodegradation and ultraviolet radiation can be improved by bonding chemicals to cell wall or by adding polymer to the cell matrix. Biodegradation of cellulose causes weakening the strength of the natural fibre. Photo degradation primarily takes place in the lignin component which is responsible for the colour changes [59]. The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptible to ultraviolet degradation.

1.2.5 Matrix materials

Since fibres cannot transmit loads from one to the other, they have limited use in engineering applications. When they are embedded in a matrix material to form a composite, the matrix serves to bind the fibres together, transfers loads to the fibres, and protect them against environmental attack and damage due to handling. The matrix has a strong influence on several mechanical properties of the composite such as modulus and strength, shear properties and properties in compression. Physical and chemical characteristics of the matrix such as melting or curing temperature, viscosity and reactivity with fibres influence the choice of fabrication process. The matrix material for a composite system is selected, keeping in view all of the above factors. The commonly used matrix materials are polymers, metals and ceramics.

Polymers

Polymers are the most widely used matrix materials for fibre reinforced composites. Their chief advantages are low cost, easy processability, good chemical resistance and low specific gravity. On the other hand low strength, low modulus and low operating temperature limit their use. Polymers are further classified into plastics and rubbers.

a. Plastics

Organic polymeric materials which can be made into desired shape through extrusion, moulding, casting etc. are termed as plastics. According to their structure and thermal behaviour, plastics are classified into thermoplastics and thermosetting plastics. Plastics that soften or melt on heating are called thermoplastics. Melting and solidification of these polymers are reversible and they can be reshaped by application of heat and pressure. They are semi crystalline or amorphous in nature. Examples include polyethylene, polypropylene, polyamides, polystyrene, polyacetate, polycarbonate, polyether ether ketone etc. Thermosetting plastics have cross-linked or network structures which do not soften but decompose on heating. Once solidified by cross linking process, they cannot be reshaped. Common examples of thermosets are polyester resins, epoxies, phenolics, melamines, silicons etc. Thermoplastics are almost exclusively used when no reinforcement is included in non structural applications and dominates also when short fibres are incorporated. However thermosets clearly dominate in structural composite applications. Thermoplastics have lately received increased attention in continuous fibre reinforced composite due to a number of attractive potential applications.

b. Rubbers

Rubber is a versatile and adaptable material that has been successfully used as matrix for composite preparation. Rubber is defined as a material that is capable of recovering from larger elastic deformations quickly and forcibly. They can be modified to a state in which it is essentially insoluble but can swell in solvents like benzene, toluene, methyl ethyl ketone etc. [60]. Rubber is unique but to following properties. Its elastic strain is much higher than that of metal. Hence it can function at high strains. It is stretched rapidly even under small load to about 1000% elongation. On releasing the applied forces, rubber retracts rapidly almost fully. There are different types of rubber including Natural rubber (NR) and a variety of synthetic rubbers.

(i) Natural rubber

Natural rubber is a high molecular weight polymer of isoprene in which essentially all the isoprene's have the cis 1-4 configuration.

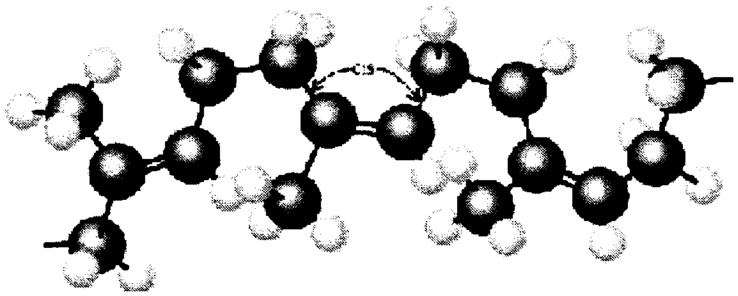


Figure 1.8 Structural formula of natural rubber

The chemical structural formula of natural rubber is shown in figure 1.8.

In its very natural state, rubber exists as a colloidal suspension in water in the latex of rubber producing plants – Hevea Brasiliensis.

Approximate composition of the field latex is given in Table 1.3.

Table 1.3 Composition of field latex

Constituents	Quantity
Rubber hydrocarbon	33 %
Water	60 %
Protein	2-3 %
Fatty acids	1-3 %
Sugars	1 %
Ash content	1 %
Trace elements (Cu, Mn)	2-3 ppm
Impurities	8-10 ppm

Among various rubbers, natural rubber is very important since it possess the general features of other rubbers in addition to the following highly peculiar characteristics. Since it is of biological origin, it is renewable, inexpensive and creates no health hazard problems. It possesses high tensile strength due to strain induced crystallization. It possesses superior building tack, which is essential in many products like tyres, hoses, belts etc. It possesses good crack propagation resistance also. The field latex is concentrated by centrifugation, creaming or electrodecantaion. Generally the latex is coagulated by formic or acetic acid. Technical grading of rubber is done according to composition of rubber, source material, initial plasticity etc. The main criterion is the dirt content which is the residue left after the rubber sample was dissolved in an appropriate solvent, washed through a 45µm sieve and dried.

Table 1.4 ISNR specifications for technically graded Natural rubber

Property	Grade 5	Grade 10	Grade 20	Grade 50
Dirt (% max)	0.05	0.10	0.20	0.50
Ash (% max)	0.60	0.75	1.00	1.50
Volatile matter(% max)	0.08	0.08	0.08	0.08
Nitrogen (% max)	0.60	0.60	0.60	0.60
Nitrogen(% min)	0.25	0.25	0.25	0.25
Initial plasticity(min)	40	40	35	30
Plasticity retention index(min)	60	50	40	30

Table 1.4 gives the Indian standard Natural rubber (ISNR) specifications of natural rubber. In addition to the different grades certain modified forms of natural rubber are also available like deproteinised natural rubber which is having high reproducibility, oil extended natural rubber also called freeze resistant rubber and cyclic natural rubber with high adhesive property.

(ii) Synthetic Rubbers

Synthetic rubbers have become necessary materials in rubber goods manufacturing industry. Any synthetic polymeric substances that exhibits the properties of rubber especially its elasticity and flexibility at room temperature are called synthetic rubbers or Elastomers. There are two broad classes of synthetic rubbers. They are General Purpose Synthetic Rubbers (GPSR) and Special purpose synthetic rubbers (SPSR).

The important GPSR's are,

(a) Styrene butadiene rubber (SBR) a copolymer of styrene and butadiene. In some properties like heat build up and tackiness, SBR is inferior to those of NR. It is marketed generally at a lower viscosity than NR and this permits its use in industry without premastication. Abrasion resistance and resistance to degradation under heat are better for SBR than NR.

(b) Polybutadiene rubber (BR) which is a homopolymer of butadiene monomer. BR is cis-1, 4 Polybutadiene. BR has very good low temperature properties due to its low Tg value. As the trans content in the polymer increases, tendency for crystallization increases. BR has high air permeability, low heat build up, high resilience, better flex resistance, heat stability etc. it is used in manufacture of mechanical goods and as modifier for plastics to improve impact resistance.

(c) Ethylene propylene rubbers are available in two types. EPM-Ethylene propylene co polymer and EPDM- Ethylene propylene diene monomers. The alternating distribution of monomers in the EPM and EPDM rubbers provide most amorphous or least crystalline rubber. In EPDM, small amount of diene is incorporate along with ethylene and propylene at the time of polymerization. The dienes are added to ethylene propylene rubber to make it sulphur curable. These rubbers have a remarkable resistance to ozone and UV radiation. The combination of weather resistance, excellent electrical properties and the ability to be cured rapidly with peroxide has been made use of this rubber in production of good quality electrical cables.

(d) Poly isoprene rubber (IR): In general this rubber can be used in areas where NR is used due to the inherent tack, high gum strength, good hysterisis, good hot tear and tensile properties.

(e) Butyl rubber (IIR): It is a copolymer of isobutylene and butadiene or isoprene. Butyl rubber is not as resilient as natural rubber. It is extremely resistant to oxidation and to the action of corrosive chemicals. Because of its it low permeability to gas, butyl rubber is used widely for inner tubes in automobile tyres.

Special purpose synthetic rubbers include chloroprene rubbers, nitrile rubbers, polyacrylic rubbers, fluorocarbon rubbers, silicon rubbers, polyurethane rubbers and polysulphide rubbers. These types of rubbers are used in specific applications which require solvent resistance, fire resistance and thermal resistance [61].

1.2.6. Fibre matrix interface and interfacial modifications

The term interface has been defined as the boundary region between two phases in contact. The composition, structure and properties of the interface may be variable across the region and may also differ from composition, structure or properties of either of the two contacting phases [62], fiber and matrix. This interfacial region exhibits a complex interplay of physical and chemical factors that exert a considerable influence in controlling the properties of reinforced composites. The interfacial interaction depends on the fiber aspect ratio, strength of interactions, fibre orientation and aggregation etc. [63-65]. Extensive research has been done to evaluate the interfacial shear strength (ISS) of man made fibres [66-69] and natural fibres [70-73] by using methods such as fibre pull out tests, critical fibre length and micro bond tests.

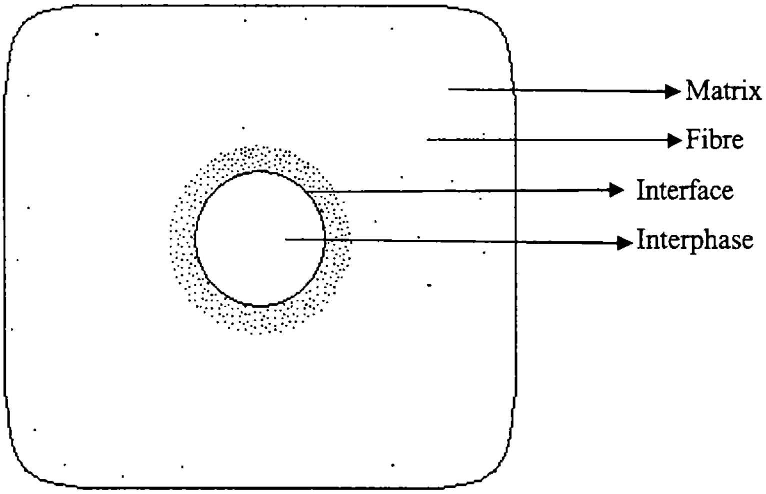


Figure 1.9 Interface/Interphase in a fibre reinforced composite

[Ref: Newaz G.M., Polym Comp (1986) 7: 421]

In fibre composites, stresses acting on the matrix are transmitted to the fibre across the interface. For efficient stress transfer, the fibres have to be strongly bonded to the matrix. Composite materials with weak interface have relatively low strength and stiffness but high resistance to fracture whereas materials with strong interface have high strength and stiffness but are very brittle. The effects are related to the ease of debonding and pull out of fibres from the matrix during crack propagation. The interface/interphase concept in fibre composite is clear from the figure 1.9 [74]. Interface is defined as a two dimensional region between fibre and matrix having zero thickness. The interphase in a composite is the matrix surrounding a fibre. There is a gradient in properties observed between matrix and interphase. The interface is an area whereas interphase is a volume.

The fibre matrix interface adhesion can be explained by five main mechanisms.

(i) Adsorption and Wetting

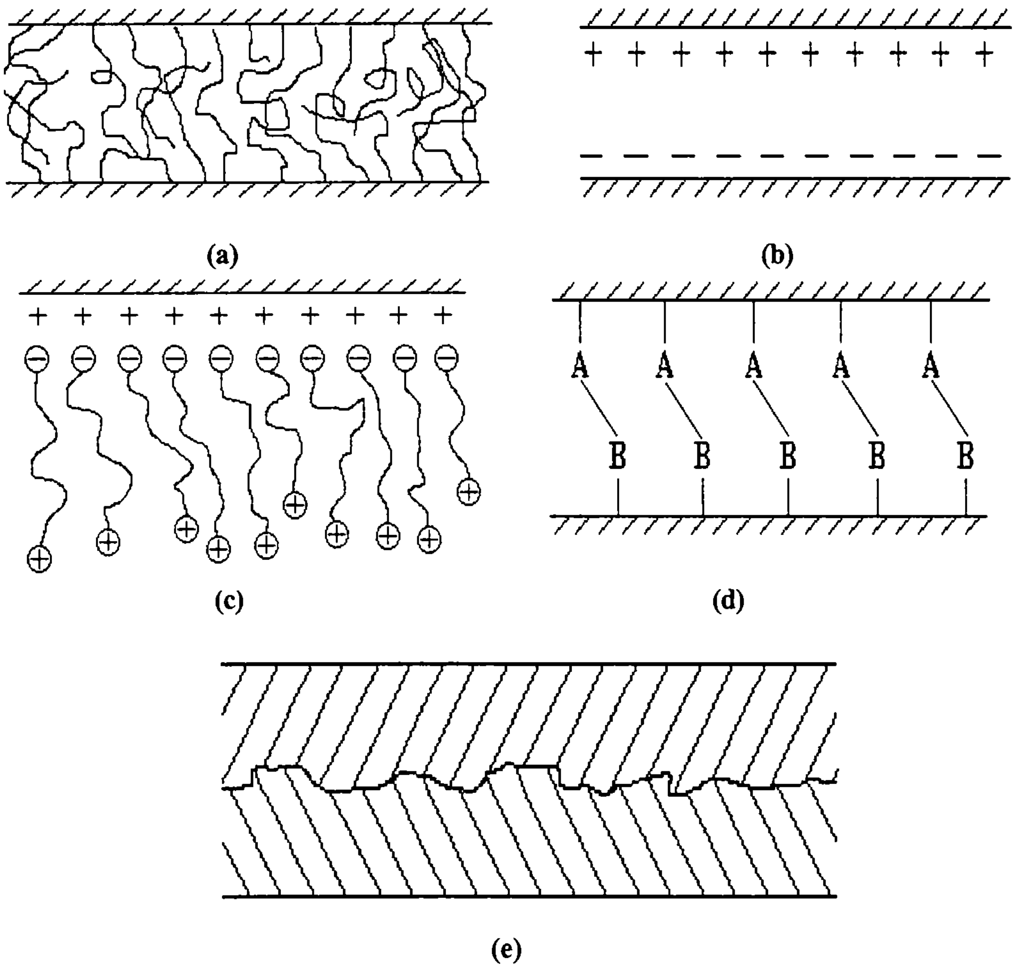
This is due to the physical attraction between the surfaces, which is better understood by considering the wetting of solid surfaces by liquids. Between two solids, the surface roughness prevents the writing except at isolated points. When the fiber surface is contaminated, the effective surface energy decreases. This hinders a strong physical bond between fibre and matrix interface.

(ii) Interdiffusion

Polymer molecules can be diffused into the molecular network of the other surface say fibre as shown in figure 1.10 a. The bond strength will depend on the amount of molecular conformation, constituents involved and the ease of molecular motion.

(iii) Electrostatic attraction

This type of linkage is possible when there is a charge difference at the interface. The electrostatic interaction at the interface is shown in figure 1.10 (b) & (c). The anionic and cationic species present at the fibre and matrix phases will have an important role in the bonding of the fibre matrix composites via electrostatic attraction. Introduction of coupling agents at the interface can enhance bonding through the attraction of cationic functional groups by anionic surface and vice versa.



(a) (b) (c) (d) (e)

Figure 1.10 Schematic representations of various fibre matrix adhesions.

(iv) Chemical bonding

Chemical bonds can be formed between chemical groups on the fibre surface and a compatible chemical group in the matrix as shown in figure 1.10 (d). The type of bond determines the strength. Interfacial chemical bonding can increase the adhesive bond strength by preventing molecular slippage at a sharp interface during fracture and by increasing the fracture energy by increasing the interfacial attraction.

(v) Mechanical adhesion

Mechanical interlocking at the fibre-matrix interface is possible as given in fig 1.10 (e). The degree of roughness of the fibre surface is very significant in determining the mechanical and chemical bonding at the interface. This is due to the larger surface area available on a rough fibre. Surface roughness can increase the adhesive bond strength by promoting wetting or providing mechanical anchoring sites.

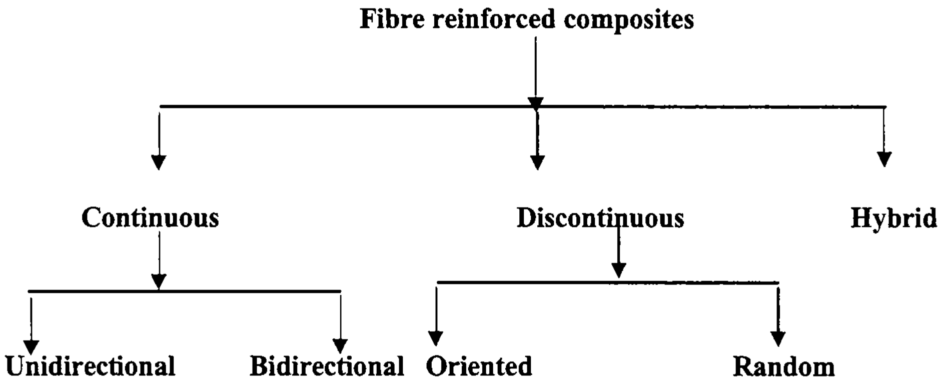
Natural fibres are hydrophilic in nature and are incompatible with the hydrophobic polymer matrix and have a tendency to form aggregates. Since they are hydrophilic fibres they are very sensitive to moisture absorption. To eliminate the problems related to high water absorption, treatment of fibres with hydrophobic reagents has been attempted. These reagents contain reactive functional groups that are capable of bonding to the reactive groups in the matrix polymer. The modification of natural fibres is done to make fibres hydrophobic and to improve the interfacial adhesion between the fibre and the polymer matrix [75-85]. In addition to the surface treatments of fibres, use of a compatibilizer or coupling agent for effective stress transfer across the interface can also be explored [86-91]. The compatibilizer can be a polymer with functional groups grafted in to the chain of the polymer. The coupling agents are generally tetra functional organometallic compounds based on silicon, called silanes [92]. Pedro *et al* found that pre impregnation of cellulose fibres in a LDPE/xylene solution and the use of a coupling agent result in small increment in mechanical properties of LDPE, reinforced with green cellulosic fibre composites which are attributed to an improvement in the interface between fibres and matrix. The fibre treatment also improved the shear properties of the composite and fibre dispersion in the matrix [93]. Ishak *et al* [94] used silane coupling agents and compatibilizers to improve the mechanical properties of oil palm fibre filled high density polyethylene composites. In all cases it seems that the mechanical properties of the composites have improved significantly. The use of silane coupling agent enhanced the tensile properties and tear strength of bamboo fibres filled rubber composites [95]. The silane coupling agent is believed to improve the surface functionality of bamboo fibres and subsequently enabled the bamboo fibres to bond chemically to the rubber matrix. The wetting of cellulosic fibres in rubber matrix is also improved by the use of coupling agent. According to Damka, [96] the use of silanes permits within a shorter vulcanization time, an increase in rubber bound sulphur and gives vulcanizates of increased strength.

Usually natural fibres are treated with NaOH to remove lignin, pectin and waxy substances. Alkalization gives rough surface topography to the fibre. It also changes the fine structure of native cellulose I to cellulose II [97]. The increase in the percentage crystallinty index of alkali treated fibre occurs because of the removal of cementing materials which leads to better packing of cellulose chain and increase in molecular orientation. The elastic modulus of the fibre is expected to increase with increasing degree of molecular orientation [98]. Superior mechanical properties of alkali treated jute based biodegradable polyester composites was attributed to the fact that alkali treatment improves the fibre surface characteristics by removing the impurities if the fibre surface thereby producing a rough surface morphology [99]. The effect of alkalization and fibre alignment on the mechanical and thermal properties of kenaf and hemp fibre reinforced polyester composites were studied by Aziz and Ansell [100]. Samal *et al* [101] studied the effect of alkali treatment and cyanoethylation on coir fibres and found that the modified coir fibre showed significant hydrophobicity, improved tensile strength and moderate resistance to chemical reagents. Hill *et al* [102] studied the benefit of fibre treatment by chemical modification (acetylation) of the fibres and by the use of silane coupling agent on the mechanical properties of oil palm and coir fibre reinforced polyester composites. They found that acetylation of coir and oil palm fibres results in the increase in the interfacial shear strength between the fibre and the matrix and increase in the mechanical properties of the composites. George *et al* [103] analyzed the improved interfacial interaction in chemically modified pine apple leaf fibre reinforced polyethylene composites. They used various reagents like NaOH, silanes and peroxides to improve the interfacial bonding. The influence of fibre surface modification on the mechanical performance of oil palm fibre reinforced phenol formaldehyde composites were studied by Sreekala *et al* [104]. The effects of various chemical modifications of jute fibres as a means of improving its suitability as reinforcement in biopol based composites were done by Mohanty *et al* [105]. Sisal fibres were chemically treated with a two step treatment with sodium sulphate solution followed by acetic anhydride to promote adhesion to a polyester resin matrix [106]. It was found that the chemical treatment improved the fibre matrix interaction as revealed by the brittle behaviour of the composites reinforced with treated fibres. Though the treatment improved the fibre behaviour in relation to moisture, the water absorption capacity of the composites was increased by the treatment. This should be due to the failure to remove all the unreacted hydrophilic species left by treatment or to the formation of acetyl cellulose micro tubes in the treated fibre. Rozman *et al* [107] employed lignin as compatibilizers in coconut fibre polypropylene composites. Since lignin contains both polar hydroxyl groups and nonpolar hydrocarbon and benzene ring it can play a role in enhancing the compatibility between both components. The composite with lignin as a compatibilizer possessed higher flexural properties compared to the control composites. Lignin also reduces water absorption and thickness swelling of the composites. Thomas and coworkers [108-113] have carried out systematic studies on the chemical modification of various natural fibres like sisal, coir, oil palm, banana and pineapples and its reinforcing effect on various rubbers, thermoplastics and thermosets. In all cases it was observed that the composite properties have greatly improved by using treated fibres due to better fibre matrix interaction.

The studies so far reported proved that the utilization of natural fibres in polymeric matrices offer economical, environmental and qualitative advantages. Owing to the uncertainties prevailing in the supply and price of petroleum based products, it is highly important to use the naturally occurring alternatives. Proper utilization of indigenously available raw materials will open up new markets for these natural resources. Hence studies on composites containing natural fibres are important.

1.3 Classification of fibre reinforced composites

Fibre reinforced composites (FRC) can be classified on the basis of different aspects among which the fibre length is a very important parameter. Thus FRC's are grouped into two; long (continuous) fibre reinforced composites and short (discontinuous) fibre composites. In continuous fibre composites fibres are oriented in one direction to produce enhanced strength properties. In short fibre composites, the length of short fibre is not too high to allow individual fibres to entangle with each other nor too small for the fibres to loss their fibrous nature. The reinforcement is uniform in the case of composites containing well dispersed short fibres. There is a clear distinction between the behaviour of short and long fibre composites. End effects dominate in short fibre composites, so they do not act as good reinforcing agents.The schematic representation of the classification of the fibre reinforced composites is given below.



1.4 Short fibre reinforced rubber composites

Short fibre reinforced rubber composites were developed to fill the gap between the long fibre reinforced and particulate filled rubber composites. That is mainly to achieve the high performance of the fibre coupled with easy processability and elasticity of the rubber. Composites in which the short fibres are oriented uniaxially in an elastomer have a good combination of good strength and stiffness from the fibres and elasticity from the rubber. These composites are being used for the fabrication of a wide variety of products such as v-belts, hoses and articles with complex shapes (114-115). Short fibre reinforced rubber composites possess several advantages over continuous fibre composites (116-119). Short fibres can be easily incorporated into the rubber compound along with other ingredients. They are amenable to standard rubber processing operations such as extrusion, calendaring, compression moulding, injection moulding etc. These composites provide high green strength and high dimensional stability during fabrication. Design flexibility is another advantage of these composites. Complex shaped articles which is quite difficult to accomplish with long fibre composites can be fabricated using short fibre composites. Mechanical properties like specific strength and stiffness, reduced shrinkage in moulded products, resistance to solvent swelling, abrasion, tear and creep resistance are greatly improved in the case of short fibre composites. Moreover short fibres are cheaper than long fibres. There are some disadvantages also for short fibre composites. Difficulty in achieving uniform dispersion, fibre breakage during processing, difficulties in handling and bonding etc. are some among them.

1.5 Factors affecting the properties of short fibre rubber composites

By controlling the factors such as aspect ratio (length to diameter ratio) of the fibre, orientation of fibres, by establishing a high degree of fibre dispersion and fibre matrix adhesion, reasonably good rubber products can be fabricated using short fibres. The rubber compounds containing short fibres have been found to possess good dimensional stability and higher green strength. The reinforcement caused by short fibres with the polymer matrix is governed by the following factors.

These include mixing of rubber compounds, fibre dispersion, fibre orientation, fibre breakage, critical aspect ratio of the fibre, fibre matrix adhesion, fibre concentration etc.

1.5.1 Mixing of rubber compounds

The conventional mixers like Banbury and open two roll mixing mill can be utilized for mixing of short fibres with rubbers as described Boustany and Coran (120). The mixing procedure may be distributive or dispersive depending on the type of the fibre used. The distributive mixing increases randomness of spatial distribution of the minor constituent within the major base material without further size reduction, while dispersive mixing serves to reduce the agglomerate size. Thus brittle fibres like glass or carbon which break severely during mixing require more distributive mixing but for organic fibres such as nylon, and natural cellulosic fibres dispersive mixing is preferred since these fibres tend to agglomerate during mixing procedure.

1.5.2. Fibre dispersion

Good dispersion of short fibres in the rubber compounds is an essential requisite for high performance composites. The naturally occurring cellulosic fibres tend to agglomerate during mixing due to hydrogen bonding. A pretreatment of fibres at times is necessary to reduce fibre-fibre interactions. Natural fibres treated either with carbon black or compositions containing latex were found to be dispersing well in the rubber matrix [121]. Fibre length has also a small effect to facilitate better dispersion. Derringer [122] has used commercially available fibres such as nylon, rayon, polyester and acrylic flock cut into smaller lengths of 8-10 cm for better dispersion.

1.5.3. Fibre breakage

The importance of fibre length and its influence on the properties of the composites were studied by several researchers [123-126]. In a composite material fibre length is a critical factor which should not be too long so that they entangle with each other causing problems of dispersion. But a very small length of fibre does not offer sufficient stress transfer from the matrix to the fibre. The severity of fibre breakage mainly depends on the type of fibre and its initial aspect ratio. Fibres like glass and carbon are brittle and they posses a low bending strength than cellulosic fibre which are more flexible and resistant to bending. For each type of fibre there exists a certain aspect ratio below which no further breakage can occur depending on its resistance to bending. The aspect ratio of glass fibre is very low compared to cellulosic fibres. If the mix viscosity is high, more shear will be generated during mixing and thus exceeding the critical bending stress of the fibre which eventually results in severe breakage. O'Connar [127] has reported the fibre breakage during mixing. The lower reinforcing ability of the glass fibre has been attributed to severe reduction in their length compared to cellulosic fibres during mixing. Murthy and De [128] suggested that the breakage of the fibre is due to the buckling effect. De *et al* [129-131] have studied the breakage of jute and silk fibres in natural rubber, and NBR and found that the breakage of silk fibres is less than that of jute fibres.

1.5.4. Critical fibre length and aspect ratio of fibre

In a perfectly oriented unidirectional continuous fibre reinforced polymer composite containing fibres of uniform radius, the rate of increase of fibre stress is proportional to the interfacial shear stress and the fibre ends have very little influence on the properties of the composites. But the fibre ends in short fibre composites play a major role in the determination of ultimate properties. The concept of critical fibre length over which the stress transfer allows the fibre to be stressed to its maximum, or at which efficient fibre reinforcement can be achieved has been used to predict the strength of the composites. Broutmann and Agarwal [132] have done a theoretical analysis on the mechanism of stress transfer between matrix and fibre of uniform length and radius and have given the following expression for the critical fibre length (l_c).

$$l_c/d = sf_u/2t_y \quad \ldots\ldots\ldots\ldots\ldots \quad 1.1$$

where d is the diameter of the fibre, sf_u is the ultimate fibre strength, and t_y is the matrix yield stress in shear. The aspect ratio (the length to diameter ratio) (l/d) of fibres is a major parameter that controls the fibre dispersion, fibre matrix adhesion that gives the optimum performance of short fibre polymer composites. If the aspect ratio of the fibre is lower than the critical aspect ratio, insufficient stress will be transferred and the reinforcement will be inefficient. Several researchers [129,133-135] have suggested that an aspect ratio in the range of 100-200 is essential for high performance fibre rubber composites for good mechanical properties. However Chakraborthy [130] has observed that an aspect ratio of 40 gives optimum reinforcement in the case of carboxylated nitrile rubber composite reinforced with jute fibre. Murthy and De [136-137] have reported that an aspect ratio of 15 and 32 are sufficient for reinforcement of jute fibre in natural rubber and styrene butadiene rubber respectively. It was reported that for synthetic fibre like polyester and nylon an aspect ratio of 220 and 170 gives good reinforcement in natural rubber vulcanizates [138-139].

1.5.5. Fibre orientation

Fibre orientation has a significant influence on the physico mechanical properties of fibre reinforced rubber composites. The preferential orientation of fibres in the matrix results in the development of anisotropy in the matrix. With respect to orientation three limits are explained as longitudinal (along machine direction), transverse (across machine direction) and random as given in figure 1.11 below. It was observed that during mixing procedure, lower the nip gap higher the anisotropy in tensile properties of the composites implying greater orientation of fibres. This has represented as anisotropy index, which reduces gradually with increasing nip gap. During processing and subsequent fabrication of short fibre polymer composites, the fibres oriented preferentially in a direction depending upon the nature of flow i.e., convergent and divergent as explained by Goettler [140].

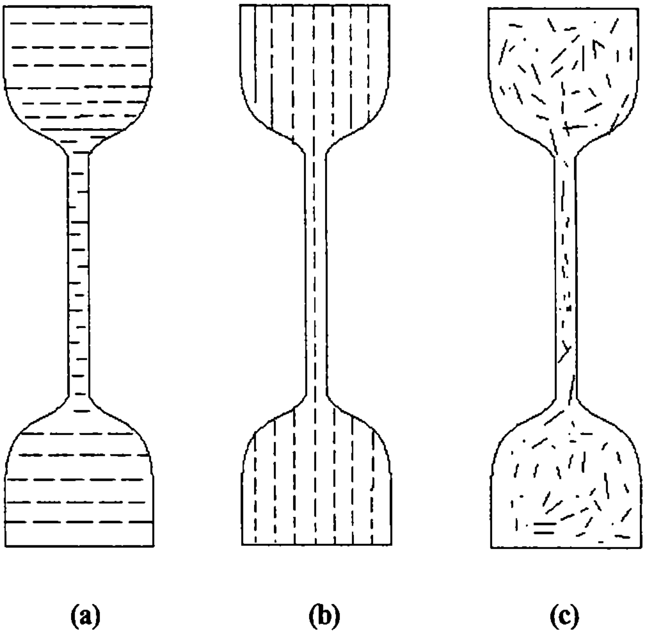

(a) (b) (c)

Figure 1.11 Schematic representation of the (a) transverse (b) longitudinal (c) random orientation of the fibres in the rubber matrix

If the flow is convergent the fibres align themselves in the longitudinal direction and if it is divergent they orient in the transverse direction. In longitudinally oriented composites the effective stress transfer from the matrix to the fibre occurs in the direction of fibre alignment and greater strength and reinforcement will be experienced by the composite. In transversely oriented composites the stress transfer takes place in a direction perpendicular to the fibre alignment and hence fracture of the sample occurs at a lower tensile stress which may be equal or lower than the strength of the matrix. Randomly oriented composite shows variable strength values i.e., strength lies between the limits of longitudinally and transversely oriented composites. These composites are essentially isotropic in plane. i.e., they have desirable properties in all directions in a plane. Longitudinally oriented composites are inherently anisotropic.

Recently Thomas and co workers [141] have evaluated the % extent of orientation from green strength measurements, by using the following equation

$$\text{Orientation }\% = \frac{S_L/S_{G,L}}{S_L/S_G + S_T/S_G} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1.2$$

Where S represents green strength of the composite and subscript L, T denotes longitudinal and transverse orientation and G represents the gum compound respectively. Many researchers have used SEM of the fracture surface to determine the fibre orientation due to the ease of sample preparation [142-143].

1.5.6. Fibre concentration

Concentration of fibres in the matrix plays a crucial role in determining the mechanical properties of the fibre reinforced polymer composites. A lower concentration of fibres gives lower mechanical strength. This has been observed not only in rubbers [144] but also in thermoplastic elastomeric matrices [145-148]. This behaviour has been attributed basically to two factors, (i) dilution of the matrix which has a significant effect at low fibre loadings and (ii) reinforcement of the matrix by the fibres which becomes of increasing importance as fibre volume fraction increases. At low fibre content, the matrix is not restrained by enough fibres and highly localized strains occur in the matrix at low strain levels causing the bond between fibres and the matrix to break, leaving the matrix diluted by non reinforcing debonded fibres. At high fibre concentrations, the matrix is sufficiently restrained and stress is more eventually distributed thus the reinforcement effect outweighs the dilution effect [149]. As the concentration of fibres is increased to a higher level the tensile properties gradually improve to give strength higher than that of the matrix. The concentration of fibres beyond which the properties of the composite improve above the original matrix strength is known as optimum fibre concentration. In order to achieve improvement in mechanical properties with short fibres, the matrix is loaded beyond this volume fraction of fibre. In rubbers this optimum fibre concentration is quite often found to lie between 25 and 35 phr. This has been observed by several researchers [150-154] for various natural and synthetic fibres in rubbers. Quite often at concentration beyond 35 to 40 phr the strength again decreases, because there is insufficient matrix material to adhere the fibres together.

1.5.7. Fibre matrix adhesion

Fibre to matrix adhesion plays a very prominent role in the reinforcement of short fibres in the polymer matrices. The fibre matrix is important in determining the mechanical, dynamic mechanical and rheological characteristics of the composites since the stress transfer occurs at the interface from matrix to fibre.

Though the mechanism of stress transfer is not clear, it has been postulated that it takes place through shearing at the fibre matrix interface. In composites with low fibre matrix adhesion Derringer [155] observed that a region of yielding occurs extending over a large portion of the strain range which is accompanied by low tensile strength and high permanent set. The fibre matrix adhesion is evaluated at the interface of the composites. Interface is an essentially bi-dimensional region through which material parameters such as concentration of an element, crystal structure, elastic modulus, density and coefficient of thermal expansion change from one side to another. There are two types of interface bonding in fibre reinforced composites. They are mechanical interface bonding and chemical bonding at the interface. In the former one a simple mechanical anchoring between the two surfaces that can lead to a considerable degree of adhesion. Moreover, any contraction of the polymeric matrix on to the fibre would result in gripping of the fibre by the matrix. Chemical bonding at the interface can occur in two ways by dissolution and wettability bonding or by reaction bonding. In wettability bonding the interaction between the fibre and the matrix occurs on an electronic scale i.e., these components come into an intimate contact on an atomic scale. Hence both surfaces should be approximately wetted to remove any impurities. In reaction bonding, transport of atoms occurs from the fibre, matrix or both to the interface. These polar surfaces can form bonding owing to the diffusion of matrix molecules to the molecular net work of the fibre, thus forming tangled molecular bonds at the interface. E.g., reaction bonding by coupling agents likes silane.

Fibre matrix adhesion has been explained by the evidences like mechanism of dry bonding system, fibre treatment and determination of the adhesion level and optimization. The dry bonding system commonly used in rubbers is the HRH system consisting of hydrated silica, resorcinol and hexa methylene tetramine to create adhesion between fibre and rubber matrix. If the fibres are not properly bonded with the matrix it will slide past each other under tension deforming the matrix to low strength. When the fibre matrix interface is sufficiently strong, the load will be effectively transferred to fibres to obtain a high performance composite. Hence the mechanism of load transfer may take place through the shear at the interface. O'Connar [127] have studied the effect of three bonding system like HRH system, and a resin bonding agent on NR composites containing various synthetic and natural fibres. To improve the adhesion between fibres and matrix various oxidative and non oxidative chemical treatments are available for natural and synthetic fibres [156-157]. Anthome *et al* and Coran *et al* [158-159] have reviewed the reinforcement of elastomers with various treated short cellulosic fibres and their mechanism of reinforcement. Several researchers have investigated the use of treated short natural fibres as reinforcing elements for rubber composites [153,154,160-163]. These include jute, coir, sisal, oil palm, bamboo etc.

A good extent of adhesion is required for high performance short fibre composites. The main problem with adhesion in short fibre rubber composites is that it cannot be measured quantitatively. The adhesion level can be qualitatively assessed from the shapes of the stress strain curves and the study of fracture surfaces using scanning electron microscope techniques. Restricted equilibrium swelling technique can also be used to evaluate adhesion [164]. But this measurement is inaccurate since the restriction may be due to the presence of fibres and the adhesion cannot be separated out. In the case of viscoelastic properties, with the increase of adhesion level a high shear will be experienced at the interface thereby the mechanical loss associated with it also increases. At elevated temperature the interface deteriorates and the value decreases. The studies so far reported proved that utilization of natural fibres as reinforcement in polymer composites offer economical, environmental and qualitative advantages. By the incorporation of natural fibres along with synthetic fibres composites with high performance can be prepared. They may find application in automotive industry as well as building industry.

1.6 Hybrid composites

The development of composite materials based on reinforcement of two or more fibres in a single matrix, which leads to the development of hybrid composites with a great diversity of material properties. Research revealed that the behaviour of hybrid composites appears to be the weighed sum of the individual components in which there is a more favorable balance between the advantages and disadvantages inherent in any composite material [165]. It is generally accepted that properties of hybrid composites are controlled by factors such as nature of matrix, nature, length and relative composition of the reinforcements, fibre matrix interface and hybrid design [166,167]. Sisal and glass fibres are good examples of hybrid composites possessing very good combined properties [168]. Due to the superior properties of glass fibres, the mechanical properties of the hybrid composites increase with increase in the volume fraction of glass fibres. Thomas *et al* [167] have studied the properties of sisal/sawdust hybrid fibre composites with phenol formaldehyde resin as a function of sisal fibre loading. It has been found that mechanical properties like tensile and flexural strength increases with sisal fibre content. This is due to the fact that the sisal fibre possesses moderately higher strength and modulus than saw dust. Mishra *et al* [169] studied the mechanical properties of sisal and pineapple /glass fibre reinforced polyester composites. They found that the addition of small amount of glass fibres to the pineapple leaf fibre and sisal fibre reinforced polyester matrix enhanced the mechanical properties of the resulting hybrid composites. Rozman *et al* [170] studied the tensile and flexural properties of polypropylene/oil palm/glass fibre hybrid composites and found that incorporation of both fibres into the polypropylene matrix improved the tensile and flexural strength by the increasing level of overall fibre loading. Junior *et al* [171] used plain weaved hybrid ramie-cotton fibres as reinforcement for polyester matrix. The tensile behaviour was dominated by the volume fraction of the ramie fibres aligned with the test direction. Cotton fibre had a minor reinforcement effect. This was due to the weak cotton polyester interface as well as poor cotton alignment. Hybrid composites containing glass fibre mat and coir fibre mat in polyester matrix was prepared by Rout *et al* [172]. Hybrid composites containing surface modified coir fibres showed significant improvement in flexural strength and reduced water absorption. Sreekala *et al* [173] prepared high performance phenol formaldehyde composite reinforced with oil palm and glass fibres. It has been found that there exists a positive hybrid effect for the flexural modulus and unnotched impact strength. Natural rubber composite reinforced with sisal/oil palm, sisal/coir hybrid fibres were prepared by Maya *et al* [174] and Haseena *et al* [175] found that the hybridization has a significant effect in improving the mechanical properties of the natural rubber composite when compared with the composite containing individual fibres.

1.7 Cellulose micro fibrils reinforced composites

Due to the biological origin, cellulose fibres display a unique structural hierarchy; they are composed of an assembly of micro fibrils which in turn consists of a number of cellulose molecules. These molecules which constitute the basic common element of all celluloses consist of long linear chains of poly-ß-(1-4)-D-glucosyl residues organized in perfect stereo regular configuration. During biosynthesis, these chain themselves get packed into slender micro fibrils of extreme length, whose diameters range from 2 to 20 nm depending upon the sample origin. Within each micro fibril, the cellulose molecules are organized in a crystalline order which results from a regular network of intra molecular hydrogen bonds. The cellulose micro fibrils which make the cellulose chains can be used as a new type of raw material that could be used in a number of applications ranging from particles for plastic reinforcement to gel forming and thickening agent has been reported [176-178]. Methods have been developed to extract micro fibrils not only from wood pulp fibres [179] but also from parenchyma cell walls that constitute major leftovers from the food industry [180]. The cellulose micro fibrils can also be employed in the preparation of nanocomposites, which can be used in various optical as well as biomedical applications. These micro fibrils on reaction with strong acids break down into short crystalline rods or cellulose micro crystals [181].

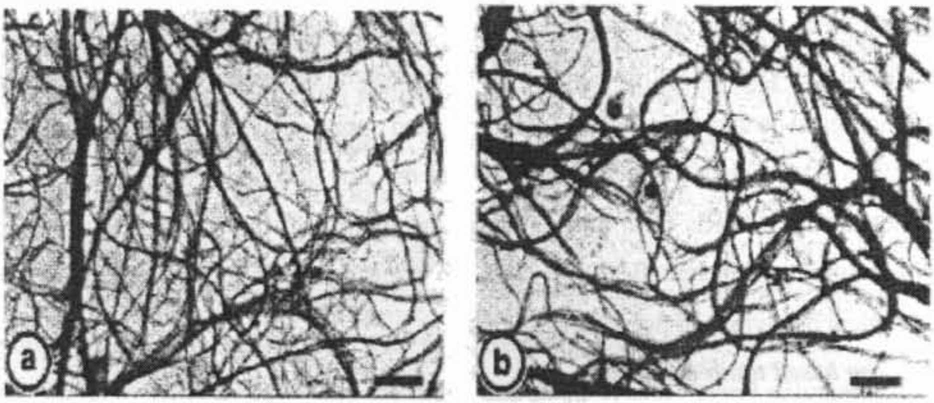


Figure 1.12 Morphology of the cellulose micro fibrils before (a) and after (b) silylation.

[Ref: Gousse' H Chanzy., Cerrada m.L., Fleury E., Polymer, (2004) 45: 1569]

Natural fibres, which are rich in cellulose, can be used as a starting material for the preparation of cellulose micro fibrils. Cellulose micro fibrils can be separated by methods like cryo-crushing where the frozen pulp is crushed with liquid nitrogen [182]. In addition, methods to mechanically homogenize and stabilize food ingredients could also be adopted for the preparation of cellulose micro fibrils [183]. The morphology of the cellulose micro fibrils before and after silylation is given in Figure 1.12 a & b.

Steam explosion is another excellent process which can be used to defibrillate the fibre bundles [184]. This method being fast and well controlled is well adapted for semi retted fibres. Enzymatic hydrolysis of cellulose is also accelerated by steam explosion. Grunert and Winter [185] developed cellulose nanocrystals from bacterial cellulose which are modified by trimethylsilynation. The untreated and the trimethyl silylated crystals were exploited as the particulate phase in nanocomposites with cross linked poly dimethyl siloxane as the matrix material. They found that these cellulose nanocrystals could be successfully incorporated into various polymer matrices for the preparation of nanocomposites. The untreated and surface silylated fibre samples consists of a random dispersion of long and rather stiff micro fibrils that occur individually or packed into bundles. The mild silylated micro fibrils, which had some morphological features as those of the untreated samples, were dispersible into non polar solvent to yield stable suspensions that did not flocculate. Gousse *et al* [186] developed micro fibrils from natural fibres and found that the silylated micro fibrils have acquired an inherent flexibility with the result that their suspensions present the rheological behaviour of polymer solutions.

Cellulose based nano composites

The concept of nanostructured material design is gaining widespread importance among the scientific community [187]. The strong reinforcement effects at low volume fraction resulted in tremendous interest from the industry and research circles. The concept of cellulose nanocomposites for load bearing applications is fairly new.

Property enhancements are expected due to higher Young's modulus of pure cellulose reinforcement and finally distributed reinforcing microfibrils. A major problem in the commercial use of cellulose microfibrils in structural materials is the disintegration of cellulose from plant cell wall at reasonable cost and without severe degradation. Another major problem is dispersion of cellulose micro fibrils in a polymer matrix. Cellulose nanocomposites are usually fabricated by utilizing microfibrils of 10-50 nm on width as reinforcement in a polymer matrix. Although many studies provide detailed knowledge regarding the morphology and crystallography of different types of cellulose, the Young's modulus of microfibrils from different sources and subjected to different types of hydrolysis is seldom discussed. The research group at CERMAV-CNRS has presented numerous studies based on cellulose whiskers reinforced nanocomposites [188]. Another area of interest is that of microfibrillated cellulose [MFC] nanocomposites. A review of the recent research into cellulose whiskers, their properties and their application in nanocomposite field has been presented by the same group [189]. Recently scientists achieved uniform pyrrole nanocoating on natural cellulose fibres without disrupting the hierarchical network structures of individual cellulose fibres by means of polymerization induced adsorption [190]. Researchers have also reinforced natural rubber with naofibres of sepiolite [191]. The level of reinforcement was assessed from mechanical and orientation behaviour. Nanoscale modified plant structures such as paper or bast fibres also present a different approach to preparation of nanocomposites structures. An interesting study focusing on preserving the microfibril organization of wood veneer in composites was reported [192]. The basic idea was to increase the volume fraction of cellulose microfibrils by partially removing the lignin and hemicellulose wood polymers and by compressing the veneer. Phenol formaldehyde (PF) was used to preserve the compressed microstructure of the material and to bond micro fibrils. Researchers have looked into development of cellulose nano composites based on bacterial cellulose and cellulose acetate butyrate [193]. Bacterial or microbial cellulose have also found their way as reinforcement in composites [194]. Though the microbial cellulose composites have evoked widespread interest, the industrial use of microbial cellulose composites requires the development of efficient large scale fermentation technology.

1.8 Green Composites

Significant research efforts are currently being spent in developing a new class of fully biodegradable green composites by combining natural fibres with biodegradable polymers [195-200]. These composites are environment friendly, fully degradable and sustainable. At the end of their life they can be easily disposed of or composted without harming the environment. The life cycle of a green composite is given in Figure 1.13. The green composite may be used effectively in many applications such as mass produced consumer goods with short life cycles of one or two years (non durable) or products indented for one term or short term (few times) use before disposal. A variety of natural and synthetic biodegradable resins are available for use in green composites. Most of these resins degrade through enzymatic reactions when exposed to compost environment. Many will also degrade in moist outdoor environments through microbial/bacterial attack. A review of biocomposites highlighting recent studies and developments in natural fibres, biopolymers, and various surface modifications of natural fibres to improve fibre/matrix adhesion is presented by Mohanty *et al* [201]. Goda *et al* used ramie fibres in the form of low twist yarns and starch based resins to obtain green composites [202]. These composites had tensile strength in the range of 250 MPa and would be useful for structural applications. Mohanty *et al* [203] reported that plasticized polar cellulose acetate was found to be a better matrix for hemp fibre and thus exhibited improved physico mechanical properties. Incorporation of a high content of natural fibres of about 50% in the biocomposite system along with suitable surface modification of fibres and by the use of coupling agents can generate superior bio composites.

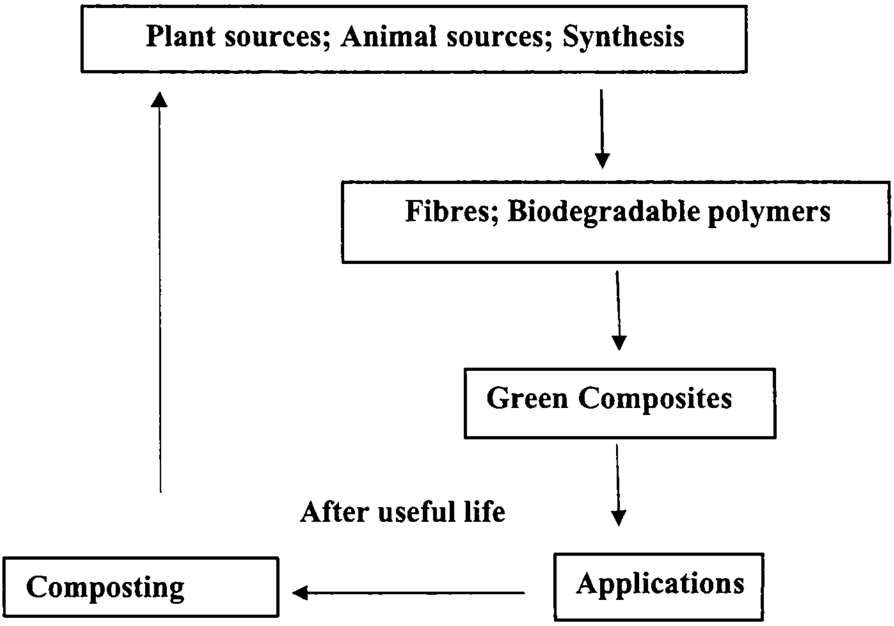


Figure 1.13 Typical life cycle of green composite

[Ref: Netravali A.N., Chabba S., Materials Today, April (2003) 22.]

Mwaikambo *et al* [204] studied the mechanical properties of hemp fibre reinforced cashew nut shell liquid composites. They found that combination of naturally occurring lignin containing fibres with natural monomers containing similar phenolic compounds provides a compatible interaction on polymerization and hence improved mechanical properties. Oksman *et al* [205] used flax fibres as reinforcement in polymers based on renewable raw materials like polylactic acid [PLA]. The mechanical properties of PLA were found to be comparable to PP/flax composites. The pure PLA has a tensile strength of 50 MPa and a modulus of 3.4 GPa. The composite had a significant improvement in tensile modulus [8.2 GPa]. The addition of flax fibres slightly improved the tensile strength [51 MPa] which is an indication of poor adhesion between flax fibres and the matrix.

1.9 Applications of short fibre reinforced rubber composites.

Short fibres have the potential for reinforcing low performance tires.In automotive and truck tires they find application in better abrasion resistance for the chafer strip and in improved cut resistance to treads especially for trucks and OTR vehicles. As short fibres have higher green strength and cut, tear and puncture resistance they can be used for sheeting. Shot fibres can be utilized as the sole reinforcement for a moderate performance hose or as auxillary reinforcement with cord constructions. They can provide stiffening to soft inner tubes for the application of metal braids and can extend hose life by bridging the stresses across weaker filaments. Other uses are belts diaphragms, gaskets, roofing, hoses, dock and ship fenders etc. Short fibres can reinforce and stiffen rubber in fenders and other impact applications in accordance with simpledesign equations.

1.10 Isora fibre

Various natural fibres like sisal, coir, jute, oil palm, bamboo etc have been proved to be a better reinforcement in rubber matrix. Incorporation of natural fibres resulted in better long term mechanical performance of elastomers. However studies on isora fibre as reinforcement have not yet been reported. Isora is a bast fibre presented in the bark of *Helicteres isora* plant. Two varieties of the plant are distinguished, *tomentosa* and *glabrescens* in which in the former the bottom side of the leaves is glabrous and in the latter both sides of the leaves are glabrous. The plant occurs as undergrowth especially as a secondary growth in forests. Seed sown during the rainy season easily propagates it. Roots stem and fruits of the plant are used for medicinal applications. The stem bark is exploited for the fibre. The best type of fibre is obtained when the plants are 1-1.5 years old; plants older than 2 years yield coarse and brittle fibre. Stalks can be harvested annually for fibre extraction from regenerated shoots. It occurs as undergrowth, especially as a secondary growth in forests. It coppices well shooting up rapidly when cut or burnt back. In some places the plant forms dense, almost impenetrable thickets covering large areas practically to the exclusion of other growths. The fibre which is present in the inner bark of the plant is polygonal in cross section with a circular or oval lumen. The cell wall of the fibre element is thick and lignified. The fibre is extracted from the stem by retting the stem in running water for 18-24 days. The retted stalks were taken out of the water, beated gently with wooden mallets and fibres are peeled off, washed with water and dried. Fibre of good quality and colour is obtained when retting is effected in running water.

Properties of natural fibres depend mainly on the nature and age of the plant, and the extraction method used. The data of production of isora fibre are not available. According to the estimate made in 1951 the yield of fibre is 50-60 md per acre [206]. The fibre is used mostly for rough sacking or canvas and as cordage for sewing gunny bags and cattle harness. It is especially valued for container bags and used as pans in lever weighing systems. The quality of fibre is amenable to considerable improvement. By selecting stalks of equal age and maturity, and retting them under proper conditions and switching the dried fibre on suitable mechanical appliances, it is possible to obtain fibre which can be spun into good yarn and woven into canvas and other durable fabrics of excellent quality. Woven materials can be dyed and printed in attractive designs for making shopping bags. Ropes and cordages made of the fibre are better and smoother than coir products [207]. Stalks and twigs of the plant with and without bark are also suitable for the manufacture of writing or printing paper in combination with long fibre pulp of bamboo species [208]. Fruits disperse during April to June, and about 620 dried seeds weigh I Kg. The seeds sown during rainy season will germinate and grow without much care or other inputs. The total turn over of the dried fruits of the plant was about 1200 Kg in one year as recorded by Kerala state SC&ST Federation 1998. The cost of the seed was around Rs 1.50 per Kg [209]. Certain quantity of seed collected from forest areas might have also gone to the general market, on which there is no quantified data available.

1.11 Scope and objectives of the present work

The present work aims at investigating the prospect of using isora fibre as reinforcement in natural rubber matrix. Research work is going on with other natural fibres like jute, sisal, oil palm, banana, flax etc. In order to achieve this major objective several fundamental investigations on the fibre and its composites have been undertaken. Helicteres isora plant from which the fibre is separated is abundantly available in India especially in Kerala. Currently the fibre is being utilized for the preparation of ropes, cordages, gunny bags etc. These fibres if put to better use, as reinforcement in polymers will definitely contribute to the development of the economy of the country and will open up new avenues for our natural resources. The factors which affect the properties of natural fibres are the cellulose content and microfibrillar angle. Isora fibre has relatively high cellulose content and a low micro fibrillar angle. These two are the desirable properties in a natural fibre to be used as reinforcement in polymer composites. Earlier reports have shown that the natural fibres are susceptible to moisture absorption, thermal degradation and biodegradation. Therefore strategies need to be worked out to overcome these limitations.For the successful design of a composite material from isora fibre and natural rubber several parameters like fibre aspect ratio, fibre orientation, chemical modification of the fibre surface, fibre matrix adhesion etc. that influences the performance of a short fibre composite have to be considered and to be optimized. Careful analysis of the literature indicates that no systematic studies have been reported about the use of isora fibre as reinforcement in polymers. The major attraction of this work is that both the matrix and the fibre are naturally available. Hence products based on this work will be both cheaper and sustainable.

The following aspects of isora and isora /natural rubber composites are proposed to be evaluated

(i) Separation and characterization of isora fibre.

Processing and evaluation of the physical and chemical properties of isora fibre is proposed to be done in detail. Chemical composition, surface morphology and thermal stability of the fibre are also proposed to be analyzed.

(ii) Chemical modification of isora fibre surface for improved interaction with the polymer matrix.

The polar natural fibre and non polar polymer matrix are likely to end up in relatively weak bonding. The bonding can be improved to an extent by varying the polarity of the fibre surface. Treatments with various chemical reagents like alkali, silane etc can be used effectively in order to change the surface polarity and thereby improve the fibre matrix interaction. In view of this, isora fibre surface is proposed to be modified by silane and alkali treatments. Effect of gamma radiation on the surface properties is also proposed to be investigated.

(iii) Characterization of the modified fibre surface.

Techniques like scanning electron microscopy, atomic force spectroscopy, and infrared spectroscopy are proposed to be tried characterize the untreated and treated fibre surface. The changes in crystallinty on chemical treatment are proposed to be studied by wide angle X- ray diffractometer. Changes in the mechanical performance of the fibres on various modifications are also proposed to be studied.

(iv) Thermal degradation behaviour of the modified fibre.

The examination of the thermal degradation behaviour of the untreated and treated fibre is proposed to be done by thermogravimeric and differential thermal analysis like TG/DTG, DSC, and DTA.

(v) Preparation of composites of isora and natural rubber

Fibre aspect ratio, fibre orientation, fibre loading and fibre matrix adhesion control the ultimate properties of the fibre rubber composites. Fibre length should not be too high so that individual fibres do not entangle or not too short so that effective reinforcing action will not be attained. So a critical aspect ratio for the fibre is proposed to be determined. Short fibre composite exhibit anisotropy in mechanical properties because of the preferential fibre orientation. Green strength measurements, mechanical properties and anisotropic swelling measurements are proposed to be used to estimate the extent of fibre orientation. A tricomponent bonding system and fibre surface modification is proposed to be used to produce better fibre matrix adhesion.

(vi) Macroscale examination of the composites to evaluate the fibre matrix interaction.

The mechanical properties of a composite are clear indication of the strength of the interface and thereby fibre matrix interaction. The fracture mechanism as evidenced by SEM and the value of strength characteristics point to the fibre matrix interaction. Therefore a comprehensive analysis of the macroscopic properties of the composite is proposed to be undertaken. The extent of interfacial adhesion between the fibre and rubber is also proposed to be analyzed by the restricted equilibrium swelling in various solvents.

(vii) Fibre breakage analysis.

During processing fibres may undergo breakage hence analysis is also proposed to be made to evaluate the extent of breakage.

(viii) Dynamic mechanical analysis.

Fibre matrix interaction in composites has been studied in detail based on the response of the material when subjected to dynamic mechanical analysis. The nature of the damping curves and modulus curves are likely to be a good indication of the fibre matrix interaction and the nature of the interface.

(ix) Ageing studies

The degradation behaviour of isora/NR composites on exposure to gamma radiation, ozone and heat is proposed to be studied. The tensile properties of the unaged and aged samples will be compared. The effect of fibre matrix adhesion on ageing and tensile fracture mechanism of the aged composites is proposed to be studied using an optical microscope and scanning electron microscope.

(x) Low temperature curing studies.

At higher temperature fibre and rubber show a tendency to degrade. Hence a novel low temperature curing accelerator is also proposed to be tried and the properties of the composites cured at low temperature are proposed to be compared with that of the composites cured using conventional accelerator system.

2. REFERENCES

1. *Encyclopedia of Polymer Science Engineering,* H.F. Mark Edition,JohnWiley and Sons, New York (1985)
2. Tjong S.C.,Meng Y.Z., *J Appl Polym Sci*, (1999) **72**: 501.
3. Gonzalez P.I.,Yong R.J., *J Mater Sci*, (1998) **33**: 5715
4. Thomas M.P., Winstone M. R., *J Mater Sci* ,(1998) **33**: 5499
5. Amash A., Zugenmaier P., *Polymer Bulletin*, (1998) **40**:251
6. Kishore., Venkatraaman S., *J Appl Polym Sci*, (1998) **67**:1565
7. Raghavan J., Wool R. P., *J Appl Polym Sci*, (1999) **71**: 775
8. Oya N., Hamada H., *J Mater Sci*, (1998) **33**: 3407.
9. Srivastava V.K., Hogg p.J., *J Mater Sci*, (1998) **33**:1119.
10. Zheng Q., Song Y.H.,Yi X.S., *J Mater Sci Lett* , (1999)**18**: 35
11. Leaity M.A., Smith P.A., Curtis P.T., *Composites,* (1992) **23**: 387

12. Richardson T., *Composites-a design guide,* Industrial Press Inc.,200 Madison Avenue,Newyork,(1987)
13. Warner S.B., *Fibre Science.*,Prentice Hall,Engle wood Cliffs, New Jersey,(1995)
14. Mallick P.K., *Fibre reinforced composite materials, manufacturing and design.*, Marcel Dekker,Inc., Newyork,(1988) Ch. 1., p.18
15. Nielsen L.E., *Mechanical properties of Polymers and composites*, Vol 1. Marcel Dekker (1974)
16. Cook J.G., *Hand book of Textile fibres and Natural fibres*, 4th Edn.Morrow Publishing,England.(1968).
17. Rubin I.I, *Plastics Materials Technology,*Wiley Interscience,*(1990)*
18. Milewski J.V., Katz H.S., *Handbook of Reinforcements for Plastics*,Van Nostrand Reinhold (1987
19. Gachter R., Muller H., *Plastics Additives Handbook*, Hanser Publishers (1990)
20. Sathyanarayana K.G., Kulkarni A.G., Rohtgi p.k., *J Scientific and Industrial Res,*(1983) **42**: 425
21. Payen A., Hebd C.R., *Seances Acad Sci*, (1938) **7**: 1052
22. Woodcock C., Sarko A., *Macromolecules,*(1980) **13**: 1183
23. Sarko A., Muggli R., *ibid* ,(1974) **7**: 480.
24. Kritschewsky G.E.,*Chemische Technology Von Textilmaterialien*, Moskau, Legprombitisdat(1985).
25. Ammalahti E., Brunow G., Robert D., *J Agri Food Chem*,(1998) **46**: 5113
26. Xiao B., Sun X.F., Sun R.C., *Polym Deg Stab*,(2001) **74**: 307.
27. Bledzki A.K., Gassan J., *Prog Polym Sci* ,(1999) **24**: 221
28. Hill S., *New Scientist* (1997) p 36
29. Satyanarayana K.G., Pillai S.G.K., *Handbook of Ceramics and Composite*

Cheremisinoff N.P., Edition Marcel Dekkar, New York Vol 1 (1990).

30. *The Wealth of India – A Dictionary of Indian Raw materials and Industrial products.,* Published by CSIR, New Delhi (1959) **5:** 27-29.
31. Wright J.R., Mathias L.J., *J Appl Polym Sci*, (1993) **48:** 2241.
32. Hednberg P., Gateholm P., *J Appl Polym Sci*, (1995)**56:** 641.
33. Maldas D., Kokta B.V., *J Comp Mater*, (1991) **25:** 375.
34. Maldas D.,Kokta B.V., *Polym Plast Technol, Eng*,(1990) **29**: 419.
35. Prasanth kumar R., Thomas S., *Bull Mater Sci*, (1995) **18(8):** 1021.
36. Geethamma V.G., Mathew K.T., Thomas S., *Polymer*, (1998) **39**: 1483
37. Ismail H., Rosnah N., Rozman H.D., *Polymer*, (1997) **38(16):** 4059.
38. Ismail H., Shuhelmy S., Edyham M.R., *Eur Polym J* ,(2002) **38**: 39
39. Harikumar K.R., Joseph K., Thomas S.,*J Reinf plast Comp,* (1999) **18**: 346.
40. Yamini S.A.K., Ahmad A.J.,Nasir N.M., *Proc. of Int Symposium on Bio Composites and Blends based on natural fibres,* (1994) p.135
41. Rowel R.M., Banks W.B., *Gen.Tech.Rep.FPL-GTR-50; USDA Forest service*, Forest Products Laboratory, Madison, WI (1985) 24
42. Feughelman M., Nordan P.J., *J Appl Polym Sci*, (1962) **6:** 670.
43. Joly C., Gauthier R., Coubles E.S., *J Appl Polym Sci*, (1996) **61:** 57.
44. Schniewind A.P., Wood and fire, M.B. Bever (ed), *Encyclopedia of Materials Science and Engineering,* Vol.7, 1st edition, Pergamon Press,Oxford (1986).
45. Shukry N., Girgis B.S., *Polym Plast Technol Eng*, (1992) **31**: 541.
46. Beall F.C., Thermal degradation of wood, M.B. Bever (ed), *Encyclopedia of Materials Science and Engineering,* Vol.7, 1st edition, Pergamon Press, Oxford (1986).
47. Tinh N., Eugene Z., Edward M.B., *J Macromol Sci*, (1981) **C20** : 1
48. Tinh N., Eugene Z., Edward M.B., *J Macromol Sci*, (1981) **C21** : 1

49. Gassan J., Bledzki a.K., *J Appl Polym Sci*, (2001) **82**; 1417.
50. Sreekala M.S., Thomas S., *J Reinf Plast Comp*, (1998) **17**: 579.
51. Pothen L.A, Thomas S., Oommen Z., *Polimetry*, (1999) **44**: 750.
52. Prasanthkumar R., Thomas S., *Polym Int*, (1995) **38**: 173.
53. Geethamma V.G.,Joseph R., Thomas S., *J Appl Polym Sci* ,(1995) **55**: 583.
54. Baiardo M., Frisoni G., Scandola M., *J Appl Polym Sci*, (2002) **83**: 38.
55. Ansell M.P.,Eichhorn S.J.,Baillie C.A., *J Mater Sci* ,(2001) **36**; 2107
56. Ge X. C., Li X.H., Meng Y.Z., *J Appl Polym Sci*, (2005) **93**: 1804
57. Alvarez V.A., Vazquez A., *Polym Deg Stability*, (2004) **84**:13.
58. Hatakeyama H., Nakayachi A., *Comp Part A*, (2005) **36**: 698.
59. Rowell R.M., The *Chemistry of Solid Wood*, Adv. Chem. Ser 207: American Chemical Society, Washington.DC (1985).
60. Vajrasthira C., Amornsakchai T., *J Appl Polym Sci* ,(2003) **87:** 1059
61. Jagannathan N., *Polym Plast Technol Eng*, (1975) **5(1):** 107
62. Schwartz M.M.,*Composite Materials Hand book*, Newyork, McGraw Hill(1984)
63. Sreekala M.S., Thomas S., Neelakandan N.R, *J Polym Eng*, (1997) **16**: 265.
64. Brahmakumar M., Pavithran C., Pillai R.M., *Comp Sci Technol* (2005) **65**: 563.
65. Ivarez P., Blanco C., Santamary'a R., Granda M., *Comp Part A*, (2005) **36**: 649.
66. Wong S., Shanks R., Hodzic A., *Comp Sci Technol*, (2004) **64**: 1321.
67. Hristov V.N., Lach R., Grellmann W., *Polym Testing*, (2004) **23**: 581.
68. Cheng T.H., Jones F.R., Wang D., *Comp Sci Technol*, (1993) **48**: 89.
69. Drazal L.T., Madukar M., *J Mater Sci*, (1993) **28**: 569.
70. Felix G.M., Gatenholm P., *J Appl Polym Sci*, (1991) **42**: 609.
71. Felix G.M., Gatenholm P., *J Appl Polym Sci*, (1993) **50**: 699.

72. Khalil H.P., Ismail H., Rozman H.D., *Europ Polym J*, (2001) **37**: 1037
73. Mani P., Satyanarayan K.G., *J Adhesion Sci Technol*, (1990) **4**: 17.
74. Liao B., Huang Y., Cong G., *J Appl Polym Sci*, (1997) **66**: 1561.
75. Rowell R.M., ACS Proceedings, *Polym Mater Sci Eng*, (1992) **67**: 461.
76. Rowell R.M., Clemson C.M, *Proceedings of the 26th International particle board/Composites Symposium,* WA, (1992) 251.
77. Bledzki A.K., Gassan J., *J Appl Polym Sci,* (1996) **59**: 1329.
78. Mohanty A.K, Singh B.C., *J Appl Polym Sci,* (1987) **34:** 1325.
79. Muzumdar P., Sanyal S., Dasgupta b., *Indial J Fibre Technol*, (1994) **18**: 286.
80. Anderson M., Tillman A.M., *J Appl Polym Sci*, (1989) **37**: 3437.
81. Sahoo P.K., Samantaray H.S., Samal R.K., *J Appl Polym Sci*, (1986) **32**: 5693
82. Samantaray H.S., Samal R.K., *J Appl Polym Sci*, (1986) **37**: 3085.
83. Mannan-Kh M.,Latifa B, *Polymer*, (1980) **21**: 777.
84. Huque M.M., Habibuddowla M.D., Mohamood A.J., *J Polym Sci, Polym Chem Ed,* (1980) **18:**1447.
85. Samantaray H.S., Samal R.K., *J Macromol Sci, Macromol Chem Phy,* (1986) C26:81.
86. Lu J.Z., Wu Q., Negulescu I.I., *J Appl Polym Sci,* (2005) **96**: 93.
87. Thielemans W., Wool R.P., *Comp Part A,* (2004) **35**: 327.
88. Harper D., Wolcott M., *Comp Part A*, (2004) **35**: 385.
89. Abdulmouleh M., Bou S., Duarte A.P., *Inter J Adhesion*, (2004) **24**:43.
90. Hernandez E.G., Claverie A.L., *Polym Comp*, (2004) **25(2)**: 34.
91. Lu J.Z., Wu Q., Negulescu I.I., *Comp Interfaces*, (2005) **12(1)**:125.
92. Saheb D.N., Jog J.P., *Advances in Polym Technol,* (1999) **18**: 351
93. Pedro J., Manuel De H.F., Vega J.A., *J Appl Polym Sci*,(1997) **21**: 197

94. Mohd Ishak Z.A., Aminullah A., IsmailH, Rozman H.D., *J Appl Polym Sci,* (1998) 68:2189.
95. Ismail H., Shuhelmy M.R., *Euro Polym J,* (2002) **38**: 39.
96. Krysztafkiewicz A., Domka L., *Plast Rubb Proc Appl,* (1986) **6**: 197
97. Mwaikambo L.Y., Ansell M.P., *J Appl Polym Sci,* (2002) **84**:2168.
98. Gassan J., Bledzki A.K., *Comp Sci Technol*, (1999)**59**:1303.
99. Bisanda E.T.N., Ansell M.P., *Comp Sci Technol,* (1991) **41**:165.
100. Aziz S.H., Ansell M.P., *Comp Sci Technol,* (2004) **64**:1219.
101. Samal R.K., Rout S.K., Mohanty M., *J Polym Mater,* (1995) **12**: 229.
102. Hill C.A.S., Akhalil H.P., *J Polym Sci,* (2000) **78**: 1685.
103. George J., Bhagawan S.S., Thomas S., *Comp Interfaces*, (1998) **5**: 201.
104. Sreekala M.S.,Joseph R., Thomas S., *App Comp Mater,* (2000) **7**: 295
105. Mohanty A.k., Khan M.A., *Comp Sci Technol,* (2000) **60**: 1115.
106. Calado V., Barreto D.W., Almeida J.R.M., *Polym Comp*, (2003) **2**:1.
107. Rozman H.D., Kumar R.N., Ismail H., *Euro Polym J* ,(2000) **36**: 1483.
108. Prasanth kumar R, Thomas S., Polym*International*, (1995) **38(2)**: 173.
109. Geethamma V.G, Thomas S., *Int J Polym Mater,* (1996) **32**: 147.
110. Sreekala M.S., Thomas S., *Comp Sci Technol*, (2003) **63**: 861.
111. Joseph P.V., Joseph K., Thomas S., *Comp Sci Technol,* (2002) **62**: 1357.
112. George J., Bhagawan S.S., Thomas S., *Comp Sci Technol,* (1998) **58**:1471.
113. Pothen L.A.,Neelakandan N.R.,Thomas S., *J Reinf Plast,* (1997) **16**: 8
114. Rogers J.W., *Rubber World,* (1981) **27**: 183.
115. Goettler l.A., Lambright A.J.,Leib R.I., *Rubb Chem Technol* ,(1981) **54**: 277.
116. Abrate S., *Rubb Chem. Technol*, (1986) **59:** 384.
117. Chakraborthy S.K., Setua D.K., De S.K., *Rubb Chem Technol,* (1982) **55**:1286.
118. Moghe S.R., *Rubb Chem Technol,* (1974) **47**: 1074.

119. Vincent J.F.V *Appl Comp Mater*, (2000) **7**: 269.
120. Boustany K., Coran Y., *US Patent No.33 679 364* (1972)
121. Dunnom D.D., Wagner M.P., Derringer G.C., Chemical Division, PPG Industries Inc., *US Patent No.3746669* (1973).
122. Derriger D.C., *Rubber World*, (1971) **45**: 165.
123. Broutman L.j., Aggarwal B.D., *Analysis and performance of fibre composites*, Soc.Plast. Ind., John Wiley and Sons,Newyork (1980)
124. Monette L., Anderson M.P., Grest G.S., *Polym Comp, (*1993) **14(2)**: 101.
125. Termonia Y., *J Mater Sci Lett*, (1993) **12**: 732.
126. Rosen B.W.,*Fibre Composite Materials*, American Society for metals, Metal Park, Ohio (1965)
127. O'Connor J.E., *Rubber Chem Technol,* (1977) **50**: 945.
128. Murthy V.M., Bhowmick A.K., De S.K., *J Mater Sci*, (1982) **17**: 709.
129. Setua D.K., De S.K., *Rubb Chem Techno*, (1983) **56**: 808.
130. Chakraborty S.K., Setua D.K., De S.K., *Rubb Chem Technol,* (1982) **55**: 1286.
131. Setua D.K., De S.K., *J Mater Sci*, (1984) **19**: 983.
132. Broutman L.J., Aggarwal B.D., *Analysis and performance of fibre composites*, Soc.Plast. Ind., John Wiley and Sons,Newyork (1980)
133. O'Connar J.E., *Rubb Chem Technol*, (1974) **47**: 396.
134. Boustany K., Arnold R. L., *J Elasto Plast*, (1976) **8**: 160.
135. Boustany K., Coran A.Y., *US Patent No. 3 397 364* ,to Monsanto C (1972)
136. Murthy V.M., De S.K., *J Appl Polym Sci*, (1982) **27**: 4611.
137. Murthy V.M., De S.K., *J Appl Polym Sci,* (1984) **29**: 1355
138. Ibarra L., Chamorro A.C., *J Appl Polym Sci,* (1991) **43**: 1805.
139. Rueda L.I., Chamorro A.C., *J Appl Polym Sci*, (1989) **37**: 1197.
140. Goettler L.A., Lambright A.J.,Leib R.I., *Rubb Chem Technol* ,(1979) **52**: 838

141. Geethamma V.G., Joseph R., Thomas S., *J Appl Polym Sci,* (1995) **55**: 583.
142. Varghese S., Kuriakose B., Thomas S., *Ind J Nat Rubb Res,* (1992) **5(1)**:18
143. Joseph K., Thomas S., *Mater Lett,*(1992) **15**: 224
144. Prasanth Kumar R., Thomas S., *J Appl Polym Sci*, (1995) **58**: 597.
145. Kutty S.K.N., Nando G.B., *J Appl Polym Sci*, (1991) **43**: 1913.
146. Roy D., Bhowmick A.K., De S.K., *Polym Eng Sci*, (1992) **32**: 971.
147. Senapati A.K., Nando G.B., *Int J Polym Mater,* (1988) **12**: 73.
148. Senapati A.K., Nando G.B., Kutty S.K.N., *Int J Polym Mater,* (1989) **12**: 203
149. Kutty S.K.N., Nando G.B., *J Appl Poym Sci,* (1991) **43**: 1913.
150. Varghese S., Kuriakose B., Thomas S., *J Adhes Sci Technol*,(1994) **8**:235
151. Geethamma V.G., Thomas S., *Int J Polym Mater*, (1996) **32**: 147.
152. Prasanth Kumar R., Thomas S.,*Bull Mater Sci,(*1995) **18(8)** :1021
153. Arumugham N., Tamaraselvy K.,*J Appl Polym Sci*, (1989) **37** : 2645
154. Ismail H., Edyham M.R., Wirjosentono B., Polymer *Testing,* (2002) **21**:139.
155. Derringer D.C., *J Elast Plast,* ((1971) **3**:230
156. Chawla K.K., *Composite Materials*, Spriger Verlarg,Newyork(1987)
157. Richardson M.O.W., *Polymer Engineering composites,* Applied Science Publishers,London (1977) p. 1
158. Anthonie G., Arnol R.L., Boustany K., *Eur Rubb J, (*1975) **157**: 28.
159. Hamed P., Coran A.Y., *Additives for Plastics*, Seymour Edn. Academic Press,Newyork (1982)
160. Murthy V.M., De S.K., *J Appl Polym Sci*,(1984) **29**: 1355
161. Varghese S., Kuriakose B., Thomas S., *Rubber Chem. Technol,* (1997)**63**: 550.
162. Ismail H., Rozman H.D., Ishiaku U.S., *Polym International,* (1997) 43: 23.
163. Geethamma V.G., Joseph R. Thomas S., *Polymer,* (1998) **39**: 1483.

164. Das B., *J Appl Polym Sci*, (1973) **17**: 1019.
165. Hartikainen J., Hine P., Friedrich K., *Comp Sci Technol,* (2005) **65**: 257.
166. Idicula M., Neelakandan N.R., Thomas S., Oommen S., Joseph K., *J Appl Polym Sci,* (2005) **96** : 1699
167. Idicula M., Malhotra S.k., Thomas S., *Comp Sci Technol,* (2005) **65**:106.
168. Kalaprasad G., Joseph K., Thomas S., *J Comp Mater,* (1997) **31**: 509.
169. Mishra S., *Comp Sci Technol,* (2003) **63**: 1377.
170. Rozman H.D., Ismail H., *Euro Polym J,* (2001) **37**:1283.
171. Junior C.Z.P., Fonseca V.M., Monteiro S.N., *Polymer Testing*, (2004) **23**:131.
172. Rout J., Misra M., Tripathy S.S., Mohanty A.K., *Comp Sci Technol,* (2001) **61**: 1303.
173. Sreekala M.S., Neelakandan N.R., Thomas S., *J Polym Eng*, (1997) **16**: 265.
174. Maya Jacob, Varghese K.T., *Comp Sci Technol*, (2004) **64**: 955.
175. Haseena A.P., Unnikrishnan G., Thomas S., *Comp Interf,* (2004) **11(7)**:489.
176. Malainine M.E., Dufresne A., Mahrouz M., *Comp Sci Technol,* (2005)**65**: 520.
177. Gousse H Chanzy., Cerrada M.L., Fleury E., *Polymer*, (2004) **45**: 1569
178. Okubo K., Fujii T., Yamamoto Y., *Comp Part A,* (2004) 35: 377
179. Turbak A.F., Snyder F.W., Sandberg K.R., *Appl Polym Sci*, Appl Polym Symp,(1983) **37**: 815
180. Weibel M.K., *U.S.Patent 4 831 127* SBP Inc. (1989).
181. Dufresne A., Cavaille J.Y., Vignon M.R., *J Appl Polym Sci,* (1997) **64**: 1185.
182. Dufresne A., Dupeyre D., Vignon M.R., *J Appl Polym Sci,* (2000) **76**: 2080.
183. Turbak A.F., Snyder F.W., Sandberg K.R., *U.S.Patent 4.374.702* (1983)
184. Okubo K., Fujii T., Yamamoto Y., *Comp Part A*, (2004) **35**: 377.

185. Grunert M., Winder W.T., *Cellulose*, (2000) 7: 21.
186. Gousse H Chanzy., Cerrada M.L., Fleury E., *Polymer,* (2004) **45**: 1569
187. Berglund L., *Natural fibres, Biopolymers and Biocomposites*, (2005) Edited by Mohanty A.K., Misra M., CRC Press, 808.
188. Favier V., Chanzy H., Cavaille J.Y., *Macromolecules*, (1995) **28:** 6365.
189. Samir M.A.S.A., Alloin F., *Biomacromolecules,*(2005) **6(2):** 612
190. Huang J., Ichinose I., *Chemical Communications,* (2005) **13:** 1717
191. Bokobza L., Chauvin J.P., *Polymer*, (2005) **46(12):** 4144
192. Yano H., Hirose A., Collins P.J., *J Mater Sci Lett* ,(2001) **20:** 1125
193. Grunert M., Winter W.T., *Polym Environ,* (2002) 10:27
194. Tokoh C., Takabe K., Fujitha M., *Cellulose,* (2002) 9: 65
195. Burguen'o R., Mohanty A.K., Mehta G., *Comp Part A* ,(2005) **36**:581.
196. Kanie O., Tanaka H., Kitaoka T., *J Appl Polym Sci,* (2005) **96**: 861.
197. Averous L., Boquillon N., *Carbohydrate Polymers,* (2004) **56**:111
198. Maezzoli A., Calo E., Mele G., *Comp Sci Technol,* (2004) **64**: 839.
199. Alvarez V.A., ruscekaite R.A., Va'zquez A.A., *J Comp Mater,* (2003) **37:** 37.
200. Tserki V., Matzinos P., Panayiotou C., *Comp Part A,* (2005) **36**:965.
201. Mohanty A.K., Misra M., *Comp Interfaces,* Sp Issue. (2001) **8(5):** 313.
202. Goda K., *International workshop on green composites*, (2002) **8**
203. Mohanty A.K., Misra M., Drzal L.T., *Comp Part A* ,(2004) **35** :363
204. Mwaikambom L.Y., Ansell M.P., C*omp Sci Technol,* (2003) **63** :1297
205. Oksman K., Skrifvars M., Selin J.F., *Comp Sci Technol,* (2003) **63**: 1317
206. Punnose G., *Ind Text Journal*, (1952) **63**: 388.

CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Materials

2.2 Chemical composition of isora fibre

2.3 Fibre preparation and surface modification

2.4 Preparation of composites and test specimens.

  2.4.1 Cure characterstics of the rubber compounds.

  2.4.2 Moulding of the test specimens.

2.5 Characterisation of fibre and composites

  2.5.1 Scanning electron microscopy.

  2.5.2 Atomic Force Microscopic measurements and Image analysis

  2.5.3 Infrared spectroscopy

  2.5.4 Optical microscopy

  2.5.5 Integrated coupled plasma –atomic emission spectroscopy

  2.5.6 Thermal Analysis

  2.5.7 Wide angle x ray diffraction studies

  2.5.8 Fibre breakage analysis

  2.5.9 Mechanical property measurements

  2.5.10 Green strength measurements

2.6 Swelling studies

  2.6.1 Swelling data analysis

  2.6.2 Swelling parameters

2.7 Ageing studies

2.8 References

CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

Abstract

This chapter gives a brief description of the materials and methods used for the preparation of composites. The chemicals used for various fibre treatments have also been discussed. A brief description about the different analytical techniques used for the characterization of fibres and composites are also given in this chapter.

2.1 MATERIALS

2.1.1 Isora fibre.

Isora fibre was separated from the bark of Helicteres isora plant by retting in water.for 18-24 days. The average length of the fibre is approximately 75-100 cm. The physical and chemical characteristics of isora fibre is discussed in Chapter 3 and are already reported else where [1]

2.1.2 Natural Rubber

Natural rubber used for the study was ISNR 5(light colour) grade obtained from Rubber Research Institute of India, Kottayam, Kerala. The molecular weight, molecular weight distribution and non rubber constituents of natural rubber are affected by clonal variation, season and methods of preparation [2]. Hence rubber obtained from same lot has been used in this study. Its properties are given in table 2.1

Table 2.1 Properties of natural rubber [3]

Dirt content % by mass	0.03
Volatile matter % by mass	0.50
Nitrogen % by mass	0.30
Ash % by mass	0.40
Initial plasticity number,P_0	38
Plasticity retention index PRI	78

2.1.3 Compounding ingredients

a) Cross linking agent: sulphur (ρ =2.05) supplied by M/s Standard chemical company Pvt. Ltd Madras.

b) Accelarators: CBS (N cyclohexyl benzothiazyl sulphanamide ρ =1.30) and ZDC (zinc diethyl dithiocarbamate ρ =1.47) supplied by ICI India Ltd Calcutta, TMTD (tetra methyl thiuram disulphide ρ=1.3) supplied by polyolefins Industries

Ltd, Bombay.

c.Activators: ZnO (ρ=5.5) supplied by M/s Meta Zinc Ltd Bombay, Stearic acid (acid number 200) supplied by Godrej Soaps pvt Ltd Bombay.

d.Antioxidant: Vulkanox HS (1, 2 dihydro 2, 2, 4, trimethyl quinoline polymerized ρ = 1.1) was obtained by Bayer India Ltd

e .Special chemicals: PF (ρ =1.3)and RF (ρ =2.3)) resins supplied by M/s west coast polymers pvt Ltd Kannur, Kerala and precipitated silica (ρ =2.03) supplied by Minar Chemicals,Alwaye,Kerala were of commercial grade and hexamethylene tetra ammine (ρ=1.33) supplied by E.Merck (A.G) U.K was of chemically pure grade.

2.1.4. Other reagents

Other reagents like toluene,n-heaxane,ethyl alcohol used were of analytical grade, and oils like petrol, diesel,kerosene and lubricating oil were of commercial grade.

2.1.5 Chemicals for fibre modification

Sodium hydroxide, used for fibre surface modification was of reagent grade. Coupling agent (silane A151) vinyl tri ethoxy silane used was of analytical grade procured from M/s Union carbide Co, Montreal, Canada.

2.2 Chemical composition of isora fibre

Chemical composition of isora fibre was estimated according to ASTM procedures. Lignin-ASTM D 1106, Cellulose- ASTM D 1104, Ash content- ASTM D 1102, Alcohol benzene solubility -ASTM D 1107, Ether solubility- ASTM D 1108, 1% NaOH solubility -ASTM D 1109, Water solubility -ASTM D 1110.

2.3 Fibre preparation and surface modification

Isora fibre was separated from the bark of Helicteres isora plant by retting in running water for 20-24 days and dried. Then it was chopped to different lengths 6, 10, 14 mm. Any physical or chemical treatments on cellulose fibres change the morphological structures, macromolecular properties and chemical structure including the accessability of –OH groups for reactions.

a. Mercerization. Fibres of average length 10 mm were immersed in 5% NaOH solution for different time intervals viz; 4, 24,48and 72 hrs both at room temperature and at boiling temperature (95°C). Finally the fibres were repeatedly washed with water containing little acetic acid and then dried in an air oven at about 70°C for 24 hrs.

Mercerization is one of the oldest methods proposed by John Mercer in 1842 which has been used for treating natural fibres [4]. The process involves the conversion of native cellulose (celluloseI) into cellulose II, when the former is swelled in NaOH followed by the removal of alkali by washing with water. This process causes significant changes in the molecular orientation, crystal structure and degree of crystallinity and morphology of the fibres [5]. This led to the formation of more flexible micro fibirils than that present in the native cellulose due to the less crystallinty in the the resulting cellulose II. The natural impurities are also removed from the surface as a result of mercerization. There are three chemically active –OH groups on each anhydro glucose units of the untreated cellulose. Even though these groups are not much reactive under normal conditions, these become more reactive on mercerization.

b. Gamma irradiation. Isora fibres are exposed to γrays from ^{60}Co source at a dose rate of 0.1Mrad per hr for different time intervals depending upon the dosage of radiation.

c. Silane treatment. Alkali treated fibres were dipped in alcohol/water mixture (60:40) containing 1% vinyl triethoxy silane coupling agent. The pH of the solution was maintained between 3.5 and 4. Fibres were washed in distilled water and dried.

2.4 Preparation of composites and test specimens.

The fibre was mxed with rubber on a laboratory two roll mixing mill with size 150 X 300 mm as per ASTM D3184-80 at a friction ratio of 1:1.25. The mill opening was set at 0.2mm. The base formulation of the rubber compound is given in Table 2.2 and the description of the mixes is given in different tables along with the respective analyses in various chapters. The rubber was first masticated by careful control of temperature, nipgap, time and uniform cutting operation. The nip gap, mill roll speed ratio and number of passes were kept the same in all mixes. The compounding ingredients were added in the following order given in Table 2.2.

Table 2.2 Basic formulation of the rubber compound.

Ingredients	Parts per hundred rubber[phr]
Natural rubber	100
ZnO	5.0
Stearic acid	2.0
TDQ	1.0
CBS	0.6
TMTD	0.1
Sulphur	2.5
RF resin	Variable
Hexa	Variable
Silica	Variable
Fibre untreated	Variable
Fibre treated	Variable

The fibres were incorporated at the end of the mixing process, to avoid breakage of fibres taking care to maintain the direction of compound flow, so that majority of fibres are aligned in the grain direction. The samples were milled for sufficient time to disperse the fibres in the matrix at a mill opening of 1.25 mm. the stock was sheeted out after complete mixing. The homogenization was done by passing the rolled ssheet six times endwise through the tight nip gap of 0.8mm and finally sheeted out at a nip gap of 3mm.This sheet was used for the processability studies and green strength measurements.

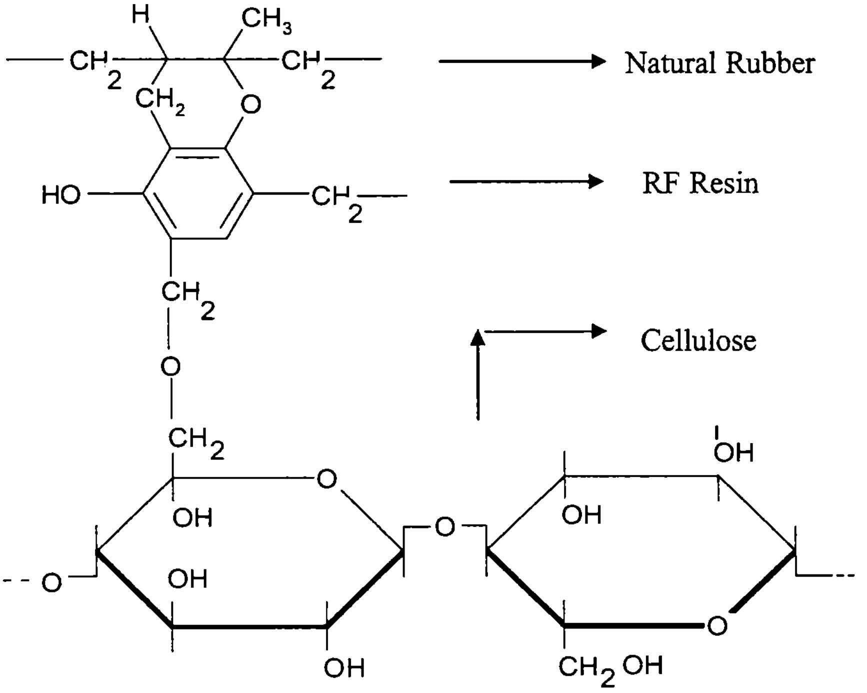


Figure 2.1 Mechanism of the RF resin bonding in Natural Rubber-Cellulosic fibre composites.

A three component bonding system consistiong of resorcinol formaldehyde resin, hydrated silica and hexa are used as the bonding agent. It was added to the mix along with other ingredients during milling process as per the same mixing sequence given in the table. The above shown schematic representation indicates the enhanced adhesion between fibre and rubber due to the presence of HRH bonding system [6].

2.4.1 Cure characterstics of the rubber compounds.

Goettfert elastograph model 67.85 was used for the determination of the cure characteristics of the mixes. It uses two directly heated, opposed biconical discs that are designed to achieve a constant shear gradient over the entire sample chamber. The specimen was kept in a lower die, which is oscillated 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.

Minimum torque (M_L): the torque obtained by the mix after homogenizing at the test temperature, the onset of cure.

Maximum torque (M_H): Torque recorded after the curing of the mix is completed

Optimum cure time (t_{90}): It is the time taken to attain 90% of the maximum torue

Scorch time (t_{10}): It is the time taken to attain 10% of the maximum torque.

2.4.2 Moulding of the test specimens.

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding on an electrically heated hydraulic press having 18 X 18 inch platens at a pressure of of 200 kg/cm^2 on the mould. The rubber compounds were vulcanized upto their their respective cure times at 150°C. Moulding were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hrs and were used for subsequent physical tests. For smpls having thickness more than 6mm (compression set, abrasion resistance etc ;) additional time based on the sample thickness was given to obtain satisfactory mouldings.

2.5 Characterisation of fibre and composites

2.5.1 Scanning electron microscopy.

The SEM photograph of the fibre surfaces and cross section of the untreated and treated fibres and fracture surfaces of the composites were taken using JEOL 35C Model scanning electron microscope. The principle of which was detailed by Johar *et al* [7]. The fracture surfaces of the composites were carefully cut from the failed test specimens without touching the surface. To avoid electron charging effects, samples were sputter coated with gold within 24 hrs in a polaron SEM coating unit SC 515. The fractured specimens and gold coated samples were stored in a descicator till SEM observations were made. The SEM photographs of the fractured surfaces will give information regarding fracture mechanism and interface adhesion of the composites.

2.5.2 Atomic Force Microscopic measurements and Image analysis

The AFM images of the untreated and chemically modified fibres were recorded with a Nanoscope IIIa SPM (Digital Instruments, Santa Barbara, CA) equipped with an extender electronics module that enables phase imaging in the tapping mode. All the images were recorded in tapping mode using silicon cantilevers with a resonance frequency between 265 and 400 kHz. The scan rate was 1.0-1.25 Hz. The Scanning Probe Image Processor (SPIP, Image Metrology, Denmark) was used for the roughness analysis of the images.

2.5.3 Infrared spectroscopy

Infrared spectra of raw and chemically modified isora fibre were obtained with Schimadzu model IR 470 infrared spectrophotometer, Scimadzu, Japan by using solid KBr pellet technique. Fibre samples were cut into small pieces and grounded well before mixing it with KBr.

2.5.4 Optical microscopy

An optical stereo microscope of Leitz metallux 3, Germany was used for calculating fibre length distribution in NR matrix and also for observing the equilibrium swelling behaviour of the composites.The crack developd on the samples after ozone ageing was also observed by optical microscope.

2.5.5 Integrated coupled plasma –atomic emission spectroscopy

Metal ions present in the fibre were estimated using ICP AES analyzer model IRIS INTREPID II XSP

2.5.6 Thermal Analysis

(i) Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were used to investigate the thermal stability of the untreated and chemically modified fibres. TGA Q 50 (TA unstruments) was used at a heating rate of 10°C/min from room temperature to 600°C with 5-10 mg of the sample in Nitrogen atmosphere.

(ii) Differntial Scanning Calorimetric and Differential Thermal analysis (DSC/DTA)

DSC studies of the fibres were carried out using a Mettler Toledo model DSC 822 thermal analyzer with a heating scheme of 30-550°C and at a heating rate of 10°C/min in nitrogen atmosphere purged at 25ml/min. DTA studies of the untreated and chemically modified fibres were also carried in an oxygen/nitrogen atmosphere using a Perkin Elmer model diamond DTA thermal analyzer. The thermal behaviour of isora/NR composites was also measured using differential scanning calorimeter. The samples were first cooled to – 80°C using liquid Nitrogen and scan was made from -80°C to 100°C at a heating rayte of 10°C/min in Nitrogen atmosphere.

(iii) Dynamic Mechanical Analysis (DMA)

The dynamic storage modulus (E'), loss modulus (E") and the loss factor (tan δ) of the composites were measured using a dual cantilever, and samples with dimensions 50x8x4 mm as function of temperature at two different frequencies 10Hz ,and 1 Hz on a Dynamic Mechanical Thermal Analyzer, DMA Q 800 TA instruments. The properties were determined over a temperature range of -100 to 140°C with dynamic tension strain amplitude of 0.325% and at a heating rate of 1°C min^{-1}.

2.5.7 Wide angle x ray diffraction studies (WAXRD)

The crystallinty index of the fibres was studied using a wide angle x ray diffractometer Bruker model D8 Advance, equipped with a scintillation counter and a linear amplifier was used. The diffraction intensities were recorded between 5 and 60° (2θ angle range).The crystallinty index was determined using the equation.

$$I_c = [(I_{002}-I_{am}) \times 100]/ I_{002} \ldots\ldots\ldots\ldots\ldots\ldots (2.1)$$

where I_c is the crystallinty index, I_{002} is the counter reading at peak intensity at a 2θ angle close to 22° representing crystalline material and I_{am} is the counter reading at peak intensity at a 2θ angle close to 18° representing amorphous material in the fibre.

2.5.8. Fibre breakage analysis

The fibre breakage analysis was carried out by dissolving 1g of the uncured composite in toluene, followed by separation of the fibres from the solution. Then the distribution of fibre length was determined using a travelling optical microscope.

2.5.9. Mechanical property measurements

(i) Tensile testing of fibres

The cleaned isora fibres were cut into 70mm, weighed and finally mounted on a manila paper card mounts with a central cut out using a strong adhesive and the tensile test was then conducted according to ASTM 2256.Tensile strength was then calculated using cross sectional area obtained from the weight and density of the fibre as shown in the equation $\sigma_T = F_{max}/A$, $\sigma_T = (\rho\ F_{max}\ l_f)/m_f$ where F is the maximum force, ρ- density of the fibre, and l_f - length of the fibre respectively.

Density measurement; The bulk density of the fibre was determined using a liquid of lower density (benzene) than the fibre.

(ii) Tensile testing of the composites

Stress-strain measurements were carried out at a crosshead speed 500mm/min on a Schimadzu Model AG1 universal testing machine. Tensile modulus, tensile strength and elongation at break were measured according to ASTM D 412-87(method A). Dum bell shaped specimens were punched out ofthe moulded sheet and tests were carried out both along and across the grain direction. Tensile strength is reported in M Pa and Elongation break is reported in percentage (Conversion factor is 1 MPa=10.197 Kg/cm^2=1 N/mm^2)

(iii) Tear resistance

Tear strength was calculated as per the ASTM D 624-86 using crescent shaped test specimens on a Schimadzu Model AG1 universal testing machine at a cross head speed of 500 mm/min. The samples were cut from the moulded sheets along and across the mill grain direction. Tear strength has been reported in kN/m (Conversion factor is 11Kg/cm=0.98kN/m)

(iv) Compression set

samples(6mm thick and 18mm diameter in duplicate compressed to constant deflection(25%) were kept for 22 hrs in an air oven at 70°C. After the heating period the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated using the following expression

$$\text{Compression set (\%)} = [t_i - t_f / t_i - t_s] \times 100 \quad \ldots\ldots\ldots\ldots\ldots (2.2)$$

where t_i and t_f are the initial and final thickness of the specimen,and t_s is the thickness of the space bar. The procedure adopted was in accordance with ASTM D 395-86 (method B).

(v) Abrasion resistance

The abrasion resistance of the samples was tested using a DIN 53516. Cylindrical samples having diameter 15mm and length 20mm was kept on a rotating sample holder and 10 N loads were applied. Initially a pre run was given and its weight was taken. The sample was then given a complete run and the final weight was noted. The difference in weight is noted as the weight loss. It is expressed as the volume of the test piece getting abraded by its travel through 42 m on a standard abradant surface. The abrasion loss was calculated as follows.

$V = m / \varrho$ where V is the abrasion loss, m is the mass loss; ? is the density of the sample.

(vi) Hardness

The hardness of the composite was measured using the Shore A type Durometer according to ASTM 2240-81. The instruiment uses a calibrated spring to provide the indenting force. The load imposed by the spring varies with indentation. Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimens.

2.5.10 Green strength measurements

Green strength values were determined using dumb bell shaped samples obtained from unvulcanized compounds on a Schimadzu Model AG1 universal testing machine at a stretching rate of 500 mm/min.

2.6 Swelling studies.

The anisotropic swelling experiments were carried out using circular specimens of diameter 2 cm. the thicknes of the composite was measured. The dry weights of the cut samples were taken before immersion in the liquid contained in an airtight weighing bottles. The samples wer removed from the bottles at periodic intervals, the wet surface was quickly dried using a piece of blotting paper and weighed immediately in air tight weighing bottles. During swelling any change in the diameter and thickness of the sample were determined bymeans of a vernier calipers and microguage respectively. The uptake of the liquid by the polymer durig swelling was expressed as moles of liquid sorbed by 100 g of the polymer. This method was found to be more convenient for comparison of sorption data and was adopted by earlier researchers [8-9].

2.6.1. Swelling data analysis.

(i) Measurement of adhesion

The extent of adhesion between fibre and rubber can be evaluated by measuring the volume fraction of rubber in the swollen and unswollen sample. In order to determine the volume fraction of the unswollen sample the test specimen was weighed both in air and water. The difference between the two weights gave the volume of the samples. Using the base formulation, the amount of rubber present in the weighed sample of each specimen and its volume were calculated. From these data the volume fraction of rubber present in dry specimen was calculated and is denoted as V_i.

The volume fraction of rubber in the swollen sample V_f was calculated by the expression

$$V_f = \frac{[(D-FT)/(\rho_r)]}{[(D-FT)/(\rho_r)] + [A_o/\rho_s]} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.3)$$

Where ρ_r and ρ_s are the densities of the rubber and solvent, D is the deswollen weight of the test specimen (dry weight), F is the weight fraction of the insoluble components, T is the weight of the specimen and A_o is the weight of the absorbed solvent corrected for swelling increment respectively.The improve adhesion between short fibre and rubber can be evaluated from V_r which is the ratio of the change in the volume fraction of the rubber due to swelling and was calculated as

$$V_r = (V_i - V_f)/V_i \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2.4)$$

Where V_i is the volume fraction of rubber in the unswollen sample, V_f is the volume fraction of rubber in the swollen sample

(ii) Calculation of Qt (mol %)

The results of sorption experiments were obtained by plotting the mol percentage uptake (Qt) of the solvent by 100 gms of the natural rubbur gum vulcanizate and fibre composites verus square root of time for different solvents. The mole percent uptake Qt for the composite samples were evaluated using the following equation,

$$Q_t = \frac{[W_2\text{-}W_1/\ M_s]}{W_1} \text{ X } 100 \quad ....(2.7)$$

Where W_1 and W_2 are the weights of the sample before and after swelling and M_s is the molar mass of the solvent.

2.6.2 Swelling parameters.

Anisotropic swelling studies provide information on the strength of interface, degree of dispersion of fibres, and their alignment in the elastomer matrix. Inorder to assess the extent of swelling behaviour of composites, gum and fibre filledvulcanizates were swollen in various solvents at room temperature and their swelling parameters were evaluated.

(i) Swelling index

Swelling index is calculated by the following equation

$$\text{Swelling index (\%)} = [W_2\text{-}W_1/W_1] \text{ x}100 \ldots\ldots\ldots\ldots \quad (2.5)$$

Where W_1, and W_2 are the intial and final or swollen weights of the sample.

(ii) Swelling coefficient

Swelling behaviour of the composites can also be analysed from swelling coefficient values. It is an index of the ability with which the samples swell and is determined by the equation

$$\text{Swelling coefficient} = [A_s\ /m] \text{ x } [1/\rho] \ldots\ldots\ldots\ldots \quad (2.6)$$

where A_s denotes the weight of the solvent sorbed at the equilibriumswelling, m is the weight of the sample before swelling, and ? the density of the solvent used.

2.7 Ageing studies.

The effect of thermal ageing was determined by ageing the samples in an air oven at

100°C for 3 and 5 days. Ozone resistance was determined according to ASTM D 518 method B. Samples were exposed to ozonised air in an ozone chamber (MAST Model 700-1) for 36 hrs. The concentration of ozone was maintained at 50 pphm and the inside temperature at 40°C. The ozone cracks developed on the samples were analyzed by optical microscopy. For radiation ageing, the samples were irradiated with gamma rays from ^{60}Co source at a dose rate of 0.3413 Mrad /hr.in a gamma chamber. Tensile and tear testing before and after irradiation and thermal ageing were carried out according to ASTM D 412-86 and D 624-87standards.

2.8 REFERENCES

1. Lovely M., Joseph K.U., Rani J., *Advances of Eco materials*, 7th International conference on Eco materials, Stallion press, Singapore, (2005) Vol. **2** Page 449.
2. Subramanyam A., *Rubb Chem. Technol*, (1972) 45: 346.
3. Subramanyam A., *Proc R.R.I.M., Planters conference*, Kaulalumpur (1971) 252.
4. Allen G.,(Ed.), *Comprehensive polymer Science- Polymer reactions*, Pergamon Press, (1989) 6.
5. Anon J., *Tex Res J* (1898) **59**: 772.
6. Blackley D.C., *Polymer Lattices*, Chapman & hall Publishers, London, Second Ed. (1997) **3**: 515.
7. Johari O., Samudra A.V., *Characterisation of solid surface*, Kane P.F., Larrabe G.B., Eds, Plenum Press, Newyork,(1974) Ch. 5.
8. Aithal U.S., Aminabhavi T.M., J *Chem Edn*, (1990) **67(1)**: 82.
9. Hargopad S.B., Aminabhavi T.M., *J Appl Polym Sci*, (1991) **42**: 2329.

CHAPTER 3

ISORA FIBRES: CHARACTERIZATION

- **3.1** Introduction
- **3.2** Results and Discussion
  - **3.2.1** Chemical analysis
  - **3.2.2** Mechanical properties
  - **3.2.3** Morphological analysis
  - **3.2.4** Chemical modifications: IR Spectroscopy
  - **3.2.5** Thermal studies
  - **3.2.6** Wide angle X ray diffractometer studies
- **3.3** Theoretical Prediction of Micro fibrillar angle and Strength of the fibre
- **3.4** Conclusions
- **3.5** References

CHAPTER 3

ISORA FIBRES: CHARACTERIZATION

Studies on chemical composition, surface modifications, morphology, chemical, mechanical and thermal properties

Abstract

'Isora' is a bast fibre separated from the bark of Helicteres isora plant by retting process. Chemical composition, morphology and physical properties of the fibre have been studied. The chemical constituents of the fibre were determined according to ASTM standards. Various surface modifications were made on the fibre. The mechanical properties of the fibre were also determined. The surface topology of the fibre has been studied by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Thermogravimetry (TGA), Differential Thermogravimetry (DTG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC) were used to determine the thermal stability of the fibre. The chemically modified fibres were characterized by IR spectroscopy. The crystallinty index of the various modified fibres was studied by wide angle X ray diffractometer (WAXRD). The micro fibrillar angle and strength of the fibre were theoretically calculated and compared with that of the experimental results.

Part of the results of this chapter has been published in *Journal of natural fibres (2006) 3(4):110* and in Advances *in Eco materials (2005) 2:44*

3.1 INTRODUCTION

ISORA is a natural fibre present in the bark of ***Helicteres isora plant***. [East Indian screw tree]. The plant belongs to the Sterculiacea family and found in the warmer parts of the world. Four species were reported to occur in India of which Helicteres isora has attained importance as a source of fibre.[1] The plant occurs often gregariously, throughout India. Fibre is extracted from the bark of the plant by retting it in water for three weeks. Fibres of good colour and quality were obtained when retting is effected in running water. Isora fibre is pale yellow in colour, soft, silky and lustrous which resembles jute in appearance, with comparable strength and durability. The photograph of raw fibre is given in Figure 3.1

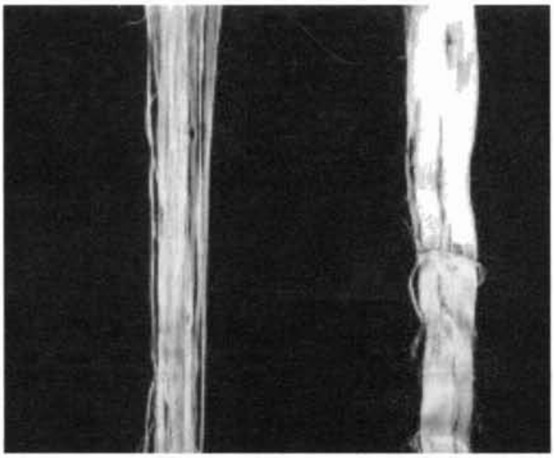
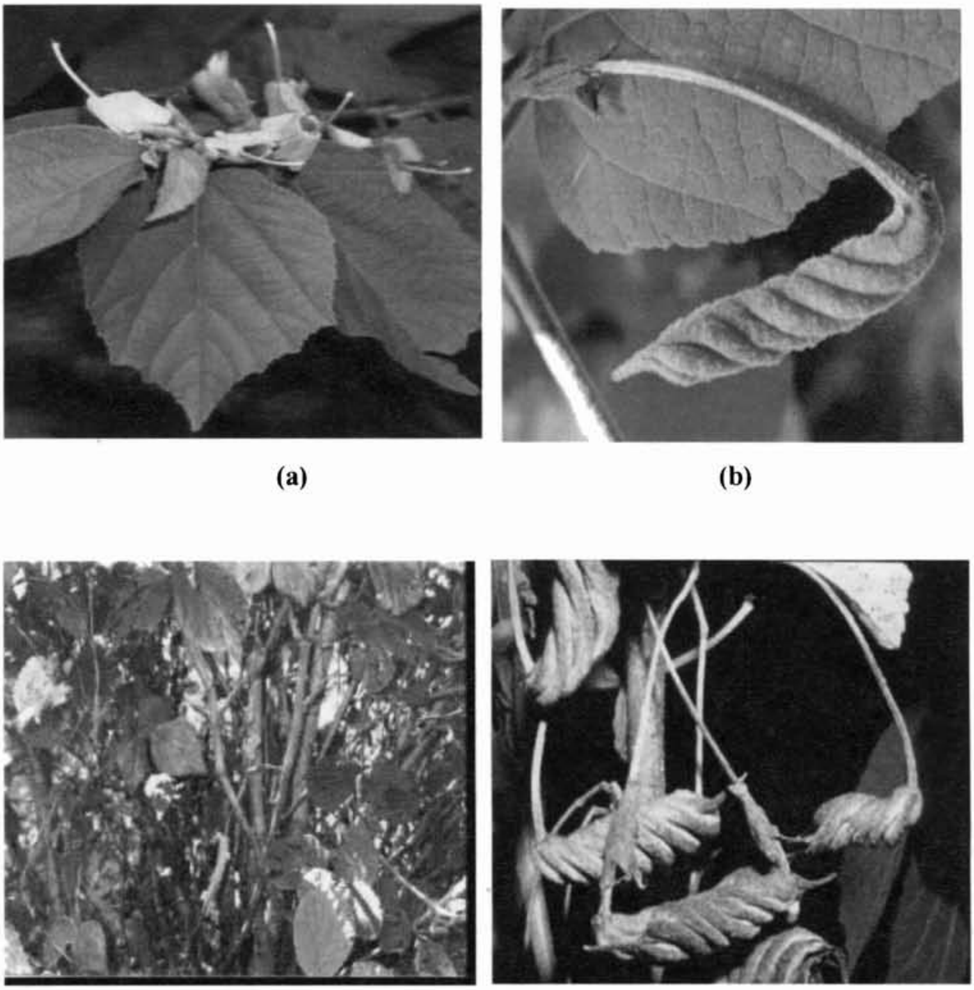


Figure 3.1 Photograph of isora fibre

The root, stem, leaves and fruits of the plant are used for medicinal purposes. The stem, leaves, fruits and the dried seeds are given in Figure 3.2.



(a) **(b)**

(c) **(d)**

Figure 3.2 Helicteres isora plant (a) leaves, (b) fruit, (c) stem (d) dried seed

Recently we have reported the possibilities of using isora fibre as a potential reinforcement in natural rubber and polyesters [2-3]. The mechanical properties of these matrices are greatly improved by incorporation of this fibre. The resultant composite product will be a cost effective and value added material for various products like conveyor belts, power transmission belts etc. Use of biodegradable matrix and natural fibres as reinforcement has open new potential applications to these composites as they are eco friendly materials. The physical properties of other natural fibres have already been reported [4-9].To date no systematic work has been reported to be undertaken to study the properties of isora fibre.

This paper reports the physical, chemical, mechanical, thermal and morphological characteristics of isora fibre. Chemical analysis of isora fibre shows that major chemical component present is cellulose. The cellulose content plays an important role in the mechanical performance of the fibre. Mechanical properties such as tensile strength, Young's modulus, and elongation at break were evaluated. Various surface modifications of the fibre by alkali and silane treatment and gamma irradiation have been tried. TGA, DTG, DTA and DSC were carried out to study the thermal stability of the fibre. The morphological analysis has been carried out by using SEM and AFM. The crystallinity and the chemical reactivity of the fibre were evaluated by using WAXRD and IR. Micro fibrillar angle and the strength of the fibre were theoretically calculated.

3. 2 RESULTS AND DISCUSSION

3. 2. 1 Chemical Analysis

Table 3.1 shows the various chemical components present in the isora fibre and the solubility of the fibre in different solvents.

Table 3.1 Chemical constituents of Isora fibre

Chemical constituents (%)		Solubility in various solvents (%)	
Cellulose	74.8	Alcohol-benzene	6.3
Lignin	23.0	Ether	5.7
Ash	0.92	1% caustic soda	14
Fat	1.09	Cold water	10
Moisture content	5-6	Hot water	12
Ca(ppm)	713.45	Acetone	5.6
Mg(ppm)	37.93		
Fe(ppm)	16.10		
K(ppm)	10.54		
Na(ppm)	10.42		

From Table 3.1 it is clear that isora is a cellulose rich fibre with comparatively low lignin content, which contributes to better performance of the fibre as reinforcement in polymers. The fine structure of cellulose materials is composed of crystalline and amorphous regions. The amorphous regions easily absorb chemicals such as dyes and resins whereas the compactness of the crystalline regions makes it difficult for chemical penetration. The fibre is hygroscopic and its moisture content is found to be 5-6%. From table 3.1 it is clear that the fibre contains about 12% water soluble materials.

3. 2. 2 Mechanical properties

The physical and mechanical properties of the fibre are given in Table 3.2

The bulk density includes all the solid material and pores within the fibre which is always less than the absolute density. The absolute density of most plant fibres is between 1.4-1.5 gm/cc [10]. The fibre density is assumed to be closely related to the mechanical properties, moisture absorption, homogeneity and degree of order of the fibre [11]. After chemical treatment there is a slight positive change in the bulk density which normally signifies cell wall densification.

Table 3.2 Physical and Mechanical properties of the fibre

Properties	**U**	**A**	**Si**	**? irradiated**
Tensile strength (MPa)	565	500	475	350
Elongation at break (%)	6	7.0	7.0	8.0
Young's modulus(GPa)	18-20	15	16	12
Density (gm/cm^3)	1.39	1.42	1.51	1.40
Crystallinity Index (%)	70.9	80.6	77.8	71.3
Micro fibrillar angle (degrees)	20-26	-	-	-
Intrinsic strength (g/denier)	0.987	-	-	-
Length to diameter ratio	99	-	-	-
Diameter (μm)	10	<10	<10	10

U-Untreated, A-Alkali treated, Si-Silane treated

The nature and texture of the fibres obtained from different regions may not be the same. Hence this will affect the properties of the fibre; therefore there is a large variation in the observed properties. An average value of the properties is reported.

Stress strain behaviour: The mechanical performance of the fibre is dependent upon the chemical composition, chemical structure and cellular arrangement. Isora fibre contains about 23% lignin and 74% cellulose. The tensile stress strain curves of the raw and modified fibres are given in Figure 3.3. Each individual fibre is composed of fibrils held together by non cellulosic substances like lignin; pectin etc. Failure of the fibre is gradual upon the application of tensile stress. It shows intermediate behaviour between brittle and amorphous materials. At the very beginning (<1% elongation) there is linearity and thereafter sharp increase is observed. As the applied stress increases, the weak primary cell wall collapses and decohesion of cells occurs resulting in the mechanical failure of the fibre. Fibre modifications lead to major changes on the fibrillar structure of the fibre.

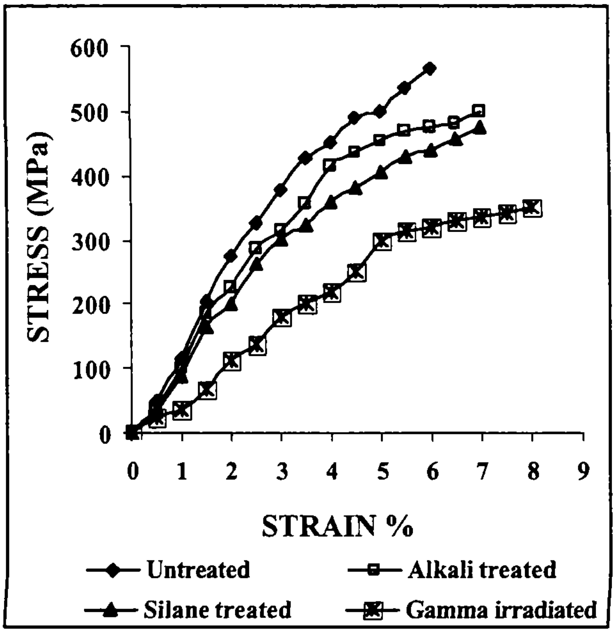


Figure 3.3 Stress strain curves of raw and modified fibres.

These modifications remove the amorphous components leading to changes in the deformation behaviour of the fibres. This is clearly observed from the stress/strain behaviour of the treated fibres. Brittleness of the fibre is substantially reduced upon treatments.

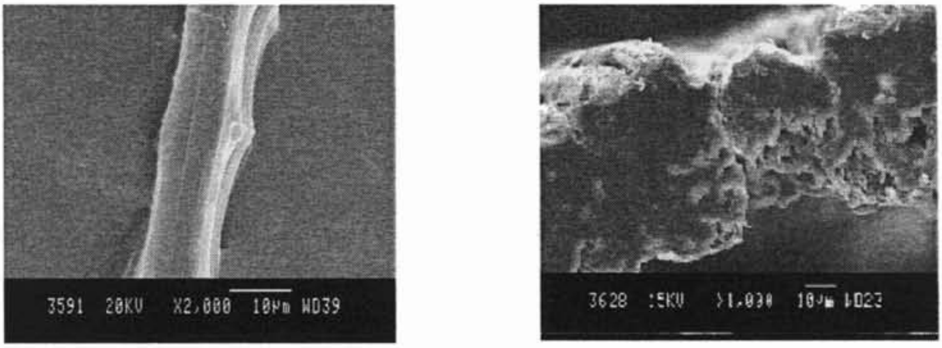
Tensile properties: Important tensile properties like tensile strength, young's modulus and elongation at break of the raw and modified fibres are given in Table 3.2. Chemical modifications of the fibre surface decreased the tensile strength due to the breakage of the bound structure and also due to the disintegration of the noncellulosic materials. Lignin, the binding material that binds the three-dimensional cellulose structures as well as the fibrils get partially removed on chemical treatment and hence tensile strength decreases. Tensile strength of the treated fibre is less than that of the untreated fibre [Figure 3.3]. Major degradation occurred as a result of gamma irradiation compared to the untreated fibre.

Results showed that on irradiation the tensile strength of isora fibre decreased from 565 MPa for untreated fibre to 350 MPa for the sample irradiated with 0.5×10^{-2} MGy dosage. This may be attributed to the scission of chain which predominates over intermolecular crosslinking. Elongation at break shows a slight increase after chemical treatment. The modification of plant fibres may involve the removal of the surface impurities, the swelling of the crystalline region and the removal of the hydrophilic hydroxyl group of the cellulose. The reinforcing ability of the plant fibres does not depend upon the mechanical strength of the fibres but on many other factors like polarity of the fibre, surface characteristics, the moisture content, presence of reactive centres and cellulose content [12]. These factors control the interfacial interaction.

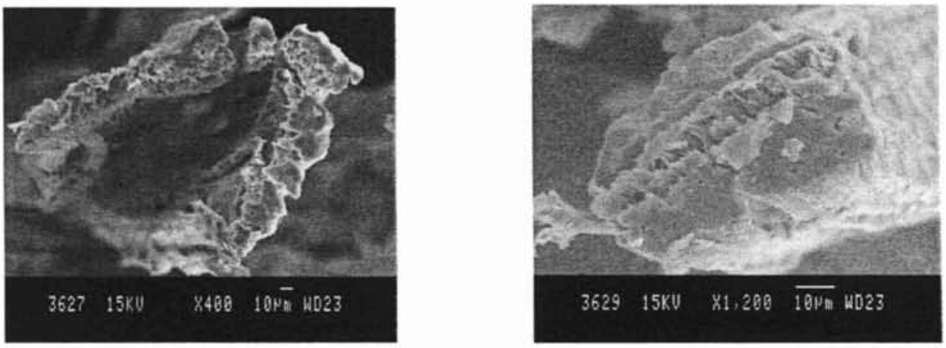
3. 2. 3 Morphological analysis of fibre

Scanning Electron Microscopic studies

Figure 3.4 is the SEM photographs revealing the morphology of untreated and alkali treated isora fibre. The scanning electron micrograph of a single fibril and the cross section of isora fibre is given in figure 3.4(a) & (b). The diameter of the fibre was found to be 10μm. The cross section is polygonal with a circular or oval lumen. The fibres are arranged in a reticulate pattern in a series of zones alternating with zones of soft tissue in the phloem region. The fibre consists of cells embedded in a matrix; the cells are the crystalline cellulose arranged in a matrix consisting of noncrystalline cellulose-lignin complex. The cell wall of the fibre elements is thick and lignified. The central core is referred to as 'lacuna' can also be seen in the figure 3.4 b. For the alkali treated fibre [Fig 3.4 c] it was observed that the size of the central lacuna is less than those of the untreated fibre indicating cell wall thickening and shrinkage of fibres during alkali treatment.



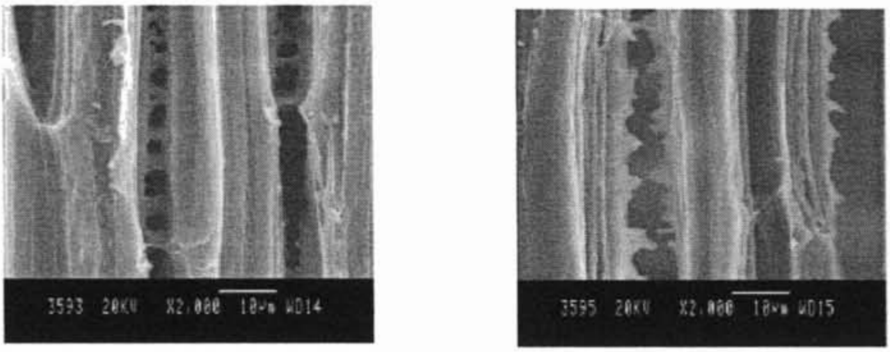
a. Single fibril **b.Cross section (untreated)**



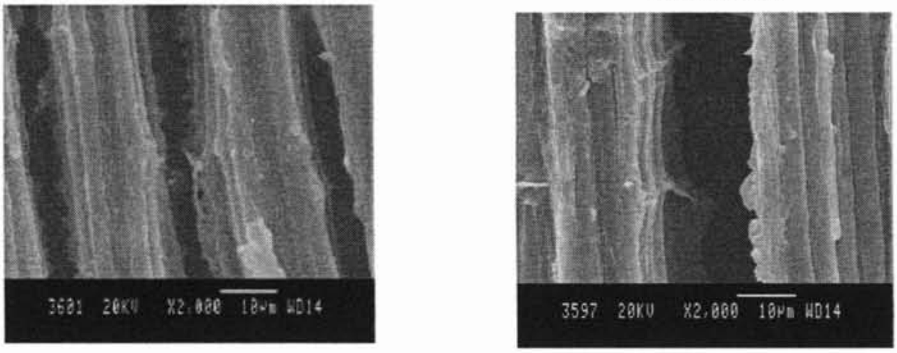
c. Cross section (alkali treated) X400 and X1200 magnifications

Figure 3.4 SEM photographs of the single fibril and cross section of untreated and alkali treated fibres

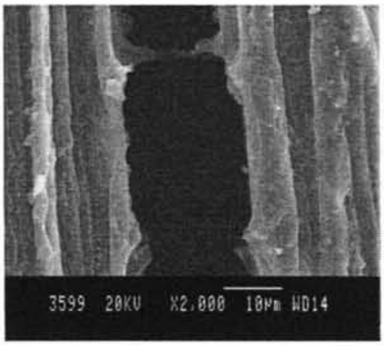
From these pictures it was found that isora fibres consisting of aligned fibrils with materials cementing the fibres together. Based on the results of FTIR and the structure of the natural fibre, the cementing material would be expected to be hemi cellulose and lignin. It is well known that hemi cellulose is a branched amorphous polymer with a low degree of polymerization, which is always associated with cellulose by hydrogen bonding.



a. 4 hours **b. 12 hours**



c. 24 hours **d. 48 hours**

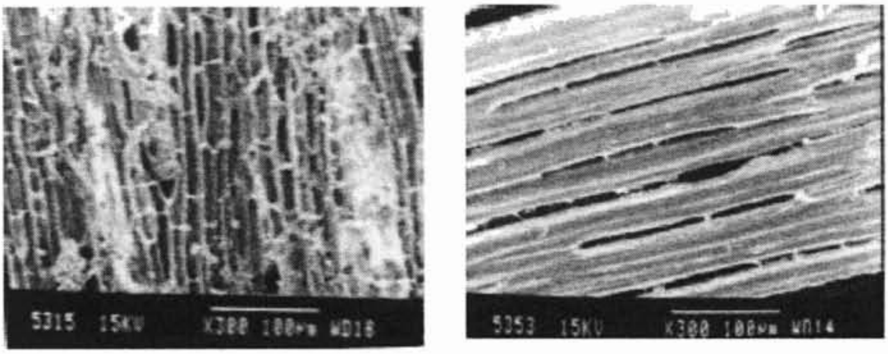


e. 72 hours

Figure 3.5 SEM Photographs of Alkali treated Fibres (at different time intervals of soaking in alkali) at X 2000 magnification

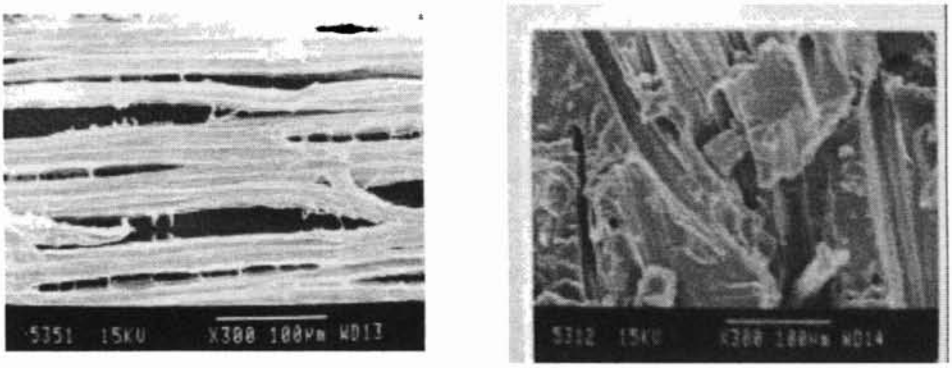
Isora fibre is a composite material with fibrous reinforcement and a mixture of hemi cellulose and lignin as matrix. SEM photographs of the alkali treated fibre at various time intervals of soaking in alkali (5% NaOH) is given in Figure 3.5. When the soaking time of the fibre in alkali was increased it can be seen that the materials in the interfibrillar region were obviously etched away and the fibrous region becomes more pronounced as interfibrillar region is removed. SEM picture of the untreated isora fibre (Figure 3.6) shown that the fibre surface to be very smooth and a series of globular particles can be seen to be embedded in the fibre surface at regular intervals. They are identified as tyloses, which covers the pits on the cell walls.

When the fibres are soaked for 4-12 hours most of the tyloses are intact but at a few isolated places it was removed creating holes as shown in figure 3.5. When the soaking time was increased to 24-48 hours a much greater proportion of the tyloses is found to be removed. At still higher soaking time the SEM pictures show complete exposure of the fibrils indicating the leaching of the intercellular binding material and the cuticle layer.



Untreated **Alkali treated**

Figure 3.6 SEM photographs of the surface of untreated and alkali treated fibres



c. Silane treated **d.Gamma irradiated**

Figure 3.6 (Contd) SEM photographs of the surface of silane treated and gamma irradiated fibres

Fibre modification by alkali and silane treatment renders roughness to the fibre surface as evident from the SEM photographs.(Figure 3.6) This will enhanced the interlocking with the matrix thereby the property of the composite increases [2-3] by the incorporation of treated fibres. Gamma irradiation eliminates the porus structure and microlevel disintegration of the fibre is observed. Major cracks are developed upon radiation treatment.

Atomic Force Microscopic studies

Topographic (a, c, e,) and phase contrast images (b, d, f,) corresponding to mechanical stiffness of untreated and modified fibres are given in figures 3.7and 3.8

The phase images shown in fig.3.7 and 3.8 represent typical surface structures of the isora fibre without treatment and after being treated with alkali, silane and gamma radiation. In each image, the main long axis of the fibre is oriented vertically, with an inaccuracy of ± 5°. The same spot demonstrate the primary result of enhanced resolution of the phase contrast image (b) compared with the topograph (a).

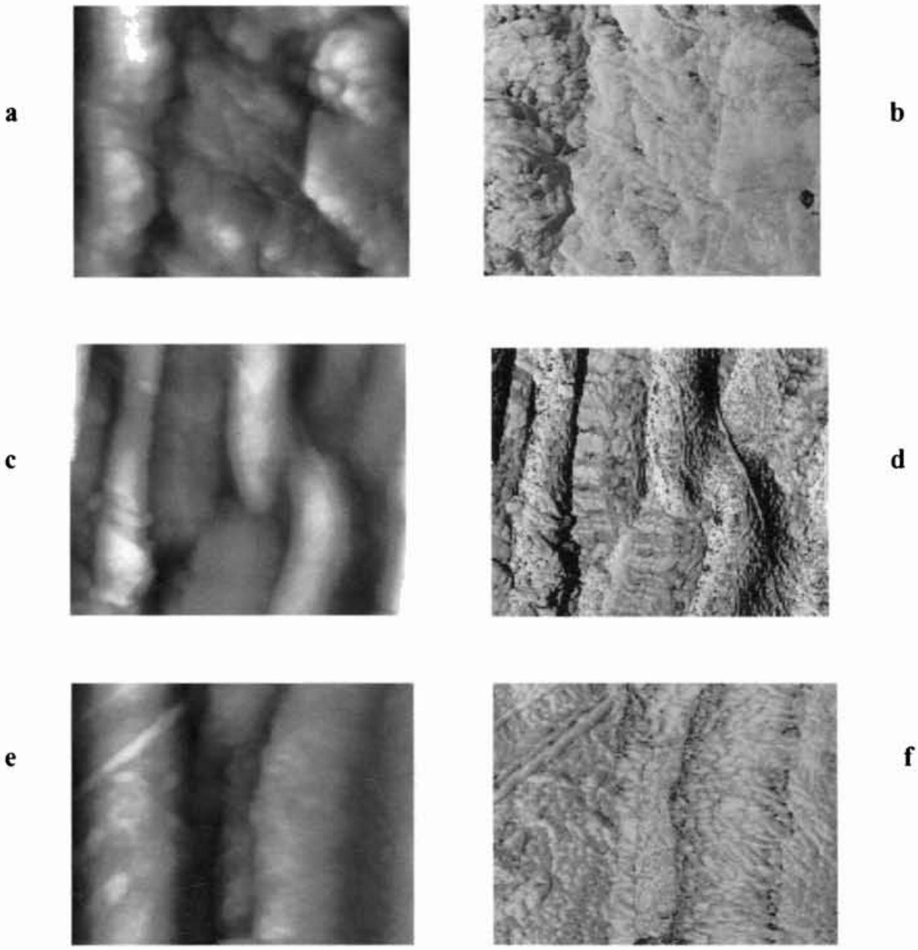


Figure 3.7 Topographic and phase contrast images of untreated (a, b), alkali treated (c, d) and silane treated (e, f) fibres.The image size is 2.5 μm

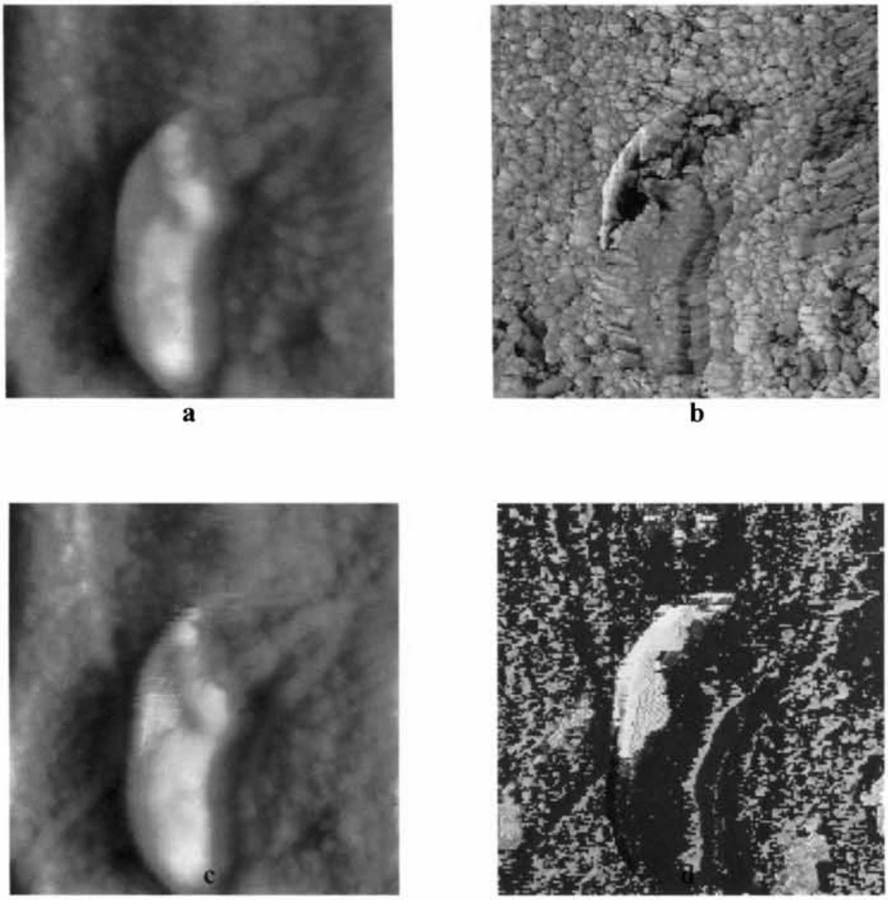


Figure 3.8 Topographic (a, c) and phase contrast images (b,d) corresponding to mechanical (stiffness) contrast (a,b) and chemical contrast (c,d) gamma irradiated fibres.The image size is 2.5 µm x 2.5 µm.

The topographs (a, c, e,) resolved the main bundles of microfibrils and their rough surface structures. The phase images resolved, in addition, the granular (Fig. 3.7 b& Fig. 3.8 b for untreated and gamma irradiated) and slightly fibrillar (Fig 3.7 d, &f for alkali treated and silane treated) fine structures of the bundles of microfibrils.

It is evident from fig. 3.7 b that the granular surface structure of untreated fibre had slightly disappeared as a result of alkali (Fig.3.7 d) and silane treatment, (Fig 3.7 f) due to partial removal of lignin or hemicellulose. However, after being irradiated by Gamma, the granular (lignin, extractives, or hemicellulose) structure [13-14] became more clear and dominant according to both mechanical and chemical contrast (Fig. 3.8 b& d).

c. The surface roughness of the fibre

Table 3.3 The roughness comparisons between untreated, alkali treated, silane treated and gamma irradiated fibres.

Parameters	Units	Untreated	Alkali treated	Silane treated	Gamma irradiated
Sq	nm	36.91	39.69	32.93	25.53
/STD		15.33	16.28	17.51	8.55
Sz	nm	233.60	236.00	174.37	141.73
/STD		96.28	109.80	89.92	40.37
Sdr	%	14.43	12.56	10.96	6.16
/STD		8.58	8.41	10.22	5.45
Ssk		-0.01	-0.13	-0.43	-0.19
/STD		0.28	0.42	0.45	0.28
Sci		1.54	1.47	1.31	1.51
/STD		0.15	0.17	0.13	0.17
Svi		0.13	0.12	0.14	0.12
/STD		0.02	0.02	0.04	0.02
Sku		3.64	3.81	3.75	2.93
/STD		0.55	1.73	1.10	0.40

A set of roughness parameters has been used for topographic characterization of surface properties in three dimensions. The surface roughness are explained in terms of the parameters like S_q, (RMS rouhness), S_z (ten point height), S_{dr} (surface area ratio), S_{sk} (skewness-height distribution asymmetry), S_{ci} (core fluid retention index), S_{vi} (valley fluid retention index) and S_{ku} (kurtosis- height distribution sharpness). The roughness parameters have been described in detail [15]. These parameters for the untreated and various modified fibres are given in Table 3.3. It is evident that the isora fibre is fairly heterogeneous according to the standard deviation. Nevertheless, after being treated with alkali or silane, the fibre surface roughness was affected slightly compared with untreated fibre. However, the gamma-irradiated fibres provided smoother surface. The reason is may be the removal of some impurities from the fibre surface. All the samples are slightly porous (small negative Ssk) by their surface.

3. 2. 4 Chemical modifications: IR spectroscopy

Figure 3.9 is the IR spectra of untreated and various chemically modified fibres
It can be understood from the spectra that some chemical reactions have occurred during the different treatments. Major changes are observed in the IR absorbance of chemically modified fibres.

Untreated fibre: The IR spectrum of raw isora fibre shows an absorption peak at 1730 cm^{-1} which is the characteristic band for carbonyl stretching associated with the carbonyl groups present in lignin and other cellulosic components. The strong broad peak at 3300-3320cm^{-1} is the characteristic hydrogen-bonded –OH stretching vibration. The peaks at 2910$cm^{-1}$and 750cm^{-1} corresponds to the C-H and C-O stretching vibrations respectively. A band at 1600cm^{-1} is due to the C-C stretching of the aromatic ring in the lignin components, while a strong peak at 950 cm^{-1} arises from the glycosidic linkages.The bands at 1370, 1330, 1310 cm^{-1} are due to the -CH deformation, -OH in plane bending and -CH_2 wagging respectively. The band near 1250cm^{-1} is due to the –C-O-C bond in the cellulose chain.

Alkali treated fibre: The important change expected as a result of alkali treatment is the removal of the hydrogen bonding in the network which is evident from the increased intensity of the -OH peaks at 3300cm^{-1}.

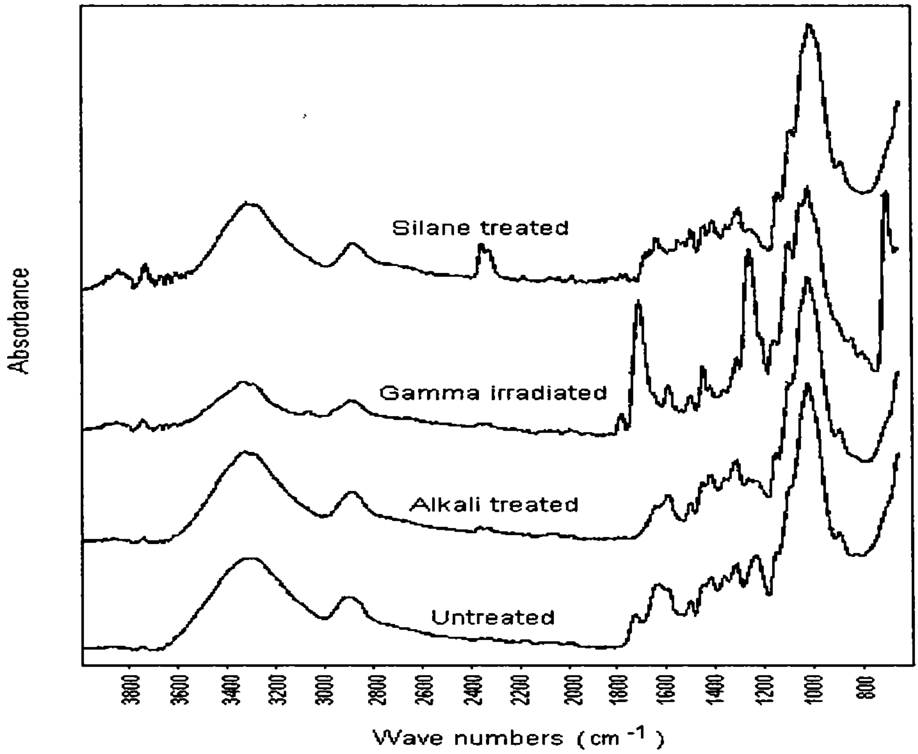
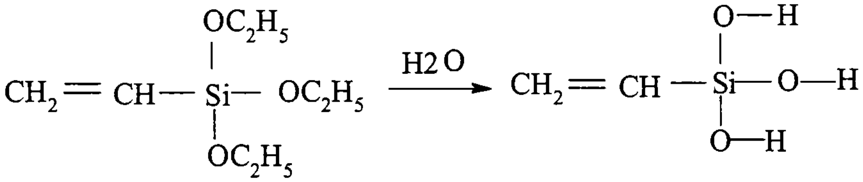


Figure 3.9 IR Spectra of Untreated, Alkali treated, Silane treated and Gamma irradiated fibre

Also, on mercerization, the peak at 1730 cm^{-1} in the spectrum of the raw fibre is disappeared. This is due to the fact that a substantial amount of uranic acid, a constituent of hemi-cellulose (xylan) is removed from the fibre, resulting in the disappearance of the peak. The dissolution of waxy materials from the fibre surface due to mercerization may cause increased mechanical interlocking between the fibre and matrix and may result in stronger composite.

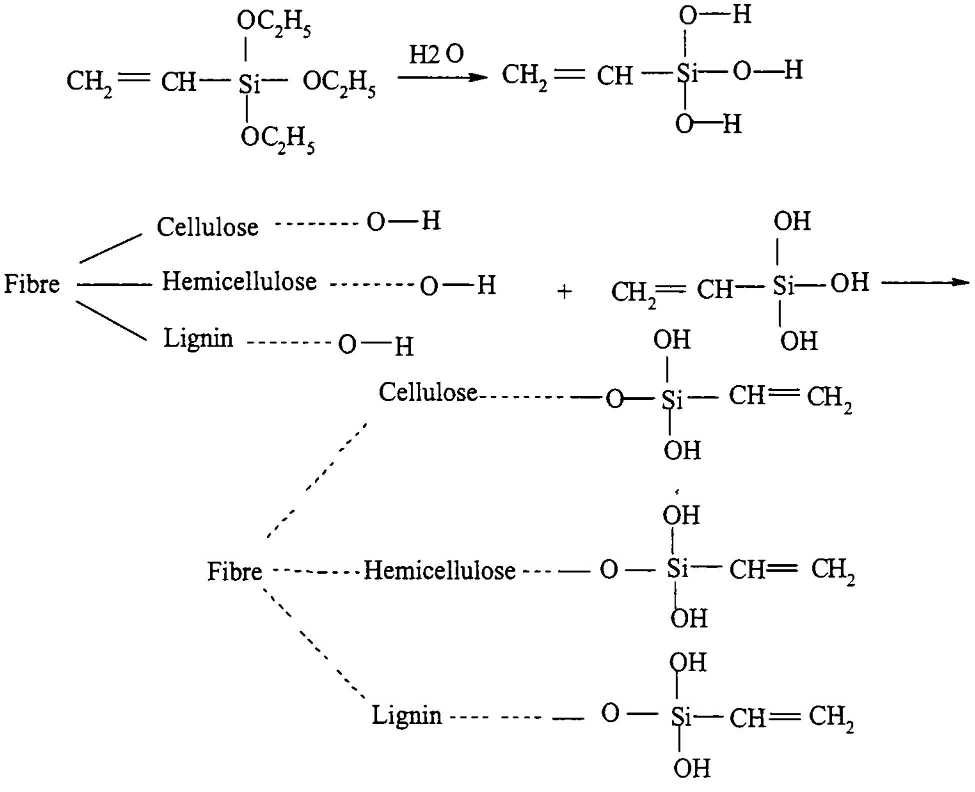
Silane treated fibre: In the case of silane treated fibre, additional peaks at 3750cm^{-1} indicating intermolecular hydrogen bonding between the silanol -OH and that of cellulosic -OH of the fibres and a peak at 2250cm^{-1} is observed due to the C=C stretching of the vinyl group.

Hydrolysis of Silane



$$CH_2=CH-Si(OC_2H_5)_3 \xrightarrow{H2O} CH_2=CH-Si(O-H)_3$$

Hypothetical reaction between fibre and silane



The cellulosic hydroxyl groups in the lignocellulosic fibre are not so reactive since they form strong intramolecular hydrogen bonds. Alkali treatment destroys the hydrogen bonding in the cellulosic hydroxyl groups and cause partial removal of lignin. This makes the -OH groups more reactive. Alkoxy silanes are able to form bonds with this free hydroxyl groups of cellulose. Silanes undergo hydrolysis, condensation and bond formation stage. Silanols can form polysiloxane structures by the reaction with hydroxyl groups of the fibres [16].

Gamma irradiated fibre: Gamma irradiation on to the fibre surface leads to major changes in the fibre. Peak at 1735 cm^{-1} intensified upon ? irradiation.

? irradiation causes depolymerization leading to the oxidative degradation of the cellulose molecules with the formation of carboxyl groups. IR spectra given in Figure 3.9 also confirmed the formation of carboxyl group as evident from a strong absorption band in the region of 1735cm^{-1} corresponding to the carbonyl stretching frequency of the carboxyl group. Prominent peaks are also observed at 1642, 1375, and 1250 cm^{-1}. This may arise from the changes in the crystalline region, C-H bending vibration and interaction between O-H bending and C-O stretching.

3. 2. 5 Thermal studies

When cellulosic fibres are heated, a series of interrelated physical and chemical changes occur. The physical properties affected include enthalpy, weight, crystallinity etc. The chemical reactions involved are the decomposition of the glycosyl units of cellulose at about 300°C. At temperatures above 400°C depolymerization of the molecule take place by the cleavage of glycosyl units. This reaction is always accompanied by the decomposition of some anhydro sugar products. At still higher temperature direct fission of the substrate and the intermediate products takes place forming low molecular weight gaseous products and metallic oxides.

The thermal degradation [DTG] of the raw and treated fibres in Nitrogen atmosphere is given in fig 3.10. In thermo-gravimetric tests, a common behaviour observed in all the samples was the dehydration process below 100°C, in which 5-8% of adsorbed water was removed. The majority of the weight loss of the raw and treated fibres took place above 300°C. The fibre treatments slightly improved the thermal stability of the fibres, showing a higher temperature of decomposition compared to the raw fibre. From the DTG curves shown in figure 3.10, it was observed that the thermal stability of the fibres increased in the following order: Untreated (361 °C) <Gamma irradiated (362.3°C) <Silane treated (375.6°C) <Alkalitreated (385.1°C).

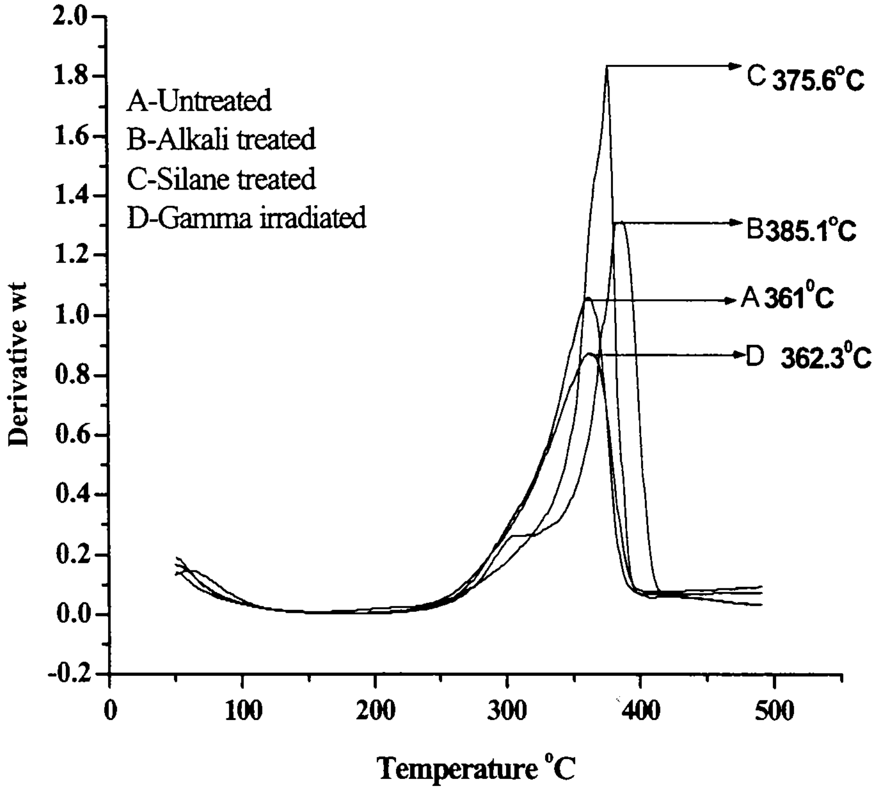


Figure 3.10 Derivative thermograms (DTG) of untreated and chemically modified fibres in Nitrogen atmosphere

DTA/TGA curves of untreated and various modified fibres in oxygen atmosphere are given in figures 3.11 and 3.12

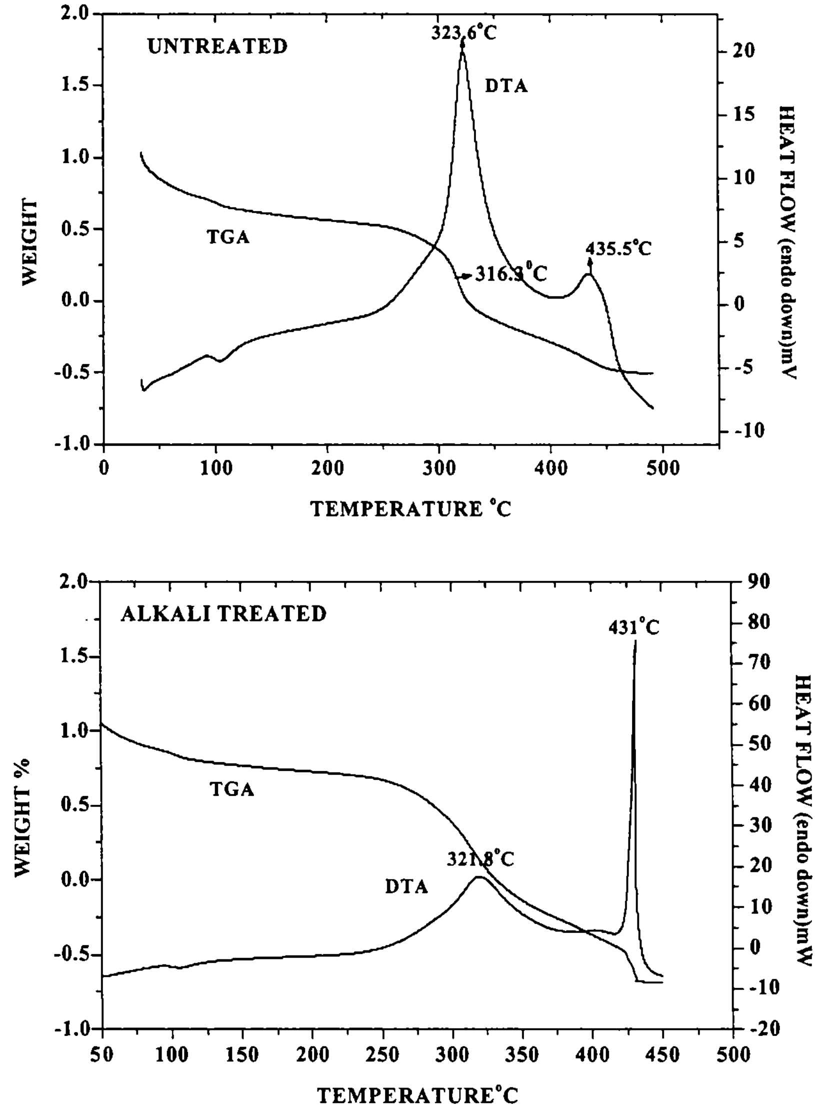


Figure 3.11 DTA/TGA Curves of untreated and alkali treated fibres in Oxygen atmosphere

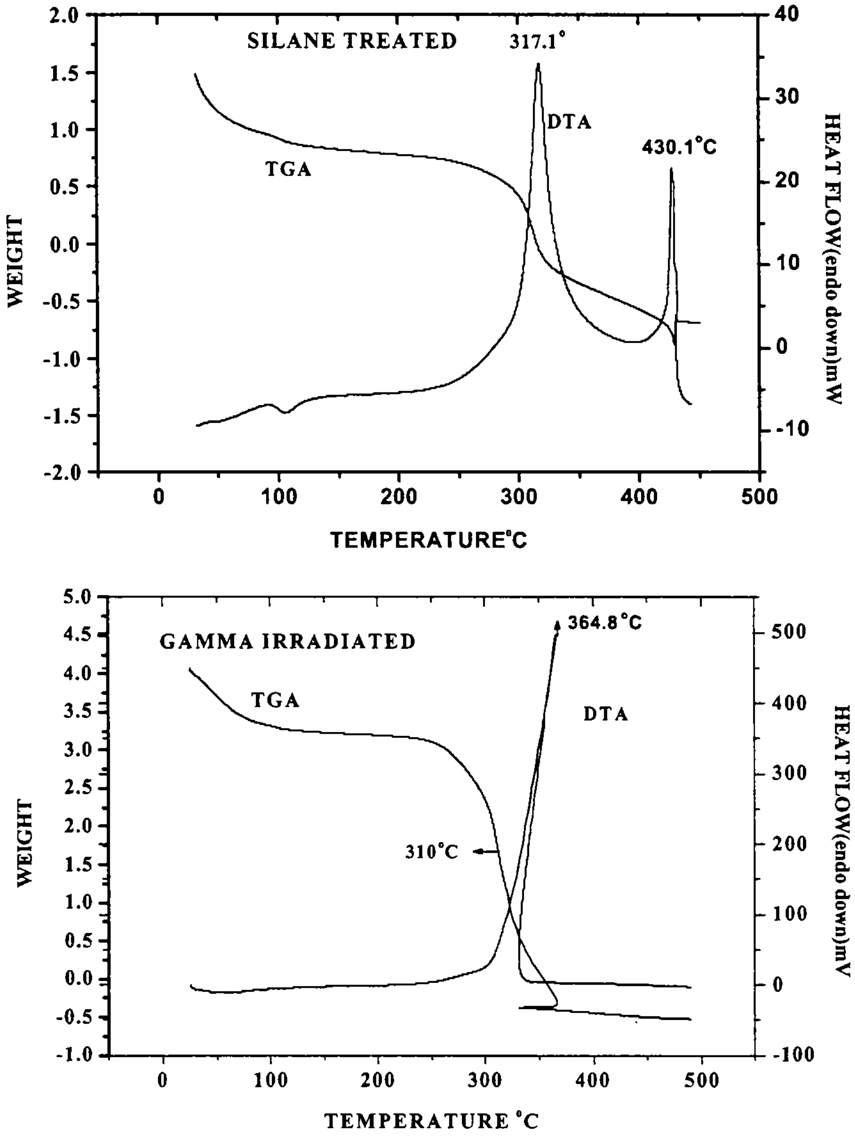


Figure 3.12 DTA/TGA Curves of silane treated and gamma irradiated fibres in Oxygen atmosphere

The DTA curves in oxygen shows a major peak between 300-350°C may be due to the thermal depolymerization of hemicelluloses and the cleavage of the glycosidic linkages of cellulose. This is an exothermic process. At the first stage of the degradation, the DTA curve shows an endothermic peak in all cases at around 100°C. This peak may be due to the removal of moisture.

Breakage of the decomposition products of the second stage (second peak) leads to the formation of charred residue. The third exothermic peak present in DTA curve is due to this oxidation and burning of the high molecular weight residues. In alkali treated fibre the second peak is not prominent and broadening of the DTA peak was observed. In DTA, (oxygen) the initial degradation temperature is higher for the untreated fibre.

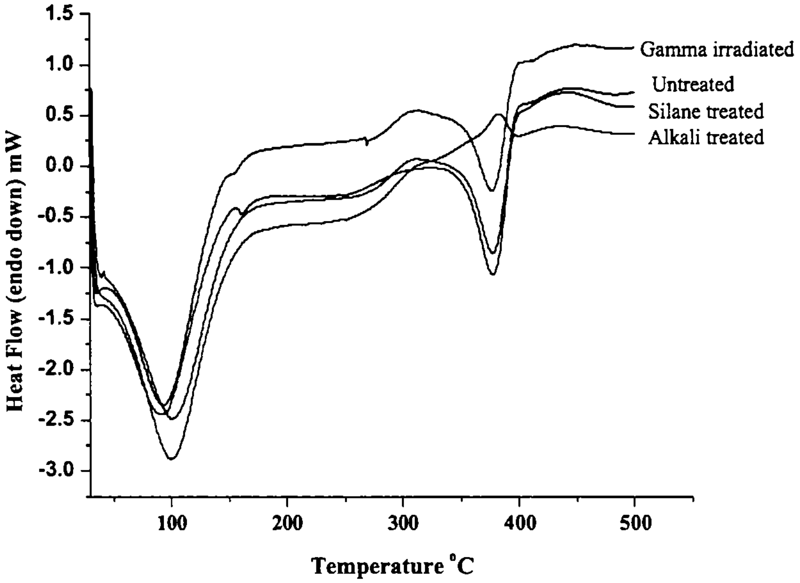


Figure 3.14 DSC curves of untreated and chemically modified fibres in Nitrogen atmosphere

The DSC studies in nitrogen also show a similar trend (Figure 3.13). A broad endotherm in the temperature range of 75-120°C was observed which may be due to the dehydration of fibres. The DSC technique is used to determine the drop in crystallinity and decomposition of plant fibre cellulose. The first exothermic DSC peak corresponds to the decomposition of cellulose.The exothermic peak of alkali treated fibre is shifted to a higher temperature. The second and strong endothermic peak corresponds to the reduction in crystallinity found at around 350°C which also shifted to a higher temperature in the case of alkali treated fibres. This is evident from the DSC curves (Fig 3.13) which is an indication of the increase in the crystalline cellulose, which is known to have good thermal resistance.

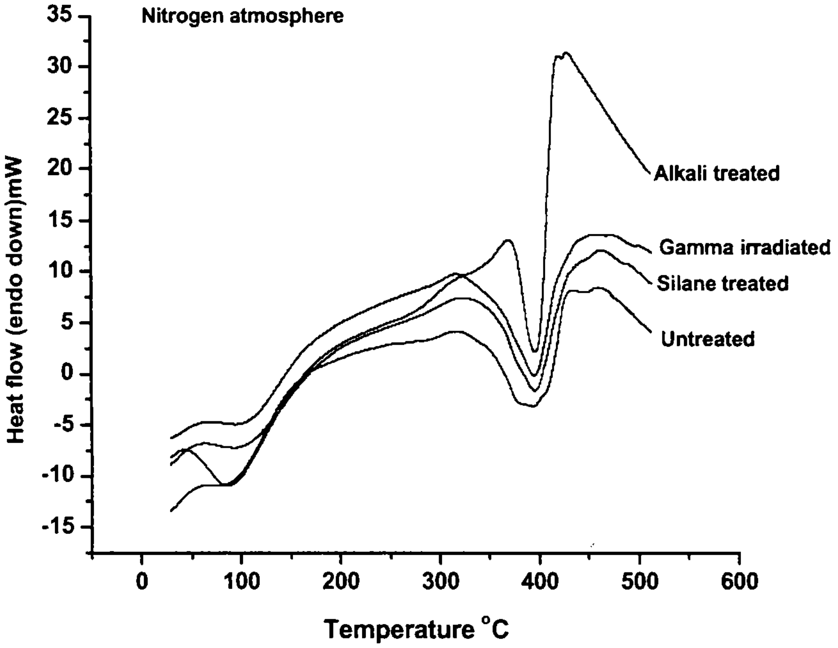


Figure 3.14 DTA curves of untreated and chemically modified fibres in Nitrogen atmosphere

In cellulose fibres lignin degrades at a temperature around 200°C [17] while the other polysaccharides such as cellulose degrade at higher temperatures. Therefore these exothermic peaks which were higher than 200°C indicate the decomposition temperature of the cellulose in the fibres. The region between 150 and 270°C shows no exothermic or endothermic reactions which suggest that the fibres are stable between these temperatures. From the first exothermic peak, it can be deduced that the alkali treated fibre is more thermally stable compared to the untreated, silane treated and gamma irradiated fibre. Similar observations have also been reported in the case of other natural fibres [18]. It was reported that alkali and silane treatment increase the thermal stability of the fibres [19]. DTA studies in Nitrogen atmosphere also show similar behaviour (See Figure 3.14). Pyrolysis of cellulosic fibres at the molecular level is strongly influenced by the degree of polymerization, supermolecular structure of the fibre and its morphology as well as by the impurities

3. 2. 6 WAXRD studies

From table 3.2 and figure 3.15 it is clear that the treated fibres show an overall initial increase in the crystallinty index, with maximum for alkali treated fibres, which is an indication of the improvement in the order of crystallites as the cell wall thickens upon chemical treatment. The use of WAXRD counts offers a simple and quick method of determining the crystallinty index and the minimum between 101 and 002 peaks (Figure 3.15) is an indication of the reflection intensity of the amorphous material. Alkali and silane treatments increase the crystallite packing order. Crystallinty index is a measure of the order of the crystallites rather than the crystallinty of the crystallites [20]. Alkali treatment is reported to reduce the proportion of crystalline material present in plant fibres as observed by several authors [21-23].

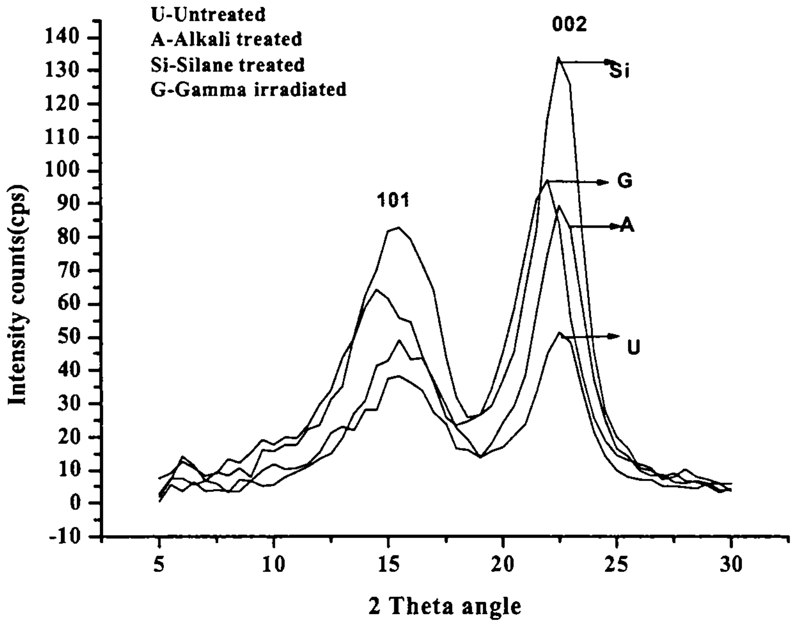


Figure 3.15 WAXRD Spectra of untreated, alkali treated, silane treated and gamma irradiated fibres

3.3 Theoretical Prediction of Micro fibrillar angle and Strength of the fibre

Strength properties of the fibre are dependent mainly on the fibrillar structure, microfibrillar angle, and the cellulose content. There is a correlation between percentage elongation e and microfibrillar angle ? [24]

$e = -2.78+7.28 X10^{-2} ?+7.7 X 10^{-3} ?^{2}$ 3.1

$s =-334.005 - 2.830 ? +12.22W$ 3.2

where W is the cellulose content of the fibre and s is the fibre strength respectively.The theoretical strength of the fibre was found to be 520 MPa, which is in close agreement to the experimental value (565MPa).

3.4 CONCLUSIONS

Chemical composition of the fibres was determined and the major constituent of the fibre was found to be cellulose. A small positive change in the fibre density was observed for the treated fibre indicating cell wall densification

Chemical treatment slightly reduced the tensile strength of the fibre as the binding component of the fibrils gets removed on alkali treatment. Elongation at break was more or less same before and after treatment. WAXRD studies indicate an increase in the crystallinity index after chemical treatment. FTIR spectroscopy has provided information about the reactivity of the fibres following treatment with alkali and silane

SEM and AFM studies revealed that chemical treatment modified the fibre surface. Fine structural changes of the fibres can be seen from the respective SEM photographs. Thermal stability and degradation characteristics of the fibre was investigated by TGA/DTG, DTA, and DSC which indicate that thermal stability of the fibres was increased upon treatment with alkali and silane. Fibres are stable up to 300°C without any considerable weight loss.

3.5 REFERENCES

1. *The Wealth of India – A Dictionary of Indian Raw materials and Industrial products.,* Published by CSIR, New Delhi (1959) **5**: 27
2. Lovely Mathew., Joseph K.U., and Rani Joseph., *Prog in Rubb Plast and Recycling Technol*, (2004) **20(4):** 337
3. Joshy M.K., Lovely Mathew.,and Rani Joseph *In the Proceedings of the first international conference ICBC 2005,* organised by M.G.University, Kottayam, Kerala. (2005) p.113
4. Barkakaty B.C., *J Appl Polym Sci.*, (1976) **20:** 2921
5. Martinez M.N.C., Herrera Franco P.J., *J Appl Polym Sci.*,(1991) **43:** 749
6. Rao D.R., Gupta V.B., *Ind J Fibre Tex Res.*, (1992) **17**:1
7. David C., fornasier R., *J Appl Polym Sci.,* (1988) **36**: 29
8. Brewis D.M., Comyn J., Fowler J.R., *Fibre Sci Technol.,* (1979) **12**:41.
9. Mahato D.N., Mathur B.K., Bhattacherjee S., *Ind J Fibre Tex Res.*, (1995) **20**: 202
10. Mwaikambo, L.Y., Ansell M., *J Mater Sci.,* (2001) **20:** 2095
11. Liu, C., Cuculo J., and Allen T., *J Appl Polym Sci, Part B Polym Phy*, (1991) **29**: 181
12. Ansell M., Mwaikambo L.Y.,*J Appl Polym Sci*, (2002) **84(12)**:2222
13. Gustafsson, J., Doctoral Thesis -"*Surface Characterization of Chemical and Mechanical Pulp Fibres by AFM and XPS*", Åbo Akademi University, Department of Physical Chemistry, Turku, Finland, 2004.
14. Sjöström, E., "*Wood Chemistry: Fundamentals and Applications*", second ed., Academic Press, New York, 1993.
15. Peltonen J., et al., *Langmuir.*, (2004) **20**: 9428-9431.
16. Bledzki A.K., Gassan J., *J Appl Polym Sci.*, (1996) **59**: 1329

17. Akita, K., Kase M., *J Polym Sci.,* (1967) *Part A* **5**:833

18. Aziz, S.H., Ansell M., *Comp Sci Technol.,* (2004) **64**:1219

19. Sreekala M.,Kumaran M., Thomas S., *JAppl Polym Sci*, (1997) **66**:821

20. Ansell, M. and Mwaikambo L.Y. (2002). *J Appl Polym Sci*, **84(12)**:2222

21. Bisanda E.T.N., Ansell M.P., *Comp Sci Technol,* (1991) **41**: 165

22. Ansell M., Mwaikambo L.Y., *Angew Makromol Chem,* (1999) **272**: 108

23. Morton W.E., Hearle J.W.S., *In an Introduction to Fibre structure, Physical properties of textile fibres*, The Textile Institute, Heinemann, London, (1975) Chap 1.

24. Satyanarayana K.G., Pilliai C.K.S., Sukumaran K., *J Mater Sci,* (1982) **17**: 2453

CHAPTER 4

CURE CHARACTERISTICS AND MECHANICAL PROPERTIES

PART I

4.1 **Isora /natural rubber composites vulcanization by conventional curing system**

4.1.1 Introduction

4.1.2 Experimental

4.1.3 Results and Discussion

4.1.3.1 Evaluation of fibre breakage

4.1.3.2 Cure characteristics

4.1.3.3 Mechanical properties

4.1.3.4 Effect of different bonding/coupling agents on cure characteristics and mechanical properties

PART II

4.2 **Isora /natural rubber composites vulcanization by low temperature curing system**

4.2.1 Introduction

4.2.2 Experimental

4.2.3 Results and Discussion

4.2.3.1 Cure characteristics

4.2.3.2 Mechanical properties

4.3 Conclusions

4.4 References

CHAPTER 4

CURE CHARACTERISTICS AND MECHANICAL PROPERTIES

Effects of fibre length, orientation, loading, chemical treatment and bonding agent.

Abstract

The effects of fibre length, fibre loading, and fibre treatments on the the mechanical properties of short isora fibre reinforced natural rubber composites is described in this chapter. The performance of the composite depends upon the interfacial strength and fibre orientation. Interfacial strength is improved by modifying the the surface topology of isora fibre and by the use of bonding agent. Attempt has been made to correlate the extent of orientation with composite performance. Effect of low temperature curing on the mechanical properties of the composite is also reported.

Results of Part I of this Chapter has been accepted for publication (in press) in *Journal of Applied Polymer Science* and Part II has been published in *Journal of Rubber Research* (2006), 9(1):21-39

PART I

4.1 ISORA /NR COMPOSITES VULCANIZATION BY CONVENTIONAL CURING SYSTEMS

4.1.1 INTRODUCTION

Short fibre reinforced rubber composites is a rapidly growing class of materials because of their improved physical and mechanical properties, easy processability and economic advantages. These materials bridge the gap between elastomers and fibres by combining the strength and stiffness of short fibres with the elasticity of rubber [1]. Complex shaped engineering components may be developed using short fibre reinforced elastomers. When used properly, short fibres generate a high degree of reinforcement, which is sufficient for many specific applications. The mechanical properties of short fibre reinforced composits̶e can be improved by maintaining a high aspect ratio, control of fibre orientation, generation of strong interface through physico-chemical bonding and establishment of high degree of fibre dispersion. The most important parameters that affect the short fibre reinforcement are fibre aspect ratio, fibre dispersion and orientation, fibre loading, fibre length and adhesion between the fibre and the matrix [2]. A considerable amount of research work has been done in the field of short fibre reinforced elastomer composites. Many researchers have studied the effect of different fibres in natural and synthetic rubbers [3-14]. Use of biodegradable matrix and natural fibres as reinforcement has opened new potential applications to these composites as they are eco friendly materials. Presently, studies have been made with an intention to conserve energy from the renewable resources and natural fibre is getting more attention from researchers. Natural cellulosic fibres when used as reinforcement imparts mechanical properties comparable to those of synthetic fibres like glass. Composites developed using these natural fibres have the potential to be an attractive alternative to synthetic fibre composites and are currently being explored in sectors like automobiles and buildings. In addition, these fibres offer an excellent opportunity to utilize and abundant source of such materials. Natural fibres have advantages over synthetic fibres due to renewable nature, low cost, easy availability, biodegradability, and ease of chemical modifications. They are also free from health hazards which are not so frequently associated with the use of synthetic fibres. It is important to mention that based on the the cost/performance ratio, natural fibres are highly cost effective form of reinforcement. These fibres however exhibit large variation in quality, and are sensitive to moisture. The main problems that are usually encountered while using natural fibres as reinforcement are that, the incorporation of a hydrophilic fibre into a hydrophobic polymer leads to a heterogeneous system with the result that they exhibit properties inferior to those of the unfilled system due to the poor adhesion at the fibre matrix interface. The surface characteristics of the reinforcing fibres are therefore important in transferring stresses from the matrix to the fiber.

In the past many attempts have been made to modify the surface properties of natural fibres in order to enhance adhesion with the polymer. Various methods such as corona treatment, plasma treatment, mercerization, heat treatment, graft co polymerization, silane treatment [15-22] etc. have been reported to enhance the compatibility in natural fibre composites. This chapter describes the cure characteristics and mechanical properties of short isora fibre reinforced natural rubber composites giving special reference to the effect of fibre length, fibre orientation, fibre treatment, fibre loading and use of a bonding agent. Fibre matrix adhesion has been analysed by scanning electron microscopy.

4.1.2 EXPERIMENTAL

Formulations of mixes with different fibre length and loading are given in Table 4.1.1 and 4.1.2

Table 4.1.1 Mixes with varying fibre length (phr[a])

Ingredients	Gum	L_1	L_2	L_3
Natural rubber	100	100	100	100
Zinc oxide	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
TDQ[b]	1.0	1.0	1.0	1.0
CBS[c]	0.6	0.6	0.6	0.6
TMTD[d]	0.1	0.1	0.1	0.1
S	2.5	2.5	2.5	2.5
Untreated isora fibre	0	15	15	15
Fibre length [mm]	0	6	10	14

[a]parts per hundred rubber, [b]2,2,4 Trimethyl 1,2 dihydroxy quinoline polymerized, [c]N-cyclohexyl benzothiazyl sulphenamide, [d]Tetramethyl thiuram disulphide

Table 4.1.3 Formulation of mixes with varying fibre loading [phr]

Mixes	Gum	X_{10}	X_{20}	X_{30}	X_{40}	Y_{10}	Y_{20}	Y_{30}	Y_{40}
Fibre [U]	0	10	20	30	40	-	-	-	-
Fibre [Y]	0	-	-	-	-	10	20	30	40
Mixes	-	X_{10b}	X_{20b}	X_{30b}	X_{40b}	Y_{10b}	Y_{20b}	Y_{30b}	Y_{40b}
RF resin	0	2.5	5.0	7.5	10	2.5	5.0	7.5	10
Hexa	0	1.6	3.2	4.8	6.4	1.6	3.2	4.8	6.4
Silica	0	1	2	3	4	1	2	3	4
Fibre [U]	0	10	20	30	40	-	-	-	-
Fibre [Y]	0	-	-	-	-	10	20	30	40

Basic recipe: NR -100, ZnO-5, Stearic acid-2, TDQ-1, CBS-0.6, TMTD-0.1, S-2.5, Composites are also prepared with silane treated (S_{30}) and gamma irradiated (R_{30}) fibres with 30 phr fibre loading. X-Untreated, Y-Alkali treated

4.1.3 RESULTS AND DISCUSSION

4.1.3.1 Evaluation of fibre breakage

Mixes L_1, L_2, and L_3 are the NR mixes containing fibres of lengths 6mm, 10mm, and 14mm respectively. The control of fibre length and aspect ratio of fibres in rubber matrix is difficult because of fibre breakage during processing. The severity of fibre breakage depends mainly on the type of fibre, the initial aspect ratio and the magnitude of stress and strain experienced by the fibres during processing [23]. Shear force during mixing orients most of the fibres along the mill grain direction. It may cause breakage of fibres also. The average diameter (10μ) of the fibre remained unchanged after mixing. The results of the fibre breakage analysis are given in Table 4.1.3.

Table 4.1.2 Distribution of fibre length after mixing

Length of fibre after mixing(mm)	Percentage available in the mix after mixing		
	L_1	L_2	L_3
0-2	51.7	9.0	11.4
2-4	27.9	22.0	23.3
4-6	20.4	30.3	25.6
6-8	-	33.0	32.7
8-10	-	5.7	7.0

*Mixes L_1,L_2 and L_3 contain fibres of length 6mm, 10mm and 14 mm before mixing.

From the data it is seen that the compound L_2 contained a total of 52.3% of the fibre in the range of 2-6 mm length and 63.3% of fibre in the range of 4-8 mm length after mixing and the aspect ratio remains higher than 200 which is generally required for effective stress transfer in short fibre elastomer composites[24]. From Table 4.1.6 it is clear that the reinforcement is high for the vulcanizate L_2 containing fibres having an original length of 10mm before mixing as evident from the high tensile strength, modulus and tear strength of the vulcanizate L_2 compared to that of L_1. The tensile strength and modulus of the vulcanizate L_3 are comparable to those of L_2, even though it contained almost the same level of fibres (48.9%) having a length in the range 2-6mm as that of the vulcanizate L_1 (48.3%). This is likely to be due to the presence of 39.7% of fibres having a final length in the range of 6-10 mm in L_3, which is almost comparable to that present in L_2 (38.7%). These observations indicate that an original fibre length of 10mm is the critical fibre length which is essential for getting better reinforcement in short isora fibre natural rubber composites.

4.1.3.2 Cure characteristics

Effect of fibre length and fibre loading

Variation of cure characteristics of composites with varying fibre length and loading are given in Tables 4.1.4 and 4.1.5. The maximum torque is a measure of cross link density and stiffness in the rubber. In general for all the mixes the torque initially decreases, then increases and finally levels off. The initial decrease in torque to a minimum value is due to the softening of the rubber matrix while the increase in

Table 4.1.4 Vulcanization parameters for mixes with varying fibre length

Mixes	Gum	L_1	L_2	L_3
ML[Nm]	.01	.03	.02	.02
M_H [Nm]	.21	0.24	0.30	0.28
t_{10}[min]	2.36	1.8	1.76	1.76
t_{90}[min]	4.32	4.62	5.42	5.46

torque is due to the cross linking of rubber. The leveling off is an indication of the completion of curing. It is found that the addition of fibres into the mix generally increases the torque values. It also shows that the torque increases with increase in fibre length and reaches a maximum at 10mm fibre length. This increase is due to the presence of longer fibres, which imparts more restriction to deformation. However the maximum torque was slightly higher for 10mm than 14mm.This may be due to the fact that longer fibres undergo fibre entanglement and breakage during mixing. The maximum torque also increases with increase in fibre loading. This is due to the increase in the stiffness and hardness of the composite [25]. This torque values are also increased by alkali treatment as the treated fibre may provide better surface for polymer interaction resulting in better reinforcement. It is observed that the curing time is not very much affected by the modification of fibre surface. The optimum cure time is found to increase with addition of bonding agent. According to Chakraborty[25] the longer curing time is due the better bonding between the fibre and the matrix when bonding agent is used.

Table 4.1.5 Cure characteristics for mixes with varying fibre loading

Mixes	**X_{10}**	**X_{20}**	**X_{30}**	**X_{40}**	**Y_{10}**	**Y_{20}**	**Y_{30}**	**Y_{40}**
t_{90}[min]	5.4	5.5	5.7	5.85	4.61	4.91	5.22	5.64
M_H[Nm]	0.29	0.32	0.35	0.40	0.32	0.34	0.40	0.51
Mixes	**X_{10b}**	**$X_{20\,b}$**	**$X_{30\,b}$**	**$X_{40\,b}$**	**$Y_{10\,b}$**	**$Y_{20\,b}$**	**$Y_{30\,b}$**	**$Y_{40\,b}$**
t_{90}[min]	7.24	7.76	8.12	8.36	6.9	7.0	7.32	7.68
M_H[Nm]	0.33	0.35	0.52	0.64	0.35	0.47	0.58	0.69

M_H- maximum torque,t_{90} –optimum cure time

Maximum torque values also increases in the presence of bonding agent. This is due to the strong bonding at the fibre/rubber interface and consequently the composite become stronger harder and stiffer.

4.1.3.3 Mechanical properties.

a. Effect of Fibre length

The effect of fibre length and orientation on the properties of the composites is given in Table 7. The properties are found to increase with increase in fibre length. The increase in strength with increase in fibre length is attributed to the fact that the extent of load transmittance is a function of fibre length and magnitude of fibre matrix interfacial bond [26]· In fibre reinforced composites there exists a critical fibre length at which the load transmittance from the matrix to the fibre is maximum. Critical fibre length is that length which is required by the fibre to develop its fully stressed condition in the matrix. Longer fibres impart more restriction to deformation while shorter fibres create friction and heat generation due to the increased number of fibre ends. Tensile and tear strengths show a maximum value for the composite with fibres having an original length of 10mm before mixing. The interaction between the fibre

Table 4.1.6 Mechanical properties of vulcanizates with varying fibre length

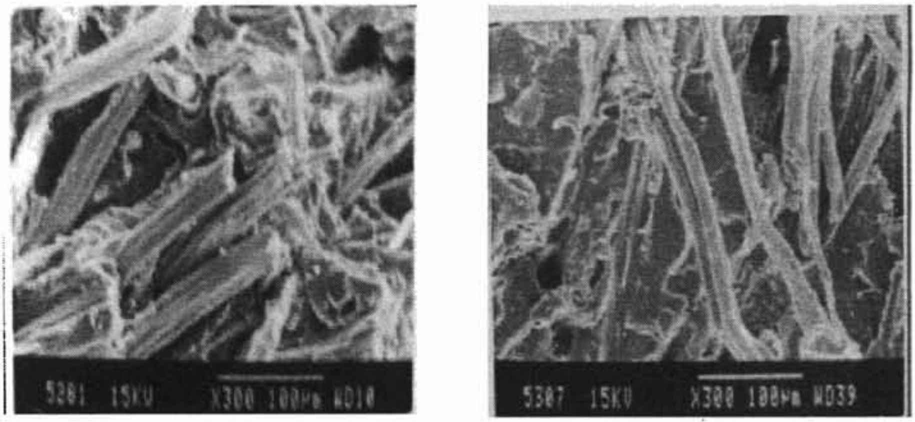
Properties	O	Gum	L_1	L_2	L_3
Tensile modulus	L	2.3	2.71	2.95	2.80
(300% E) MPa	T	2.3	2.30	2.40	2.30
Tensile strength	L	25.9	14.0	16.2	15.9
MPa	T	25.0	12.1	13.8	14.0
Elongation break	L	1050	700	625	695
%	T	1045	725	650	715
Tear Strength kNm^{-1}	L	35.1	37.5	42.0	42.5

O-Orientation; L- longitudinal; T- transverse; L_1, L_2, L_3 are mixes with fibre length 6, 10, and 14 mm respectively.

and the matrix reaches its maximum at this fibre length and the effect of fibre length decreases with longer fibres because of fibre entanglement and breakage. At higher fibre length the dispersion of fibre in rubber matrix is difficult. Hence a further increase in the length of fibre ie; above 10mm decreases the mechanical properties like tensile strength, tear strength etc. These observations indicate that an original fibre length of 10mm is the critical fibre length which is essential for getting maximum reinforcement in its composites with natural rubber.

b. Effect of fibre orientation

Fibre orientation affects the performance of composites. During milling of rubber composites, majority of the fibres tend to orient along the flow direction, causing the mechanical properties to vary in different directions [27]. In case of short fibre reinforced composites, longitudinal and transverse orientations are possible. In longitudinal orientation the fibres are aligned along the mill grain direction and in transverse one the fibres are aligned across the grain direction.



(a) **(b)**

Figure 4.1.1 SEM photographs showing (a) longitudinal and (b) transverse orientation of fibres in the composite X_{30}

Properties like tensile modulus, tensile strength tear strength etc; of the composites with longitudinal orientation are always higher than the composites with transverse fibre orientation (Table 4.1.6). The extent of fibre orientation can also be understood qualitatively from the SEM photographs.

Figures 4.1.1(a) and (b) are tensile fracture surfaces of the longitudinally and transversely oriented composite (X_{30}). The broken fibre ends protruding from the fracture surface [Fig.4.1.1 a] indicate that the fibres are well aligned longitudinally in the direction of applied force. While in transverse orientation the fibres are aligned across the direction of applied force [Fig.4.1.1 b]. The tensile strength of the composites depends on the fibres, which obstruct the progress of the fracture front. In longitudinal orientation the crack progresses in the direction perpendicular to the fibre alignment causes greater obstruction by the fibres and hence tensile strength showed a higher value. Breakage and pulling out of fibres take place when fibres are oriented longitudinally where as in transverse orientation crack progresses in the direction of fibre alignment experiencing a lower resistance by the fibres. The increase in tear strength in longitudinal orientation is due to the obstruction caused to the tear path by the short fibres.

c. Extent of fibre orientation from green strength measurements

The green strength of short fibre reinforced composites depends on the degree of fibre orientation. The extent of fibre orientation can be calculated by using the following equation

$$\text{Orientation \%} = \frac{S_L/S_{G,L}}{S_L/S_{G,L}+S_T/S_{G,T}} \qquad \text{.......................4.1.1}$$

Where S is the green strength and subscripts G, L, and T denotes gum, longitudinal and transverse respectively. The effect of fibre loading on the percentage orientation is shown in figure 4.1.2.

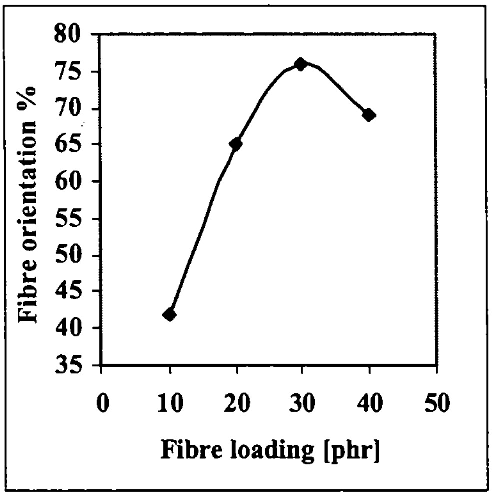
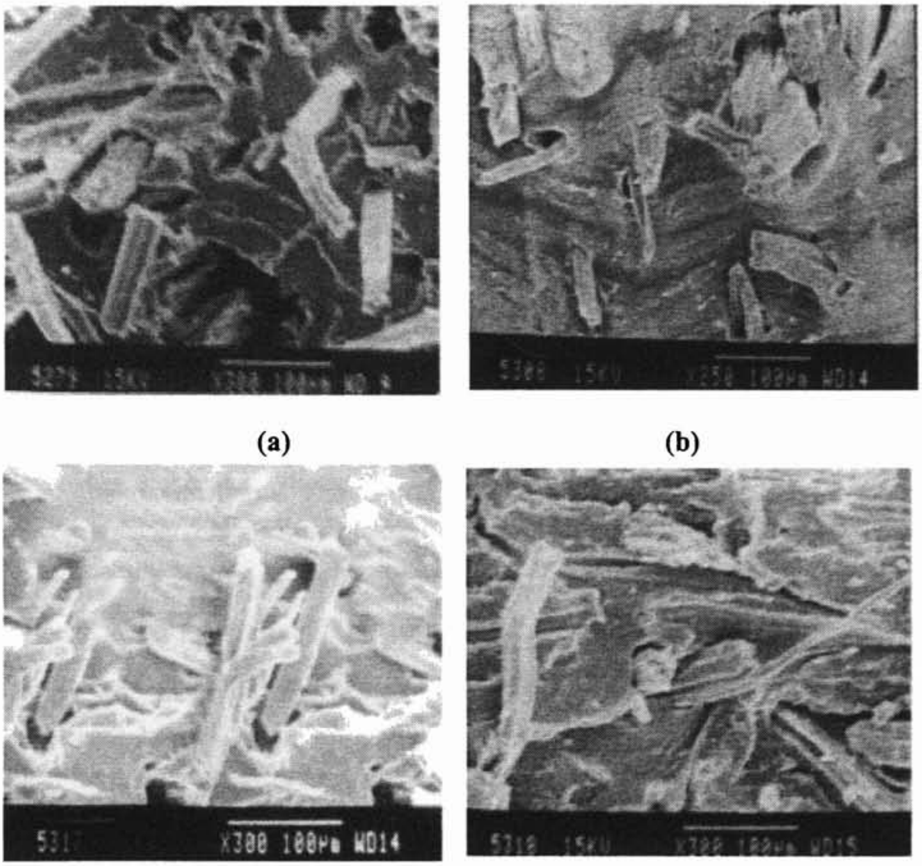


Figure 4.1.2 Effect of fibre loading on percentage of fibre orientation of the composites.

At low fibre loading the percentage orientation is the lowest as the fibres can randomly move around leading to increased chaocity and decreased levels of orientation. As fibre loading increases, percentage orientation increases with the maximum value for composite containing 30 phr fibre. At 40 phr fibre loading the percentage orientation decreases indicating that the fibres cannot orient themselves due to the entanglement caused by the increased content of fibres

d. Effect of chemical treatment and fibre loading

Good interfacial strength between the fibre and rubber is the essential factor to achieve good fibre reinforcement. The interfacial strength depends on the surface topology of the fibre. The cellulose fibres even though possess hydroxyl groups on its surface the lignin and other waxy contents make it a less effective reinforcement. Hence to improve adhesion between isora fibre and rubber it should be subjected to some chemical treatment to remove the lignin and other waxy impurities. So the mixes Y_{30}, S_{30} and G_{30} are prepared using alkali treated, silane treated and gamma irradiated fibres respectively. The surface topology of untreated and various chemically modified isora fibre was studied by SEM, and is explained in detail in Chapter 3.



(a) **(b)**

(c) **(d)**

Figure 4.1.3 SEM of the tensile fractured surfaces of the composites containing (a) untreated (b) alkali treated (c)gamma irradiated and (d) silane treated fibres

The fibrillar nature and porosity of the fibre is revealed from the fibre topography. The porous surface morphology is useful to have better mechanical interlocking with the matrix for composite fabrication.

Table 4.1.7 Mechanical properties of the various chemically modified isora fibre-natural rubber composites

Properties	X_{30}	Y_{30}	R_{30}	S_{30}
Modulus [300%elongation] [MPa]	3.2	3.8	3.4	5.4
Tensile strength [MPa]	9.8	10.9	10.4	14.9
Elongation at break [%]	437	400	467	385
Tear strength [kN/m]	46.8	47.9	40.5	53.6
Hardness [Shore A]	69	73	70	75

X-untreated, Y-Alkali treated, R Gamma irradiated, S-Silane treated

The SEM photographs of the chemically modified fibres given in Chapter 3 gives strong evidence for the physical and microcellular structural changes that occurred on the fibre surface on chemical treatment. This renders roughness to the fibre thereby enhancing the mechanical interlocking at the interface. The development of a rough surface topography offers better fibre rubber interface adhesion and increase in mechanical properties for the modified fibre composites [Table 4.1.7].

Figures 4.1.3 (a) to (d) are the SEM of the tensile fracture surfaces of composites X_{30}, Y_{30}, R_{30} and S_{30} with untreated and chemically treated fibres.

In the case of untreated fibre composites, due to the weak interfacial adhesion between the fibre and rubber, fibre pull out takes place leaving holes on the surface when stress is applied [Fig.4.1.3 a]. Fig.4.1.3 b shows the presence of broken fibres on the fracture surface which is due to the strong adhesion between the fibre and rubber matrix for composites with treated fibres. Fracture surfaces of gamma irradiated and silane treated fibre composites also contain broken fibres which again supports the improved adhesion between treated fibres and the matrix.Composites containing treated fibres show enhancement in modulus compared to the untreated ones for similar fibre loadings. Table 4.1.8 shows the mechanical properties of the composites containing alkali treated and untreated fibres for varying fibre loadings.

The tensile properties (tensile modulus, tensile strength), tear strength etc; of the composites filled with alkali treated fibres are higher than those with untreated fibres at similar loadings. To obtain good fibre reinforcement in rubber composites, the adhesion between the rubber and the fibre is very important.

Table 4.1.8 Mechanical properties of vulcanizates with varying fibre loadings

Properties	O	X_{10}	X_{20}	X_{30}	X_{40}	Y_{10}	Y_{20}	Y_{30}	Y_{40}
Modulus [MPa]	L	2.8	2.9	3.2	3.0	3.1	3.3	3.8	3.5
	T	2.0	2.1	2.2	2.4	2.5	2.6	2.8	2.9
Tensile strength (MPa)	L	20.9	14.0	9.8	9.0	21.1	15.2	10.7	9.8
	T	13.2	10.1	6.8	6.2	15.2	11.5	8.2	7.8
EB %	L	860	615	437	380	790	605	400	310
	T	900	690	480	425	612	625	412	395
Tear strength kN/m	L	36.5	42.8	46.8	40.9	38.1	44.6	47.9	43.1
	T	35.5	40.1	43.9	39.5	37.5	41.9	44.2	40.8
Hardness (Shore A)	-	50	63	69	72	55	65	73	76

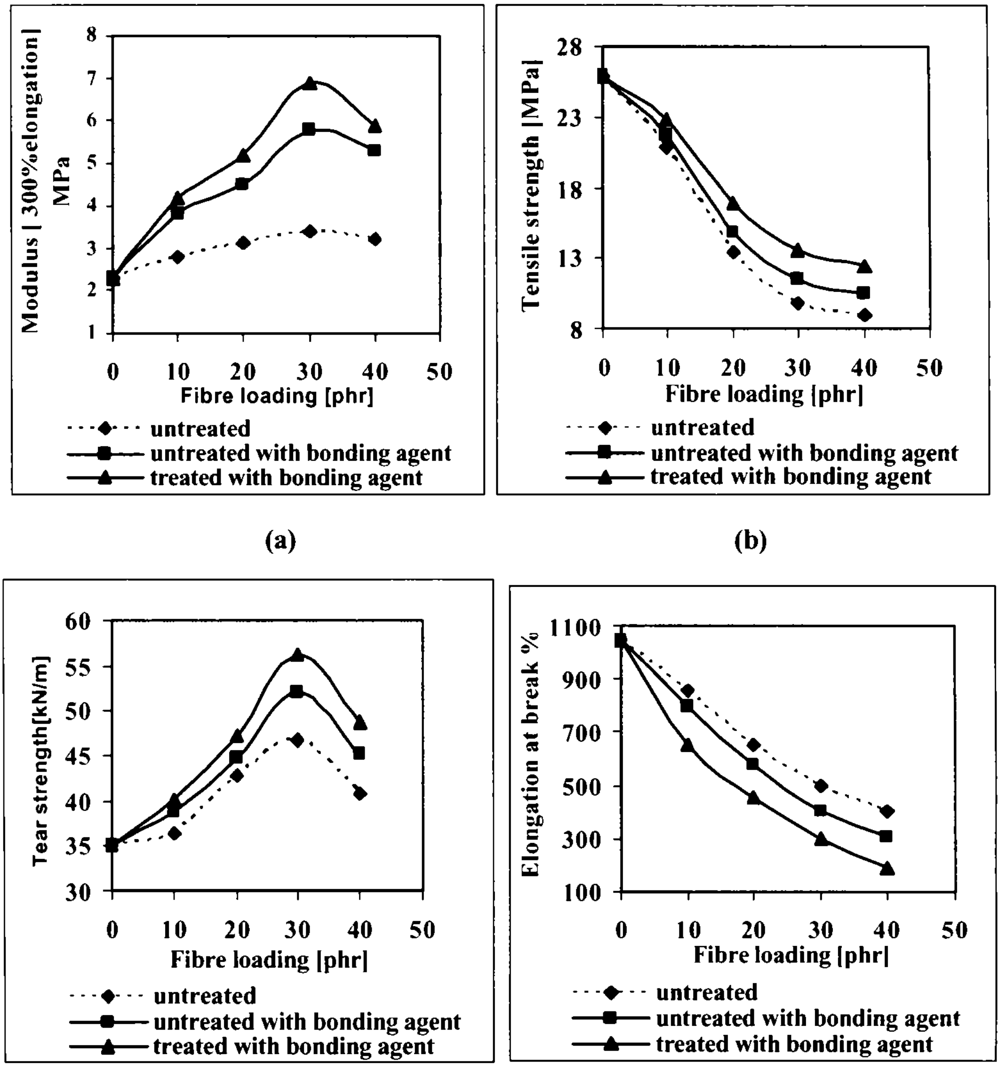
O-Orientation, L-Longitudinal, T-Transverse

From these results it is clear that the aqueous alkali treatment of isora fibre has improved the fibre adhesion to rubber matrix. It is reported that the surface of fibres can be modified by aqueous alkali treatment at elevated temperatures, and this was found to improve the adhesion properties significantly [28]. According to Flodin [29] fibre treatment can be used to prevent the debonding at the fibre polymer interface since it can form covalent bonds between the rubber matrix and fibre. Strong adhesion between treated fibre and rubber leads to higher shear strength at fibre rubber interface. Stronger force must be used to overcome the shear strength, which resulted in higher tensile strength. The elongation at break for composites with treated fibres is lower than composites with untreated fibre at similar loading. This is due to the better strength and stiffness achieved from strong adhesion between fibre and rubber. Consequently the toughness of the composites is reduced resulting in lower elongation at break. Higher toughness is obtained from weak interfacial adhesion as shown by higher elongation at break for composites filled with untreated fibres.

Natural rubber inherently possesses high tensile strength due to strain-induced crystallization. When fibres are incorporated into NR, the regular arrangement of rubber molecules is disrupted and hence the ability of crystallization is lost. Hence the fibre reinforced natural rubber composites possess lower tensile strength than gum vulcanizate. When fibre reinforced rubber composites is subjected to a load, the fibres act as carriers of load and stress is transferred from matrix along the fibres which results in a composite having good mechanical properties. The uniform distribution of stress is dependant on the population and orientation of fibres. At low levels of fibre loading, the orientation of fibres is poor and the fibres are not capable of transferring load to one another and stress get accumulated at certain points of composite leading to low modulus. From Table 4.1.8 it is clear that modulus shows a continuous increase up to 30 phr fibre loading in the case of longitudinal orientation. At higher levels of fibre loading the increased population of fibres leads to agglomeration and stress transfer get partially blocked. On transverse orientation, the modulus increases gradually but with a lower value than longitudinal orientation. Also with the increase of fibre loadings, tensile strength of the composites shows an abrupt decrease up to a loading of 30 phr and there afterwards a gradual decrease both in longitudinal and transverse orientations. At intermediate levels of loading (30phr) the population of fibres is just sufficient for maximum orientation and fibres actively participate in stress transfer. As fibre loading increases tear strength gradually increases and reaches a maximum at 30 phr fibre loading. When the fibre loading increased further, tear strength again decreases as the increased strain in the matrix between closely packed fibres increases tearing and reduces the tear strength. Maya et al also have observed similar results [30]. There is a reduction for elongation at break with increasing fibre loading. Increased fibre loading in the rubber matrix resulted in composites becoming stiffer and harder. This will reduce the composite's resilience and lead to lower elongation at break. Fliink [31] *et al* and Akhtan [32] also reported similar observations. The elongation at break for composites with treated fibres is lower than composites with untreated fibre at similar loading. This is due to the better strength and stiffness achieved from strong adhesion between fibre and rubber. Consequently the toughness of the composites is reduced resulting in a still lower elongation at break. Higher toughness is obtained from weak interfacial adhesion as shown by higher elongation at break for composites filled with untreated fibres.

e. Effect of bonding agent

Further increase in properties is seen by the incorporation of bonding agent to the system. It has already been established that a tricomponent system consisting of hexamethylene tetrammine, resorcinol and fine particle of silica can be used as a bonding agent for most rubber and fibre combinations [33]. Figure 4.1.4 shows the effect of bonding agent on the mechanical properties of the composites



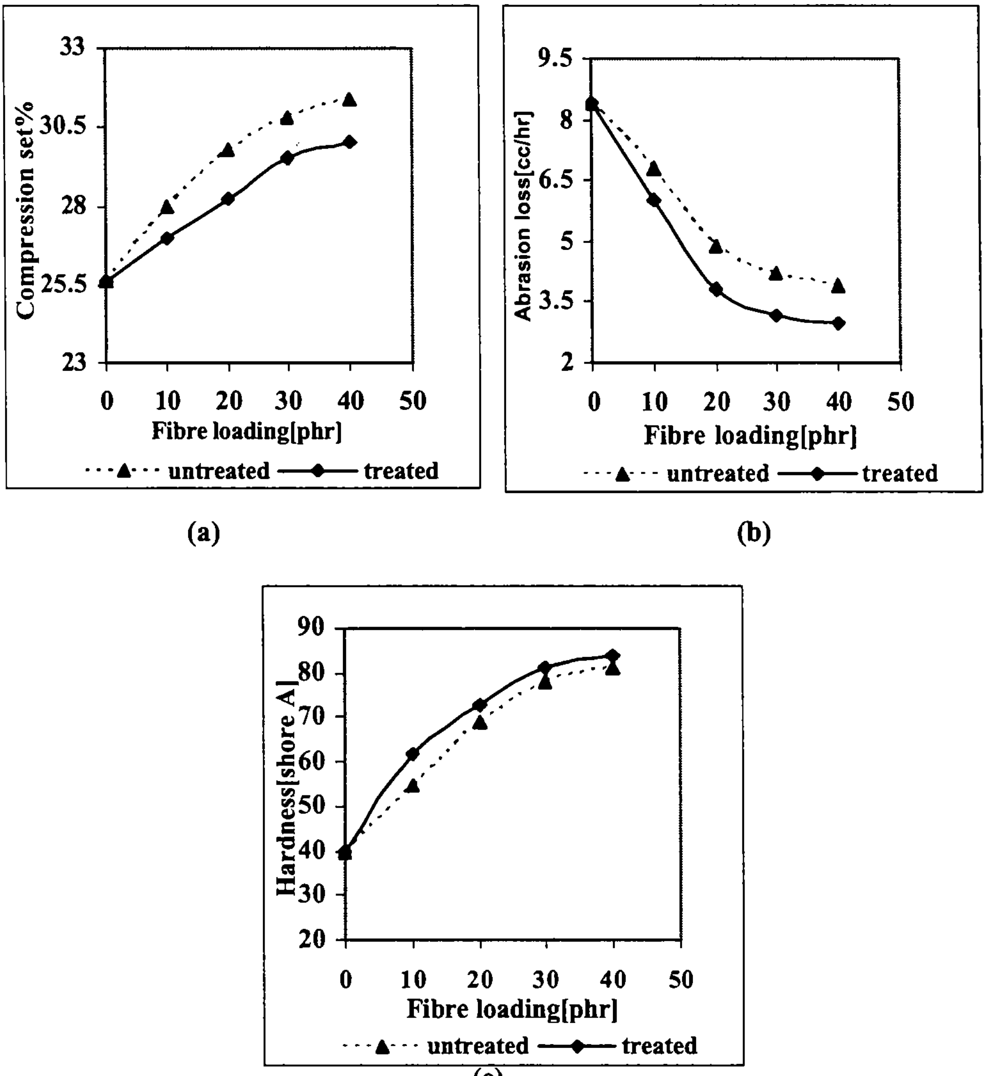
(a) (b)

(c) (d)

Figure 4.1.4 Effect of fibre loading on (a) Tensile modulus, (b) Tensile strength, (c) Tear strength and (d) Elongation at break of the composites

Presence of bonding agent in the mixes improved the mechanical properties like modulus, tensile strength, tear strength etc; Alkali treatment of fibres further enhances the effect of bonding agent as seen from the higher modulus, tensile strength, tear strength etc from figures 4.1.4 (a) to (d). The treated fiber provides a better surface for strong adhesion between fiber and matrix, and the stress transfer becomes more efficient and consequently and better enhancement in the properties. Elongation at break for composites with bonding agent has a lower value than composites without bonding agent. Again treated fibers show a lower elongation at break than untreated fibers.

The variation of compression set, abrasion loss and hardness with fibre loading for the treated and untreated fibre composites with bonding agent are given in figures 4.1.5 (a), (b), and (c). Compression set increased steadily with increase in fibre loading. The rate of increase in set however decreased as loading was increased. But the set was lower for the composites having alkali treated fibres (Figure 4.6 a). It has been reported that this behavior is due to the buckling of the fibre, taking place invariably when the closely packed fibres are compressed in the direction of their alignment [34]. Due to the strong adhesion between the treated fibres and rubber, the extent of buckling is reduced in treated fibre composites resulting in a low compression set. Abrasion loss decreases with increase in fibre concentration in the composite. (Figure 4.1.5 b). Here also the treated fibre composites showed better resistance to abrasion compared to those containing untreated fibres. The better abrasion resistance of the treated fibre composites may be resulting from the combination of higher tear strength, tensile strength and modulus achieved through better bonding with the rubber matrix. The hardness of the composites also increases in the presence of bonding agent (Figure 4.6 c). Ismail *et al* also reported similar observations [35].



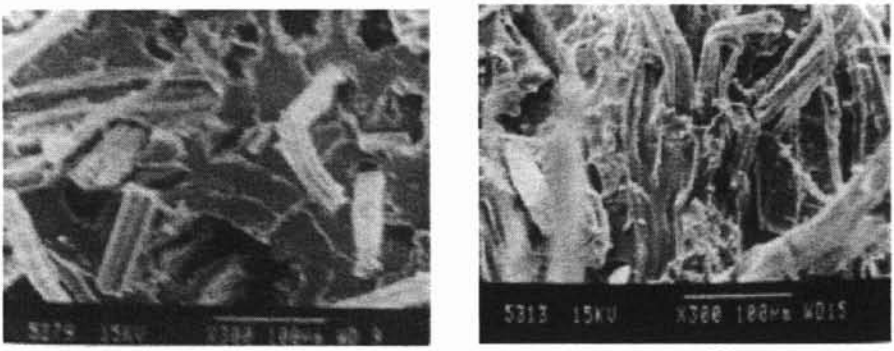
(a)

(b)

(c)

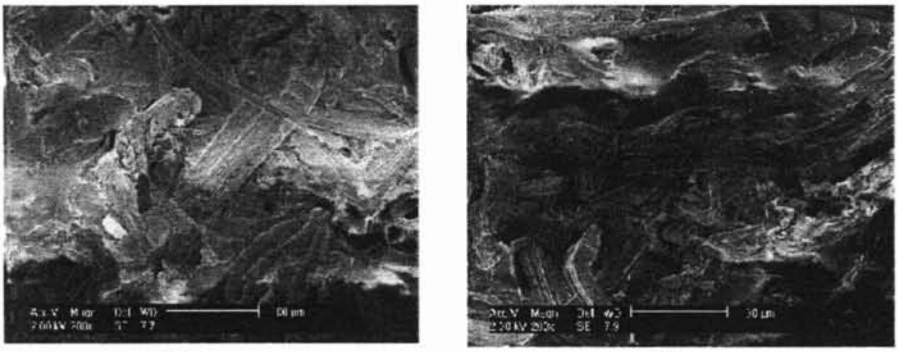
Figure 4.1.5 Variation of (a) Compression set, (b) Abrasion loss (c) Hardness with fibre loading for the composites with bonding agent

Figures 4.1.6 (a) & (b), 4.1.7 (a) & (b) shows the SEM photographs of the tensile and tear fracture surfaces of composites $[X_{30}\&Y_{30b}]$ with and without bonding agent. SEM studies also revealed that for composites without bonding agent, failure occurred at the weak fibre/rubber interface while for composites containing treated fibre and bonding agent failure occurred at the fibre due to strong adhesion between fibres and matrix.



(a) **(b)**

Figure 4.1.6 SEM of the tensile fractured surfaces containing (a) untreated fibre without bonding agent (b) alkali treated fibre with bonding agent



(a) **(b)**

Figure 4.1.7 SEM of the tear fractured surfaces containing (a) untreated fibre without bonding agent (b) alkali treated fibre with bonding agent

4.1.3.4 *Effect of different bonding/coupling agents*

Table 4.1.9 Formulation of mixes with different bonding/coupling agents

Ingredients	X0[a]	X_1	Y_1	X_2	Y_2	S_0
PF Resin[1]	-	10	10	-	-	-
RF Resin[2]	-	-	-	7.5	7.5	-
Hexa[b]	-	-	-	4.8	4.8	-
Fibre (untreated)	30	30		30		
Fibre (alkali treated)			30		30	
Fibre (silane treated)						30

Basic recipe: NR-100, ZnO-5.0, Stearic acid-2.0, TDQ-1.0, CBS-0.6, TMTD-0.1, S-2.5 [a]referencecompound, [1]Phenol-Formaldehyde resin, [2]Recorcinol-Fomaldehyde resin, [b]Hexamethylene tetra ammine,
X- Untreated, Y- Alkali treated, S- Silane treated.

a. Cure Characteristics

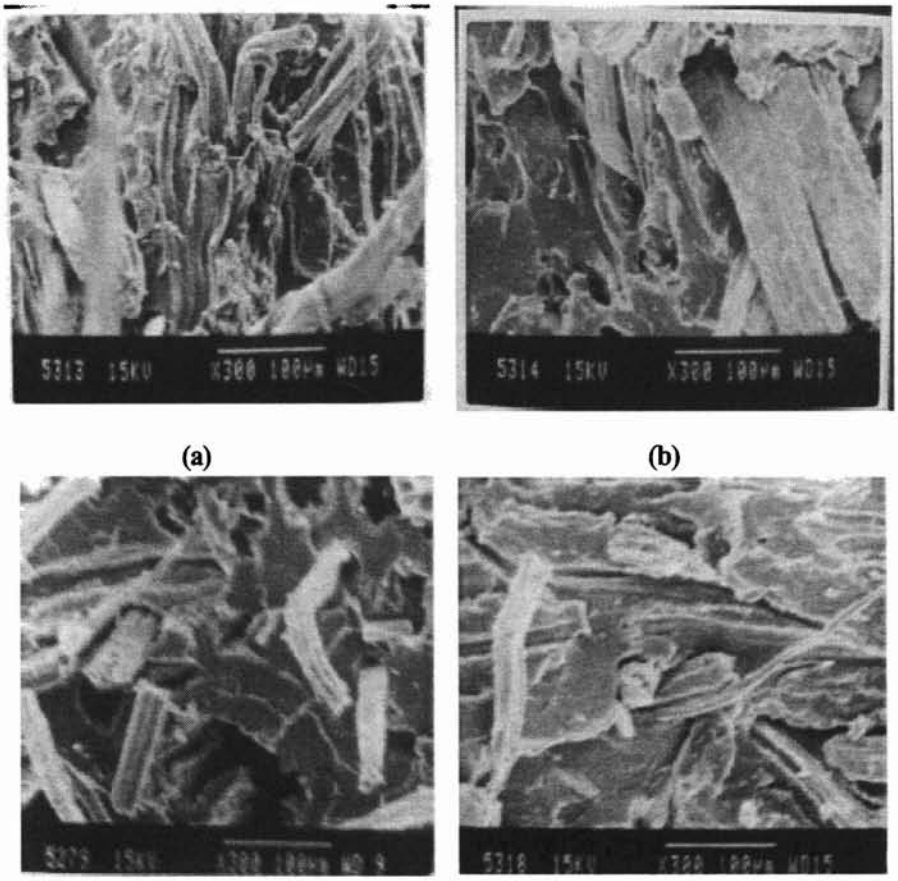
Cure characteristics and mechanical properties of compounds containing different bonding/coupling agents are given in Table 4.1.10. It is observed that there is a significant difference in the vulcanization parameters for compounds with and without bonding/coupling agents. The presence of various bonding/coupling agents in the compounds prolonged the curing time which is due to the better bonding between the fibre and matrix when various bonding/coupling agents are used [25]. Maximum torque values also increases in the presence of different bonding/coupling agents in the composites. This is due to the strong bonding at the fibre/matrix interface and consequently the composite became stronger, harder and stiffer. It is observed that the composites with treated fibre show a higher torque value compared to the untreated fibre due to the better adhesion between the fibre and rubber. Bhattacharya *et al* [36] also made similar observations.

Table 4.1.10 Cure characteristics and Mechanical properties

Compound	X_0	X_1	X_2	Y_1	Y_2	S_0
Mini.Torque[Nm]	0.02	0.01	0.03	0.02	0.04	0.05
Max.Torque[Nm]	0.28	0.44	0.75	0.46	0.54	0..71
Scorch time[min]	2.3	1.6	1.04	1.76	1.08	2.4
Cure time[min]	4.0	8.1	8.4	5.7	5.9	7.3
Tensile Modulus [MPa]	3.2	4.3	4.6	4.7	5.0	5.4
Tensile Strength [Mpa]	9.8	11.5	12.8	13.3	14.0	14.9
Elongation at break%	437	425	405	395	380	385
Tear Strength [kN/m]	42.8	41.8	47.8	44	49.1	53.6
Hardness [Shore A]	69	68	72	70	75	75

b. Mechanical properties.

From Table 4.1.10 it is clear that the mechanical properties of the composites with bonding/coupling agents are found to be higher than the reference compound (untreated fibre without bonding agent). It can be seen that tensile and tear strength increases when different bonding/coupling agents are used in the composites. Also it is observed that the mechanical properties for vulcanizate with treated fibres are higher than vulcanizate with untreated fibres. Treated fibres provide a better surface for strong adhesion between the fibre and the matrix. The presence of bonding /coupling agents also leads to strong adhesion at the fibre rubber interface. According to Miwa *et al* [37], the strong adhesion between the fibre and matrix resulted in higher shear strength at the interface and stronger force must be used to overcome the shear strength at the interface, which resulted in a higher tensile strength. Presence of bonding/coupling agents is found to enhance the composite hardness



(a) (b)

(c) (d)

Figure 4.1.11 Tensile fractured surfaces of the composites containing (a) Without bonding agent (b) PF Resin (c) RF Resin and (d) Silane

It is clear from the table 4.1.10 that different bonding/coupling agents give different cure characteristics and mechanical properties. This is due to the difference in the compatibility of various bonding/coupling agents with the fibre and rubber. The final vulcanizate properties depend on the bonding system, fibre and matrix used. From the results it is clear that silane coupling agent act as a good compatabiliser between fibre and rubber. The mechanisms of the bonding action of the resin and the coupling action of silane with the fibre are explained in chapter 2 and 3 respectively.

PART II

4.2 ISORA/NATURAL RUBBER COMPOSITES VULCANIZATION BY LOW TEMPERATURE CURING SYSTEM

4.2.1 INTRODUCTION

Elastomers constitute an important class of engineering materials without which modern technology would be unthinkable. Even though gum natural rubber vulcanizates shows high tensile strength it is not suitable for many commercial applications. Fillers are generally incorporated for improved processability, reinforcement and cost reduction. The fundamental aspects of rubber-filler interaction have been studied in detail in a number of elastomers [38-41]. Vulcanization temperature is very important in determining the quality of a rubber product. Optimum properties are obtained when curing is done at the lowest possible temperature [42] Rubbers like NR, NBR, etc; are degraded when the temperature is raised [43]. The high modulus developed by the incorporation of fillers decreases, as cure temperature is raised [44]. Low temperature curing results in products of good quality and fine appearance. The additional advantage is that low temperature curing can reduce energy consumption. Moreover it will be extremely useful in the area of repair of defective products, since subjecting finished products to high temperatures during process of repair will adversely affect the quality of the product. A new accelerator consisting of zinc xanthate-ZDC system for low temperature curing of natural rubber with particulate fillers has been prepared and reported [45]. Although xanthates are known to act as accelerators for low temperature vulcanization, their use as a curing agent in natural fibre reinforced rubber composites have not been investigated. In this section, we report the use of the zinc xanthate-ZDC system for curing of NR-isora composite at different temperatures. The properties of these composite containing untreated and alkali treated fibres vulcanized at low temperature are compared with the composite cured at 150°C by conventional accelerator system.

4.2.2 EXPERIMENTAL

Formulation of the mixes prepared is given in table 4.2.1

Table 4.2.1 Compound formulation (phr)

Ingredients	X_{10}	X_{20}	X_{30}	X_{40}	Y_{10}	Y_{20}	Y_{30}	Y_{40}
Fibre[untreated]	10	20	30	40	-	-	-	-
Fibre [alkali treated]	-	-	-	-	10	20	30	40
	X_{10b}	X_{20b}	X_{30b}	X_{40b}	Y_{10b}	Y_{20b}	Y_{30b}	Y_{40b}
RF resin	2.5	5.0	7.5	10	2.5	5.0	7.5	10
Hexa	1.6	3.2	4.8	6.4	1.6	3.2	4.8	6.4
Silica	1	2	3	4	1	2	3	4
Fibre[untreated]	10	20	30	40	-	-	-	-
Fibre [alkali treated]	-	-	-	-	10	20	30	40

Basic recipe: NR -100, ZnO-5, Stearic acid-2, TDQ-1, ZDC-1.0, Xantahate- 0.75, S-2.5, For low temp curing system represented by X and Y. **Conventional curing system [CBS- 0.6, TMTD- 0.1] is represented by X_0 and $Y_0$for untreated and alkali treated composites.**

Xanthate was prepared in the laboratory as per the method reported earlier[22]. The formulation of the test mixes is given in Table 4.2.1. Blanks cut from the uncured sheet were marked with the mill grain direction and the samples were vulcanized at different temperatures (80 to 140°C) for the ZDC/xanthate system and at 150°C for CBS/TMTD system in a hydraulic press for their respective cure times obtained from a Goettfert Elastograph

4.2.3 RESUTS AND DISCUSSION

4.2.3.1. Cure characteristics

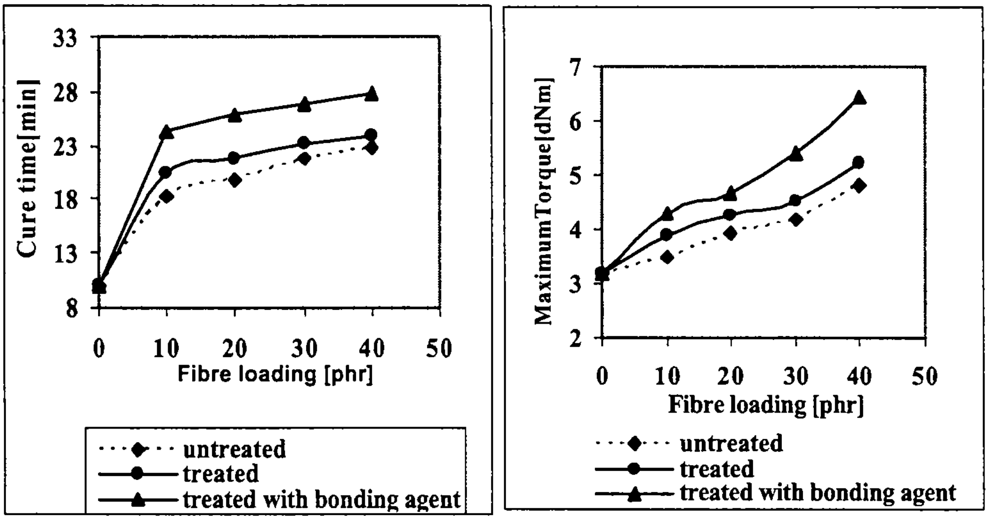
Table 4.2.2 shows the variation of cure characteristics of composites cured at various temperatures from 80°C to 140°C for a particular fibre loading [20phr]. The maximum torque is a measure of cross link density and stiffness in the rubber. It is found that the addition of fibre into the mix generally increases the torque values. It also shows that for a particular fibre loading, the torque increases with increase in temperature and reaches a maximum at 100°C. At higher temperatures the fibre may degrade resulting in a lower torque value. These torque values are also increased for alkali treatment as the treated fibre may provide a better surface for reinforcement. Results show that cure time decreases as temperature of curing is increased from 80°C to 140°C. Figure 4.2.1(a) & (b) shows the variation of cure time and maximum torque with fibre loading for the composites cured at 100°C. At a particular temperature when the cure time of gum compound is compared with the fibre filled compound it is seen that the curing becomes slow when fibres are added may be due to the presence of acidic groups on the fibre surface. It is made clear by gradually increasing the fibre loading from 0 to 40 phr. The presence of fibres retards the formation of cross links between the polymer chains.

Table 4.2.2 Effect of temperature on cure characteristics.

Composite X_{20} (untreated fibre without bonding agent)

Temperature (degrees)	t_{10} (min)	t_{90} (min)	Mini.Torque (dNm)	Max.Torque (dNm)
80	22.16	51.6	0.114	3.033
100	4.98	19.4	0.078	4.032
120	1.47	7.36	0.023	3.640
140	0.487	1.57	0.020	3.360
Composite Y_{20} (alkali treated fibre without bonding agent)				
80	26.3	54.46	0.111	3.170
100	5.67	21.8	0.010	4.252
120	1.60	7.26	0.039	4.108
140	0.51	1.64	0.045	3.808
Composite Y_{20b}(alkali treated fibre with bonding agent)				
80	27.49	59.2	0.163	3.396
100	6.07	25.8	0.035	4.682
120	1.98	8.87	0.045	4.385
140	0.57	2.61	0.084	4.007

Maximum torque value also increases with the increase in fibre loading as the composite become stiffer and harder at higher loadings. Again presence of bonding agent in the composite still increases the maximum torques. This is due to the strong bonding at the fibre/rubber interface and consequently the composite become stronger harder and stiffer. It is observed that the curing time is not very much affected by the modification of fibre surface. The optimum cure time is found to increase with the addition of bonding agent. The variation of cure characteristics of the composites as a function of soaking time of isora fibres in 5% NaOH is shown in Table 4.2.3.



(a) (b)

Figure 4.2.1 Effect of fibre loading on (a)cure time and (b) maximum torque for the composites cured at 100°C

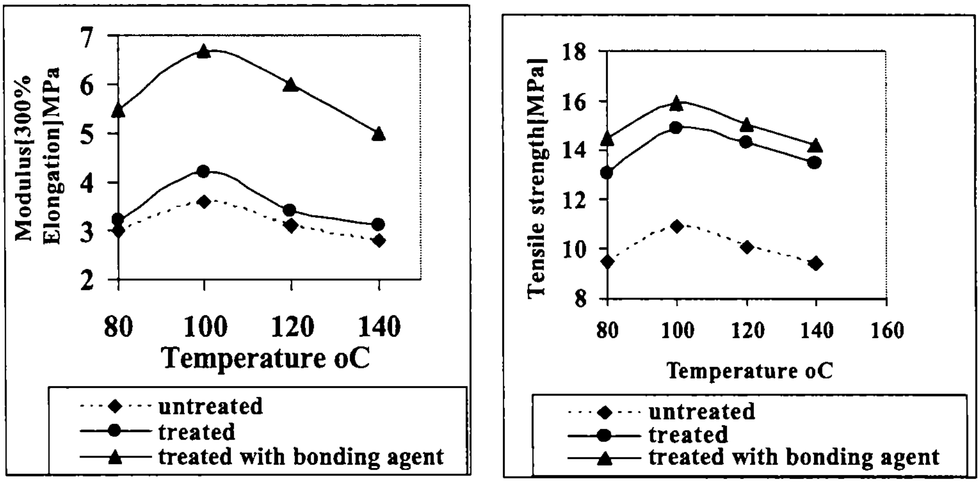
4.2.3.2 Mechanical Properties

Variation of mechanical properties of the composites as a function of soaking time of fibre in 5% NaOH is also shown in Table 4.2.3. It is seen that the tensile properties like tensile modulus, tensile strength and tear strength increases with soaking time and reaches a maximum for composites containing 4 hour treated fibres, followed by a reduction in the properties. This is associated with the better interaction between the treated fibre and rubber. However, prolonged treatment up to 72 hours decrease the properties marginally. This may be due to the excessive removal of binding material such as lignin, hemi cellulose etc.

Figures 4.2.2(a) to (f) show the properties of the composites vulcanized at various temperatures using ZDC/Xanthate systems.

Table 4.2.3 Effect of soaking time on cure characteristics and mechanical properties of the composites (X_{30}&Y_{30}) cured at 100°C

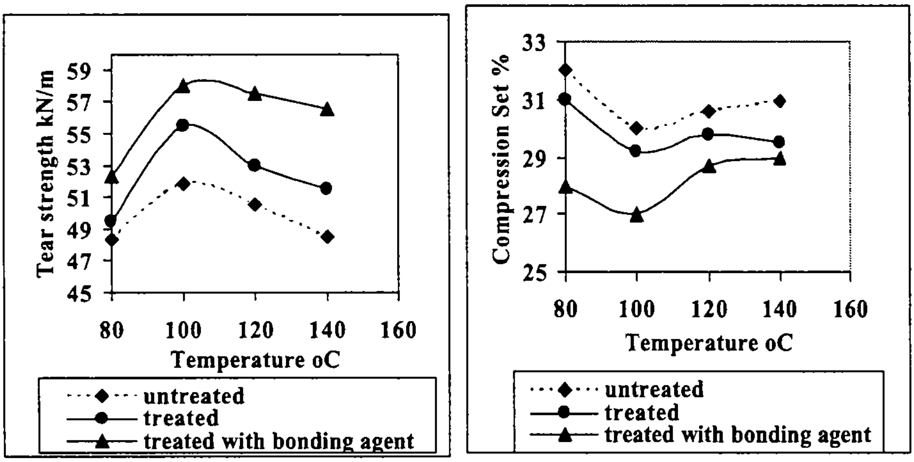
Time of soaking (Hrs)	(0h)	(4h)	(24h)	(48h)	(72h)
Cure time (min)	23.4	26.1	25.9	24.9	22.2
Max.torque(dNm)	4.69	5.39	4.25	3.96	3.85
Modulus[MPa]	5.8	6.7	6.1	5.6	4.9
Tensile strength (MPa)	11.5	13.6	12.1	11.0	10.0
Elongation at break(%)	317	300	325	357	380
Tear strength kN/m	52.1	56.3	53. 4	49.1	42.3



(a) Modulus

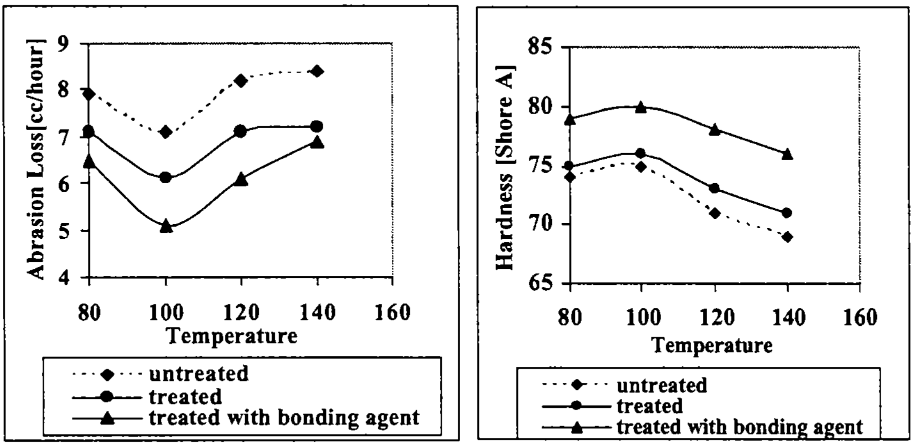
(b) Tensile strength

Figure 4.2.2 Effect of curing temperature on the mechanical properties of the composites



(c) Tear strength

(d) Compression set



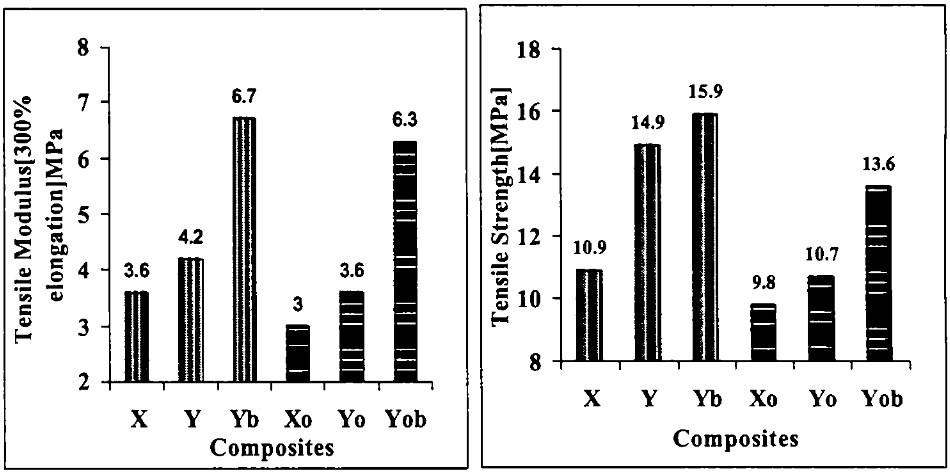
(e) Abrasion loss

(f) Hardness

Figure 4.2.2 (contd) Effect of curing temperature on the mechanical properties of the composites

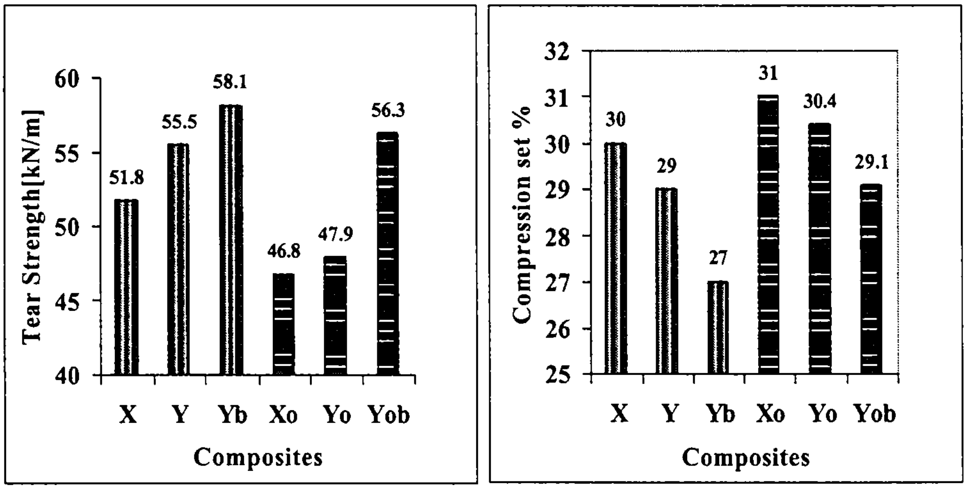
Many of the properties were found to reach a maximum for composites vulcanized at 100°C. Same trend is observed in the case of treated fibre composites and composites with bonding agent. Treated fibre composites show enhancement in properties as treated fibre provides better surface for reinforcement. Also composites with bonding agent show still better mechanical properties. The bonding resin form chemical cross-links with rubber and the cellulosic hydroxyl groups of fibres creating a strong interface between fibre and rubber [46].

Figures 4.2.3(a) to (f) show a comparison of the mechanical properties of the composites cured at 100°C with that vulcanized using conventional systems [150°C].

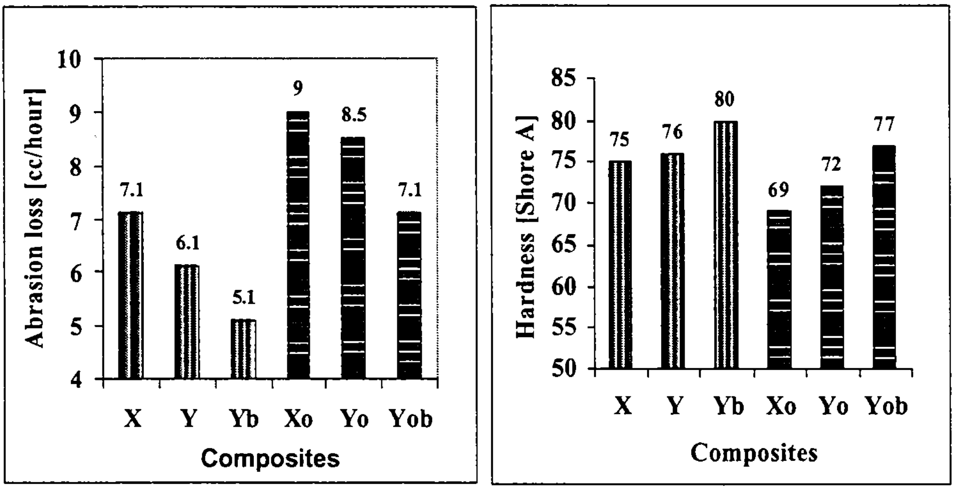


(a) Tensile modulus **(b) Tensile strength**

Figure 4.2.3 Comparison of the mechanical properties of the composites [30 phr] cured at 100°C and 150°C. X-Low temperature cured system, X_o conventionally cured system



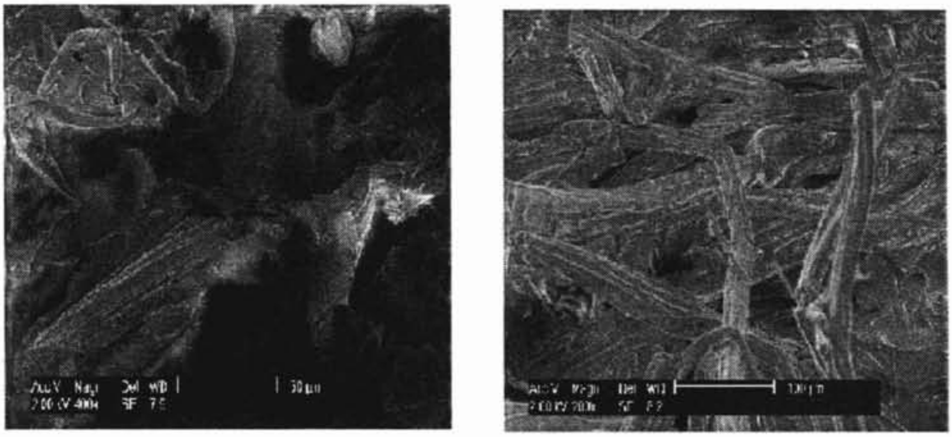
(c) Tear strength (d) Compression set



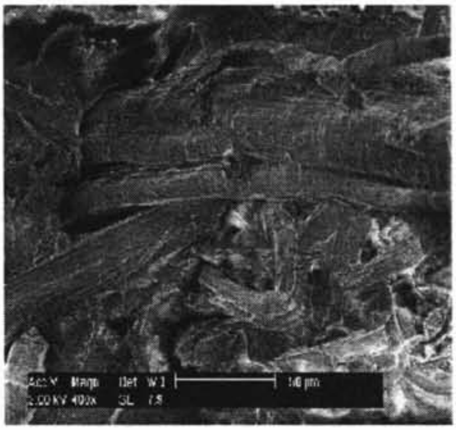
(e) Abrasion loss (f) Hardness

Figure 4.2.3 (Contd) Comparison of the Mechanical properties of the composites [30 phr] cured at100 °C and 150 °C. X-Low temperature cured system, X_0 conventionally cured system

Composites with conventional accelerator system were vulcanized at 150ºC and at high temperature fibre shows a tendency to degrade and hence a decrease in properties as evidenced from figures.



(a) Untreated **(b) Alkali treated**



(c) Alkali treated with bonding agent

Figure 4.2.4 SEM photographs of the tensile fractured surfaces of the composites [30 phr] cured at 100°C

Figure 4.2.4 is the tensile fracture surfaces of composites [30phr] cured at 100°C. Fracture surfaces of the composites [30 phr] cured at 150°C is given in figure 4.1.6. SEM studies provide additional information regarding fibre rubber interface. In both cases, for untreated fibre composites, due to the weak interfacial adhesion between the fibre and rubber, fibre pull out may take place leaving holes on the surface when stress is applied. For the treated fibre composites, broken fibres can be seen on the fracture surfaces which also revealed the indications of high interfacial adhesion for the composites with treated fibres and bonding agent.

4.3 CONCLUSIONS

The mechanical properties of short isora fibre reinforced natural rubber composites are enhanced by chemical treatment on the fibre surface and by the use of bonding agent. Longitudinally oriented fibre composites have superior properties than transversely oriented ones. The optimum length and loading of isora fibre in NR composite are found to be 10mm and 30phr respectively to achieve optimum reinforcement. The surface morphology of isora fiber is modified by chemical treatments. Xanthates are effective in low temperature curing of natural rubber composite. The composite vulcanized at 100°C showed the optimum property. At high temperature fibre shows a tendency to degrade and hence a decrease in properties. SEM analysis revealed that better adhesion is observed between modified fibres and NR in the composites. Composites with treated fibres and bonding agent show enhancement in mechanical properties in both systems.

4.4 REFERENCES

1. Ismail H, Rosnah N., Rozman H. D., *Polymer,* (1997) **38(16):** 4059.
2. Geethamma V. J., Thomas S., *J Appl Polym Sci*,(1995) **55:** 583.
3. Varghese S., Kuriakose B., Indian *J Nat Rubb Res*, (1991) **4(1):** 55.
4. Maya J., Thomas S., *Comp Sci Technol,* (2004) **64:** 955
5. Setua D. K., De S. K., *Rubb Chem Technol,* (1983) **56:** 808.
6. Arumugham N., Tamaraselvy K, *J Appl Polym Sci*,(1989) **37**: 2645
7. Ismail H., Edyham M.R., *Polymer Testing*, (2002) **21:** 139
8. Ismail H., Rozman H.D., Ishiaku U.S., *Polym Inter*, (1997) **43:**223.
9. Prasanth Kumar K, Thomas S., *Bull Mater Sci*, (1995) **18:** 1021.
10. Murthy V.M., De S.K., *J Appl Polym Sci*, (1984) **29**:1355.
11. Ibarra L., *J Appl Polym Sci,* (1993) **49:**1595.
12. Ibarra L., Chamorro C., *J Appl Polym Sci,* (1989) **37**: 1197
13. Coran A.Y., Boustany K., *Rubb Chem Technol,* (1974) **47**:396
14. Setua D.K., Dutta B., *J Appl Polym Sci*, (1984) **29**: 3097
15. Belgacem M.N., Btaille P., *J Appl Polym Sci,* (1994) **53:** 379
16. Felix J. M., Carlson C. M. G., *J Adhes Sci Technol,* (1994) **8 (2)**: 163.
17. Geethamma V. J., Thomas S., *Polymer*,(1998) **39:** 1483.
18. Sapieha S., Pupo J.F., *J Appl Polym Sci,* (1989) **37:** 233.
19. Felix J.M., Gatenholm P., *J Appl Polym Sci,* (**1991**) **42:** 609.
20. Bisanda B.T.N., Ansell M.P., *Comp Sci Technol,* (1991) **41:** 167.
21. Ismail H., Edyham M.R., Shuhelmy S., *Euro Polym J,* (2002) **38:** 39.
22. Rout J., Misra M., Mohanty A.K., *Comp Sci Technol,* (2001) **61**:1303
23. Pramanik P. K., Khastgiri D. K., *Plast Rubb Comp Proc Appl*, (1991) **5**:189
24. Goetller L. A., Shen K. S., *Rubb Chem Technol,* (1983) **56:** 619.

25. Chakraborty S.K., Setu D. K., *Rubb Chem Technol*, (1982) **55:** 1286.
26. Prasanthakumar K., Thomas S., *Bull Mater Sci*, (1995) **18 (8)**: 1021.
27. Prasanthakumar K., Thomas S., *J Appl Polym Sci*, (1995) **58:** 597.
28. Czvikovszky T., Kovacs I., *J Appl Polym Sci*, (1985) **30:** 1827.
29. Flodi P., Zadorecki Z., *J Appl Polym Sci*, (1985) **30:** 3971.
30. Maya J., Thomas S., *Comp Sci Technol*, (2004) **64:** 955.
31. Flink P., *J Appl Polym Sci*, (1988) **35:** 2155.
32. Akhtar S., De S.K., *J Appl Polym Sci*, (1986) **32:** 5123.
33. Varghese S., Kuriakose B., *J Adhes Sci Technol*, (1994) 8(**3**): 235.
34. Murthy V. M., De, S. K., *Rubb Chem Technol* (1982), **55:** 287
35. Ismail H., Rosnah, N. *Polym International*, (1997) **43:** 223.
36. Bhattacharyya T. B., Biswas A. K., J. *Plast. Rubb. Proc. Appl*, (1986) **6:** 119
37. Miwa M., Tahara K J., *J.Appl Polym. Sci*, (1980) **25:** 795
38. Blamchard A.F. *The Applied Science of Rubber*, (1961). J.S.Naunton ed., Edward Arnold Ltd.London, 414.
39. Alter H., J *Appl Polym Sci*, (1965) **9**: 1523.
40. Guth G., *J Appl Phy*, (1945) 16: 20.
41. Sato Y., Farukawa J. *Rubb Chem Technol*, (1962) **35**: 857.
42. Shiny P., Rani J., Plast *Rubb Comp*, (2001) **30:** 270.
43. Blokh G. A., *Organic accelerators in the vulcanization of rubber*, (1972) 2nd ed. Khimia, Leningrad, USSR, 293.
44. Robert F., *Vanderbilt Rubber Hand book*, (1996) 13th edn, Vanderbilt Company,Inc. N.Y.16
45. Shiny P., Rani J., J *Appl Polym Sci*, (2000) **78**: 1769.
46. Blackley D.C., *Polymer lattices*, (1966) 2nd edn.,Chapman& Hall Publishers, London, 3: 515.

CHAPTER 5

AGEING BEHAVIOUR OF SHORT ISORA FIBRE REINFORCED NATURAL RUBBER COMPOSITES

5.1 Introduction
5.2 Experimental
5.3 Results and Discussion
  5.3.1 Effect of Thermal ageing
  5.3.2 Effect of Ozone ageing
  5.3.3 Effect of Radiation ageing
5.4 Conclusions
5.5 References

CHAPTER 5

AGEING BEHAVIOUR OF SHORT ISORA FIBRE REINFORCED NATURAL RUBBER COMPOSITES

Radiation, Ozone and Thermal ageing

Abstract

This chapter gives a brief description about the degradation behavior on the mechanical properties of short isora fibre reinforced natural rubber composites with special reference to the influence of ageing condition like exposure to gamma radiations; ozone and heat. The effects of fibre treatment, fibre loading, fibre orientation and the role of bonding agent on the degradation pattern have been investigated.

Results of this chapter have been accepted for publication in ***"Journal of Natural fibres"***

5.1 INTRODUCTION

The use of polymeric materials under the influence of degrading agents such as ozonised air, gamma radiations, and heat has increased rapidly in recent years. Hence it is important to study the effects of such degrading agents on the performance of the composites. Among the external factors causing deterioration of rubber products the most important ones are oxygen and ozone. The attack by oxygen is relatively slow and activated by heat, the ozone attack is rapid. Hence even very low concentrations of ozone can cause cracks in rubber under strain. Unsaturated elastomers, especially those containing active double bonds in the main chain are severely attacked by ozone resulting in deep cracks in a direction perpendicular to the applied stress. Protection against ozone attack can be achieved by the use of antiozonants. Several studies have been reported on the protection of rubber against ozone attack [1-3]. The effects of radiation on polymeric materials and their blends and composites have also been reported by researchers [4-8]. The mechanical properties of the polymers are changed considerably under the influence of high-energy radiations. This may be due the cross-linking or by the degradation of polymer chain. Mechanical properties such as tensile strength, modulus, elongation etc; are decreased by chain degradation while cross-linking enhance these properties. Skowronski have studied the photo degradation of thermo plastic rubber blends [9]. De *et al* have reported the effect of gamma radiations on the mechanical properties of blends of hytrel/PVC and NR/PE [10-11]. Joseph *et al* reported the environmental effects on the degradation behavior of sisal fiber reinforced polypropylene composites [12]. Although ozone is present in the atmosphere at concentrations normally in the range 0-7 pphm it severely attacks nonresistant rubbers [13]. The effect of ozone and gamma radiation radiations on the degradation of NR/sisal composites were studied by Varghese and coworkers [14]. The interaction of rubber with ozone is best noted when rubber is stretched or stressed in use. A series of crack develop perpendicular to the applied stress as time proceeds. Further exposure of these cracked surfaces to ozone cause the crack to become wider and deeper until the rubber fails. The resistance of natural rubber to thermal ageing and ozone is poor. The degree of unsaturation of the elastomer is the most important factor determines its susceptibility to ozone attack. In the case of fibre reinforced composites, the fibres incorporated in the mixes prevent crack initiation and also hinder crack propagation. The fibre orientation should be perpendicular to the direction of crack propagation and also there should be a good bonding between the rubber and the fibre. Then only the fibres can prevent the crack formation. Isora fibre possesses excellent ageing resistance. Moreover in presence of high energy radiations the reactive sites formed either on the rubber or on the fibre in the composite may cause increased bonding between the fibre and the rubber. Hence the action of different degrading agents in the properties of NR-isora composites is worth investigating. In this chapter the retention of tensile strength and modulus of NR-isora composites, after exposing the test samples to different dosages of gamma radiations, heat, and ozone are reported. The surface morphology of the samples exposed to ozone has been analyzed by optical microscopy.

5.2 EXPERIMENTAL

Formulation of test mixes is given in Table 5.1

The effect of thermal ageing was determined by ageing the samples in an air oven at 100°C for 3 and 5 days. Ozone resistance was determined according to ASTM D 518 method B. Samples were exposed to ozonised air in an ozone chamber (MAST Model 700-1) for 36 hrs. The concentration of ozone was maintained at 50 pphm and the inside temperature at 40°C. The ozone cracks developed on the samples were analyzed by optical microscopy. The samples were irradiated with gamma rays from ^{60}Co source at a dose rate of 0.3413 Mrad/hr.in a gamma chamber. Tensile and tear testing before and after irradiation and thermal ageing were carried out according to ASTM D 412-68 and D 628-54 standards.

Table 5.1 Compound formulation [phr]

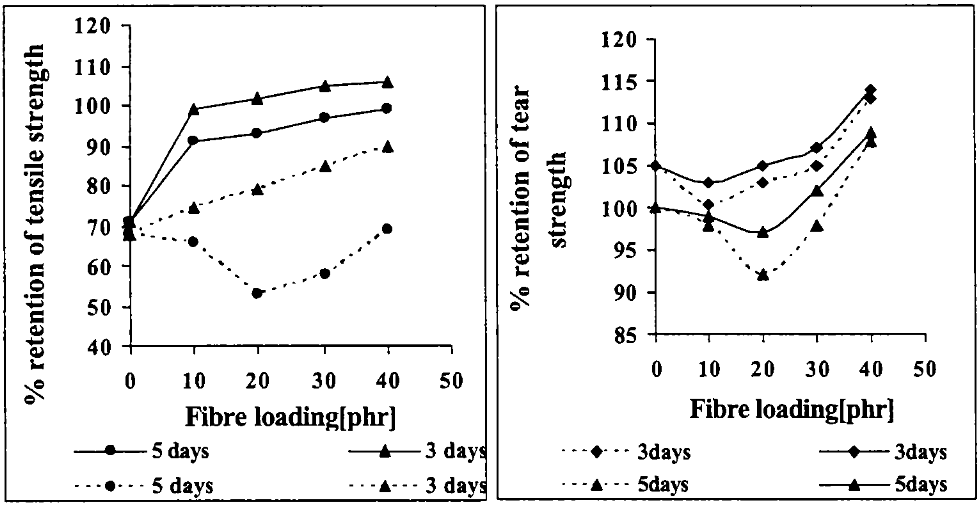
Ingredients	Y_{10}	Y_{20}	Y_{30}	Y_{40}	Y_{10b}	Y_{20b}	Y_{30b}	Y_{40b}	X_{20}	X_{20b}
RF resin	-	-	-	-	2.5	5.0	7.5	10	-	5.0
Silica	-	-	-	-	1.0	2.0	3.0	4.0	-	2.0
Hexa	-	-	-	-	1.6	3.2	4.8	6.4	-	3.2
Fibre	10	20	30	40	10	20	30	40	20	20

Basic recipe: NR-100, ZnO-5.0, Stearic acid-2.0, TDQ-1.0, CBS-0.6, TMTD- 0.1, S-2.5
X-Untreated, Y-Alkali treated

5.3 RESULTS AND DISCUSSION

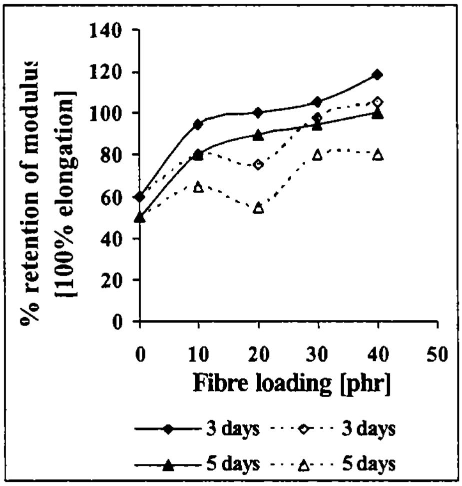
5.3.1 Effect of thermal ageing

A plot of percentage retention of tensile and tear strength after ageing the composite samples for 3 and 5 days at 100°C against fibre loading in the longitudinal orientation is given in figure 5.1 (a) and (b). For samples aged for 3 days the retention in tensile strength increases continuously with fibre loading for composites with and without bonding agent. At shorter ageing time, bonding action of the resin predominates over polymer chain degradation, which results in a higher retention of tensile strength. On increasing the ageing periods from 3 to 5 days, composites that do not contain bonding agent, show lower retention in tensile properties. This indicates that polymer degradation begins after 3 days in these composites where as bonding action of the resin continues to take place in the composites containing bonding agent. But the retention is lower than that of shorter ageing period. (3days). During thermal ageing



(a)Tensile strength

(b) Tear strength



(c)Modulus [100% elongation]

Figure 5.2 Percentage retention of mechanical properties with fibre loading after ageing the samples at 100^0C for different periods in the longitudinal orientation [........ without, ________with bonding agent] cross link formation or cross link breakage can take place or an existing cross link may break and a stable linkage can be formed. In composites, bonding action of the resin also take place during ageing. All these reactions greatly influence the performance of the composites. Tear strength and tensile modulus [100% elongation] also shows a similar trend on ageing.

For samples aged for 3 days the retention in tensile strength increases continuously with fibre loading for composites with and without bonding agent. At shorter ageing time, bonding action of the resin predominates over polymer chain degradation, which results in a higher retention of tensile strength. On increasing the ageing periods from 3 to 5 days, composites that do not contain bonding agent, show lower retention in tensile properties. This indicates that polymer degradation begins after 3 days in these composites where as bonding action of the resin continues to take place in the composites containing bonding agent. But the retention is lower than that of shorter ageing period. (3days). During thermal ageing cross link formation or cross link breakage can take place or an existing cross link may break and a stable linkage can be formed. In composites, bonding action of the resin also take place during ageing. All these reactions greatly influence the performance of the composites. Tear strength and tensile modulus [100% elongation] also shows a similar trend on ageing.

5.3.2 Effect of ozone ageing

Figure 5.3 shows the photographs of NR-isora fibre composites with bonding agent after exposure to ozone for 36 hours. The intensity of crack decreases with increase in fibre loadings. Similarly composites with higher fibre loading offer a greater resistance to crack propagation even though it experiences a greater strain. For a particular fibre loading the longitudinally oriented fibre composites show better resistance to ozone attack than transverse ones. This is because greater hindrance to the progress of fracture front is experienced when the fibres are oriented longitudinally whereas for the transverse orientation the crack progresses in the direction of fibre alignment. Thus the orientation of fibres also greatly influenced the properties of composites.

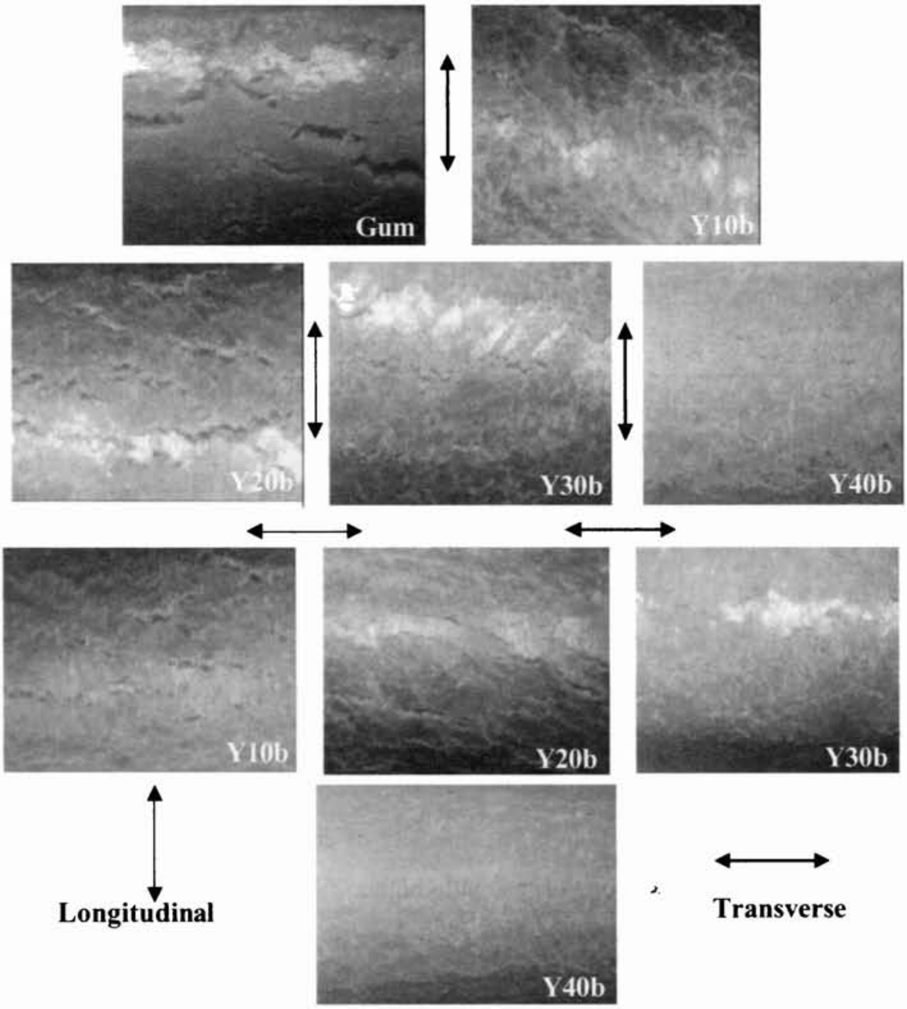


Figure 5.3 Optical photographs of NR-ISORA composites with bonding agent in the longitudinal and transverse orientations after exposure to ozone for 36 hours

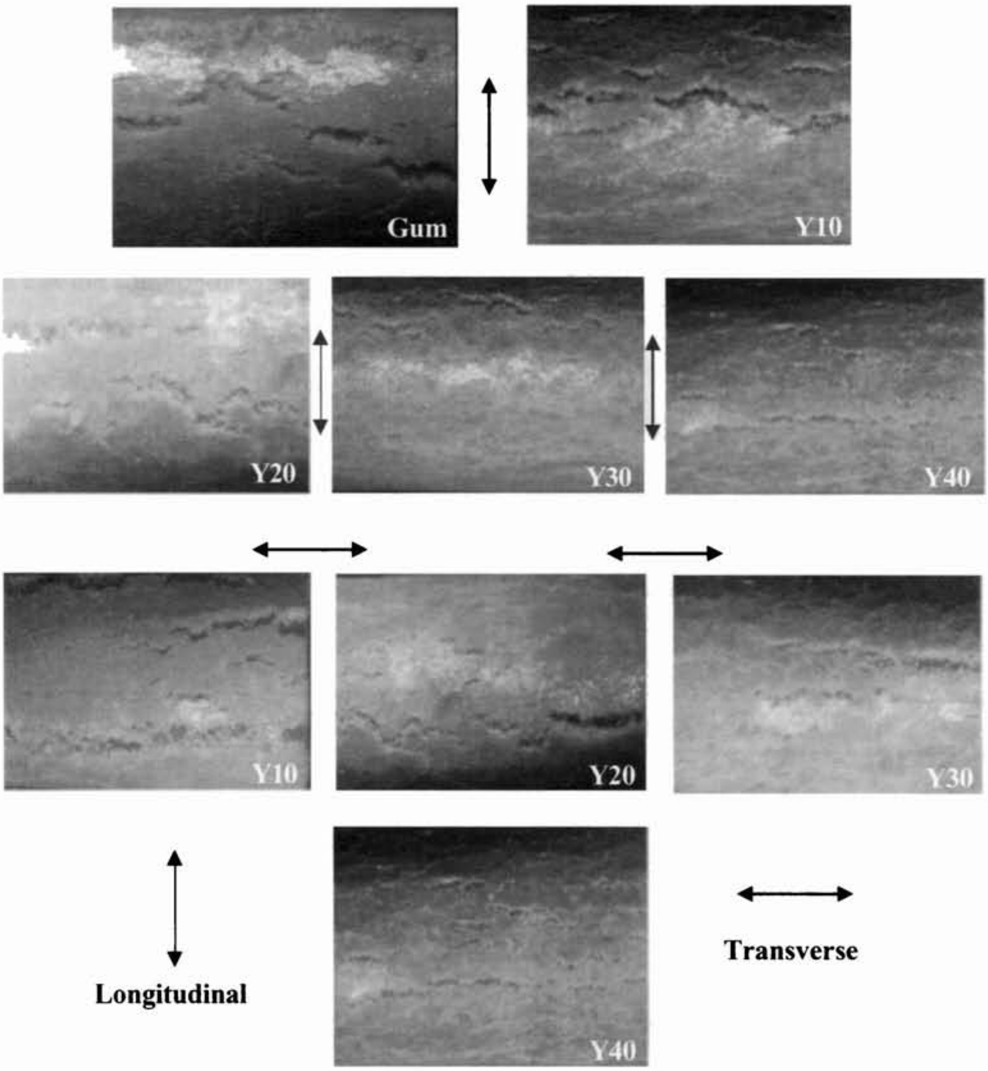


Figure 5.4 Optical photographs of NR-ISORA composites without bonding agent in the longitudinal and transverse orientations after exposure to ozone for 36 hours

Figure 5.4 is the optical photograph of NR-isora fibre composites without any bonding agent. Even in the absence of any bonding agent the composites show better resistance to ozone attack. Since the fibres are chemically treated there is sufficient interfacial bonding between the fibre and the rubber.

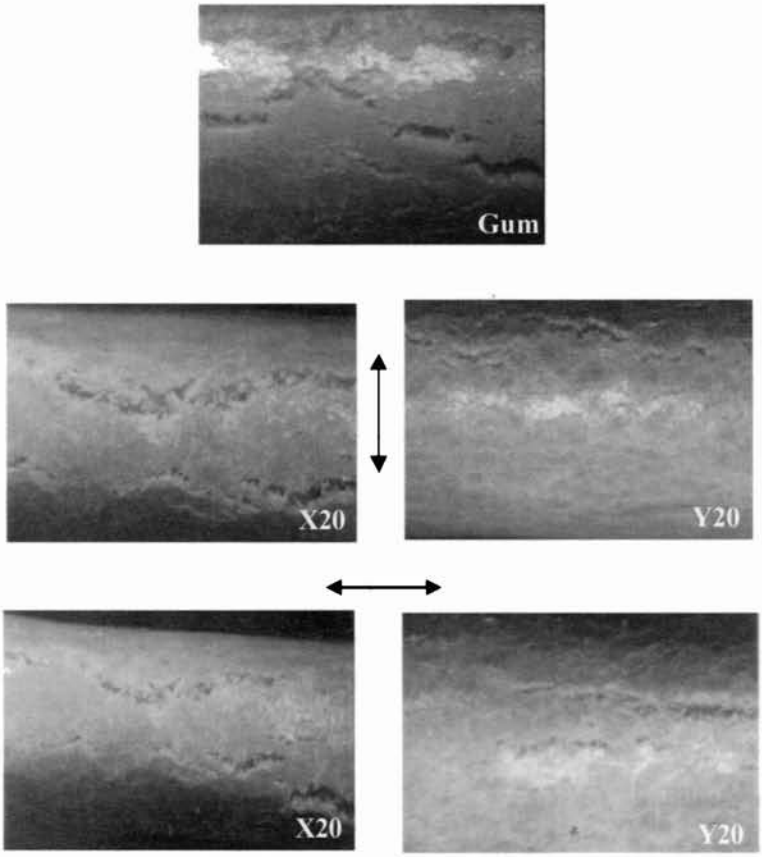


Figure 5.5 Optical photographs of NR-ISORA composites containing untreated and treated fibre without bonding agent in the longitudinal and transverse orientations after exposure to ozone for 36 hours

Figure 5.5 is the optical photograph of composite containing 20phr of untreated and treated fibre, which do not contain a bonding system. It is clear from the photograph that for the untreated composites cracks are intense even in longitudinal orientation. This is because untreated fibre fails to form sufficient bonding with the rubber, whereas for the treated fibre composites due to the improved adhesion between the rubber and fibre, fibres can efficiently hinder the crack propagation. It was reported that the addition of clay or carbon black increases the modulus of the compound [15]. Hence for a given strain, the stress in the filled sample is higher than that in the unfilled sample. Vinod et al studied the degradation behavior of Al powder filled natural rubber composites and reported that there is better retention of mechanical properties after thermal and ozone ageing compared to other fillers like HAF, Silica and acetylene black.[16].

Table 5.2 Time for the crack initiation of various samples on ozone ageing.

(a) Longitudinal orientation.

Samples	**G**	Y_{10}	Y_{20}	Y_{30}	Y_{40}	Y_{10b}	Y_{20b}	Y_{30b}	Y_{40b}	X_{20}	X_{20b}
Time in Hrs.	2.5	4.5	6.5	8.5	9.5	6.5	9.0	9.5	18	5.0	8.5

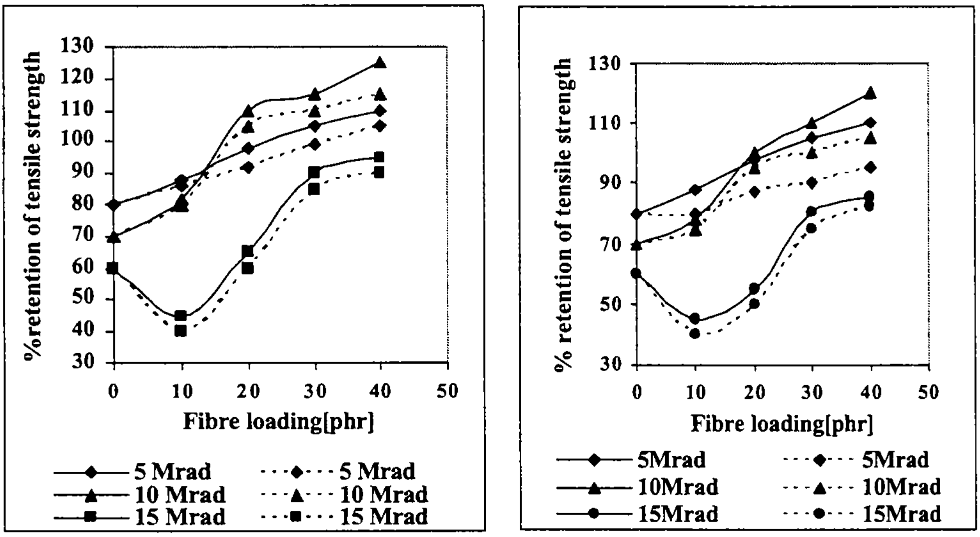
(b) Transverse orientation

Samples	**G**	Y_{10}	Y_{20}	Y_{30}	Y_{40}	Y_{10b}	Y_{20b}	Y_{30b}	Y_{40b}	X_{20}	X_{20b}
Time in Hrs.	2.5	4.0	4.0	6.5	8.0	4.5	8.0	8.5	11	4.0	7.5

G- Gum (compound without fibre)

Table 5.2 gives the time for the crack initiation of various samples on ozone ageing. It was observed that for the composites with low fibre loadings crack was initiated at the early stages of exposure. Similarly composites with bonding agent offer a greater resistance to crack initiation as evident from the longer time interval taken for the crack to be initiated. For a particular fibre loading the time for the crack initiation for the longitudinally oriented fibre composites is higher than that taken for the transversely oriented ones. This shows that the fibre orientation has a pronounced influence on the time taken for the crack initiation on ozone ageing.

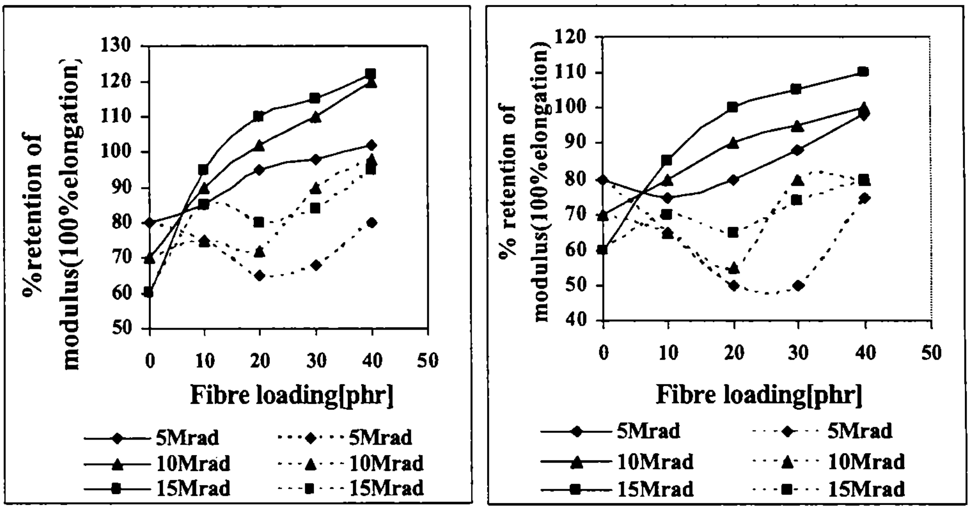
5.3.3 Effect of gamma radiation ageing



(a) (b)

Figure 5.6 Percentage retention of tensile strength with fibre loading at different radiation doses (a) longitudinal(b) transverse orientation [........without, _______ with bonding agent]

Figure 5.6 shows the plot of percentage retention in tensile strength against fibre loading with and without bonding agent at three different radiation doses of treated fibre in the longitudinal and transverse direction. The retention of tensile strength slowly increases with the increase in fibre loading for a radiation dose of 5 Mrad for composite with and without bonding agent. The slight increase in retention of tensile strength may be due to the covalent bonds formed at the interface through the reactive sites created by irradiation. But for a dosage of 10Mrad the percentage retention in tensile strength increases sharply with increase in fibre loading up to 30% and then remains almost constant. At a radiation dose of 15 Mrad degradation of the polymer chain is the main reaction-taking place at low fibre loading. But at higher fibre loading the retention of tensile properties are higher, but the actual values are lower than those of 5 and 10 Mrad radiation. A similar trend is observed in the case of transversely oriented fibre composites.



(a) (b)

Figure 5.7 Percentage retention of tensile modulus with fibre loading at different radiation doses (a)longitudinal (b)transverse orientation [........without, ________ with bonding agent]

The percentage retention of modulus for 100% elongation plotted against fibre loading in the longitudinal and transverse orientations are given in figure 5.7. With the increase in the dosage of gamma radiations, composites which contain the bonding agent show a steady increase in the percentage retention of modulus with fibre loadings. But for the composites without bonding agent, samples exposed to 5Mrad, registered a decrease in modulus retention at lower levels of fibre loading. For 10Mrad and 15Mrad dosages, modulus retention increased with increase in fibre loading. The better retention in modulus of the composites containing higher fibre loading may be due to the better interfacial adhesion between the fibre and the matrix as a result of irradiation.

5.4 CONCLUSIONS

On thermal ageing, for composites with and without bonding agent the percentage retention of tensile and tear strength increases continuously with fibre loading. The increase in retention is more in the case of composites with bonding agent.

Ozone resistance of the samples increases with increase in fibre loading especially in presence of bonding agent. The longitudinally oriented fibre composites offer better resistance to ozone attack. The treated fibre composites hindered crack propagation effectively than the composites with untreated fibres.

On exposure to gamma radiations the retention in tensile properties slowly increases with increase in fibre loading up to a loading of 30% fibre and there after remains almost constant for systems with and without bonding agent. On prolonged irradiation (15Mrad) polymer degradation is the main reaction-taking place at low fibre loadings but at higher fibre loading retention in tensile properties are slightly improved.

5.5 REFERENCES

1. Ambelang J. C., Kline R A., *Rubber Chem Technol*, (1963) **36**:1497
2. Layer R. W., Lattimer R.P., *Rubber Chem Technol*, (1990) **63**:426
3. Ungar G., *J Mater Sci*, (1981) **16**: 2635
4. Bohm G.G.A., Treekrem J.O., *Rubber Chem Technol*, (1982) **55**: 575.
5. Charlesby A., *Plast Rubb Proc App*, (1982) **2**: 289
6. Makhlis F.A., *Rad Phy and Chem of Polymers*, (1972) ed.F.A Makhlis John Wiley, Newyork; page. 288
7. Sweet G.C., *In Developments in Rubber Technology*, (1979) ed. A. Whelan, Applied Science Publishers; page 90
8. Koshy A.T., Kuriakose B., *Polym Deg Stab*, (1992) **36**: 137.
9. Skowronski T, Rabek J.K *Polym Eng Sci*, (1984) **24** : 278
10. De S.K., Thomas K.T., Thomas S., *Rad Phy Chem* ., (1986) **28**: 283
11. Akhtar S., De P.P., *J Appl Polym Sci*,(1986) **32**: 4169
12. Joseph P.V., Thomas S., Joseph K., *Comp Sci Technol*, (2002) **62:**1357
13. Thomas K.T., Mathew N.M., *Ind J Rubb Res*, (1986) **8**: 440
14. Varghese S., Kuriakose B., Thomas S., *Polym Deg and Stab*, (1994) **44**: 1
15. Bhagawan S.S., *Polym Degn Stab*, (1981) **20**:1
16. Vinod V.S., Varghese S., Kuriakose B., *Polym Deg Stab*, (2002) **75**:405

CHAPTER 6

ANALYSIS OF INTERFACE ADHESION BY EQUILIBRIUM SWELLING STUDIES

6.1 Introduction
6.2 Experimental
6.3 Results and Discussion
  6.3.1 **Equilibrium swelling of isora/NR composites in organic solvents**
  6.3.1.1 Effect of curing temperature
  6.3.1.2 Effect of fibre loading and bonding agent
  6.3.1.3 Correlation with adhesion
  6.3.1.4 Effect of chemical treatment
  6.3.1.5 Dimensional changes of the composites
  6.3.2 **Swelling of isora/NR composites in fules/oils used in automobiles**
  6.3.2.1 Effect of fibre loading and bonding agent
  6.3.2.2 Effect of chemical treatment
  6.3.2.3 Dimensional changes of the composites
6.4 References
6.5 Conclusions

CHAPTER 6

EQUILIBRIUM SWELLING STUDIES OF ISORA FIBRE REINFORCED NATURAL RUBBER COMPOSITES

Abstract

Equilibrium sorption studies have been conducted using organic solvents and commercial fuels like petrol, diesel and lubricating oil in order to understand the interfacial adhesion and performance of short isora fibre reinforced natural rubber composites under these environments. Effect of curing temperature, fibre loading and bonding agent on the equilibrium swelling of isora-natural rubber composites have also reported.

Part of the results of this chapter has been published in ***"Composites interfaces"***, Vol 13(4-6): 391; (2006) and a part has been published in "***Bulletein of Materials Science***", Vol. 29(1): 91; (2006)

6.1 INTRODUCTION

Swelling experiments of rubber composites are important for analyzing the service performance of these composites in such environments.Rubber articles come in contact with different liquids during service performance. This can happen either as a part of the service requirement as in the case of of oil seals or by accidental splashing of oils and greases that occurs with automobile components. The contact of rubbers with organic solvents can be well explained by absorption and diffusion phenomena [1]. The amount of swelling at equilibrium was treated as a special case of Flory-Rehner theory. According to Flory Rehner theory for swelling of a rubber polymer, at equilibrium

$$\ln(1-V_r) + V_r + \chi V_r^2 + V_c V_1(V_r^{1/3} - V_r/2) / V_0 = 0 \ldots\ldots 6.1$$

where V_r is the volume fraction of rubber after swelling, χ is the polymer-solvent interaction parameter,V_c is the number of moles of effective network chains in the initial or unswollen volume and V_0 and V_1 are the molar volume of the solvent and polymer. An important difference between vulcanized and raw rubber is that the former possesses a structure, which cannot be broken down completely by any solvent. The material therefore swells and cannot be dispersed. The swelling behaviour of rubber vulcanizates is influenced by different factors such as the chemical nature, dimension and shape of the filler, compatibility of the solvent with the rubber and interfacial adhesion. The degree of cure in particulate filler reinforced vulcanizates by swelling method has been studied by Kraus [2]. The degree of of restriction exerted by the reinforcing filler allows an equation of the form given by Kraus.

$$V_{ro}/V_{rf} = [1-3c(1-V_{ro}^{1/3}) + V_{ro}-1]/(1-f) \ldots\ldots 6.2$$

Where V_{ro} is the volume fraction of rubber in the unfilled vulcanizates, V_{rf} is the volume fraction of rubber in the filled vulcanizates; f is the volume fraction of the filler, 'c' the constant characteristic of the filler which indicates the degree of adhesion. Several researchers have extensively studied the transport behaviour of various organic liquids in polymer composites [3-10]. Sorption experiments provide valuable information on the transport characteristics of polymer composites, ie; at what rate the liquid diffuses into the polymer matrix. The phenomenon of transport of liquids through rubbery polymers is controlled by the polymer structure, its cross link density, presence of fillers, penetrant size etc. Das has studied the adhesion between rubber and short glass and asbestos fibres using restricted swelling measurements [11]. Coran *et al* [12] have studied the solvent swelling of unidirectional rubber fibre composites. Maximum strength and reinforcement are achieved along the direction of fibre alignment. Swelling is a uniform restrictive force induced on the vulcanizate samples and it will be anisotropic in well bonded and oriented fibre rubber composite. Because of the anisotropic nature of fibre rubber composites, the swelling is restricted in the direction of fibre alignment and consequently swelling becomes anisotropic. The improvement in reinforcement obtained by enhancing fibre matrix adhesion through the incorporation of a bonding sysem has been widely studied in the case of rubber vulcanizates [13]. Earlier researchers [14-15] have studied numerous techniques like H-block and strip adhesion; both dynamic and static conditions have been used to measure adhesion between fibre and rubber. While most of these techniques give a good relative indication of adhesion, the time dependent nature of the viscoelastic materials overshadows the real effect. Equilibrium swelling is another technique, which has been used to assess the fibre rubber adhesion. Fibres, if bonded effectively, are supposed to restrict the swelling of elastomers. Thus the procedure of restricted equilibrium swelling technique helps us to evaluate the resistivity of composites towards commonly available solvents like toluene, n-hexane etc. The resistance is strongly influenced by the strength of the fibre matrix adhesion. The solvent effects, especially when coupled with changing temperature affect a wide variety of mechanical and thermophysical properties.

The diffusion of solvents and relaxation process in a rubber sample above its T_g are governed by the segmental mobility of the chains, which in turn are considered to be affected by the total free volume and its distribution within the elastomer matrix [16]. Aminabhavi *etal* have studied the sorption and transport of organic solvents by polymer membrane [17]. This chapter presents the restricted equilibrium swelling of isora natural rubber composites with respect to the effects of curing temperature, fibre loading, chemical modification of fibre surface and bonding agent. The equilibrium swelling is studied in relation to the interfacial adhesion also.

6.2 EXPERIMENTAL

The formulation of the mixes used in this investigation is given in Table 6.1. The procedure for the swelling data analysis and their vulcanization characteristics are reported in Chapters 2 and 4 respectively.

Circular specimens of diameter 20 mm. were punched out from the vulcanized sheets. Thicknesses and diameters of the specimens were measured by means of a screw gauge and vernier calipers respectively. Specimens of known weight were immersed in the solvents (toluene and hexane) and automobile fuels and oils in diffusion test bottles and kept at room temperature. Samples were removed from the bottles at periodic intervals and the wet surfaces were quickly dried using tissue paper and the weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected. Thickness and diameter of the specimen after equilibrium swelling were also measured.

Table 6.1 Compound Formulation [phr]

Ingredients	X_{10}	X_{20}	X_{30}	X_{40}	X_{10b}	X_{20b}	X_{30b}	X_{40b}	Y_{30}	Y_{30b}
RF^a resin	-	-	-	-	2.5	5.0	7.5	10	-	7.5
Silica	-	-	-	-	1.0	2.0	3.0	4.0	-	3.0
Hexa	-	-	-	-	1.6	3.2	4.8	6.4		4.8
Fibre [U]	10	20	30	40	10	20	30	40	30	
Fibre [T]	-	-	-	-	-	-	-	-	-	30

Basic recipe: NR-100, ZnO-5.0, Stearic acid-2.0, TDQ-1.0, S-2.5 low temp curing system [ZDC-1.0,Xantahate- 0.75] For conventional system [CBS- 0.6,TMTD- 0.1]. [**Conventionally cured composites are represented by X_0** eg; X_o30b -30 phr loading with bonding agent cured by conventional systems] U-untreated, T- alkali treated

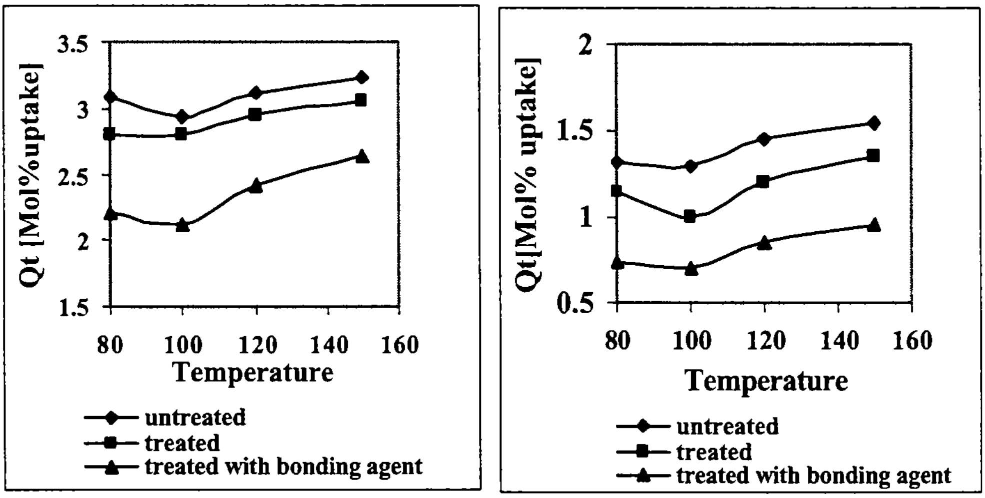
6.3 RESULTS AND DISCUSSION

6.3.1 Equilibrium swelling of isora/NR composites in organic solvents

6.3.1.1 Effect of curing temperature

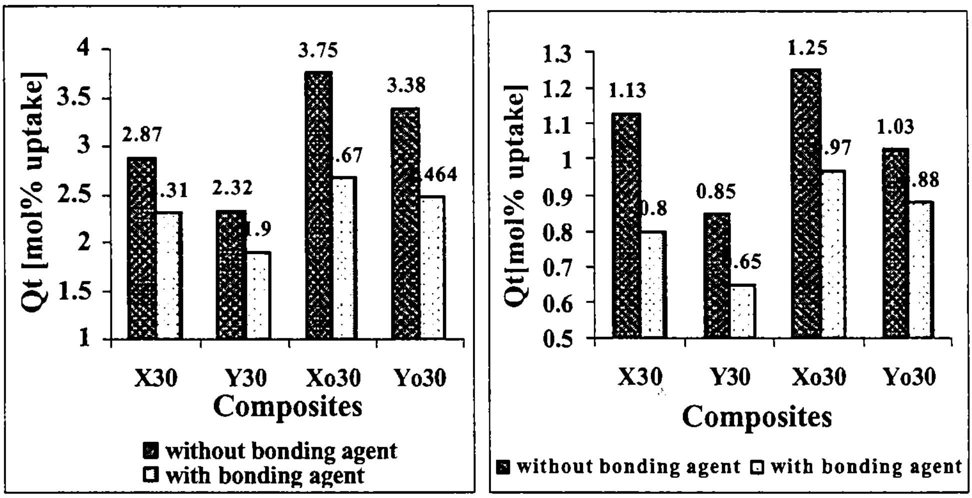
Figures 6.1(a) and (b) show the variation of the mol% uptake in toluene and hexane with curing temperature of the composites. In both solvents the uptake of solvent is lowest for the composite vulcanized at 100°C. The same trend is observed in the case of composites containing treated fibres and treated fibres with bonding agent.

A comparison of the mol% uptake of the solvent for the composites cured at 100°C and 150°C in toluene and n-hexane is given in Figure 6.2. It may be observed that in both solvents the uptake of solvent is high for the composites cured at high temperature (150°C). This shows that there is better fibre rubber adhesion when the composite is cured at 100°C and it is likely that at higher temperature (150°C) the



(a) Toluene (b) n- Hexane

Figure 6.1 Variation of mol% uptake of solvents with curing temperature of the composites



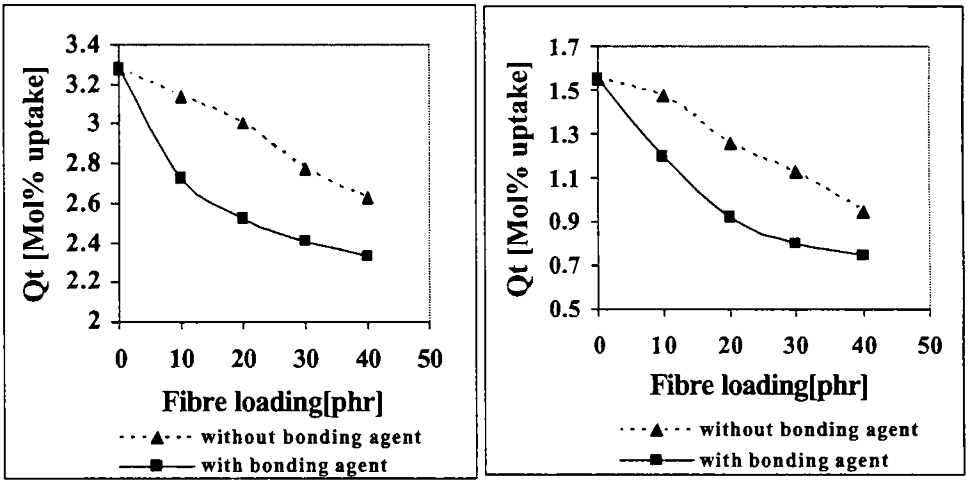
a) Toluene (b) n-Hexane

Figure 6.2 Comparison of the mol% uptake of the solvents for the composites (30 phr) cured at 100°C and 150°C

fibre and rubber shows a tendency to degrade as evident from the results of our earlier studies [18].

6.3.1.2 Effect of fibre loading and bonding agent

Figures 6.3 (a) and (b) give the variation of mol% uptake of the solvents (toluene and n-hexane) with fibre loading for the composites cured at 100°C. For both the solvents it is clear that as fibre loading increases, equilibrium solvent intake decreases. This is obviously due to the increased hindrance exerted by the fibres at higher loadings. It is also observed that for the composites containing bonding agent there is a sharp decrease in the uptake of solvents. A highly bonded system would exhibit high resistance to swelling compared to the nonbonded systems.



(a) Toluene **(b) n-Hexane**

Figure 6.3 Effect of fibre loading and bonding agent on equilibrium sorption of NR/isora composites cured at 100°C

6.3.1.3 Correlation with adhesion.

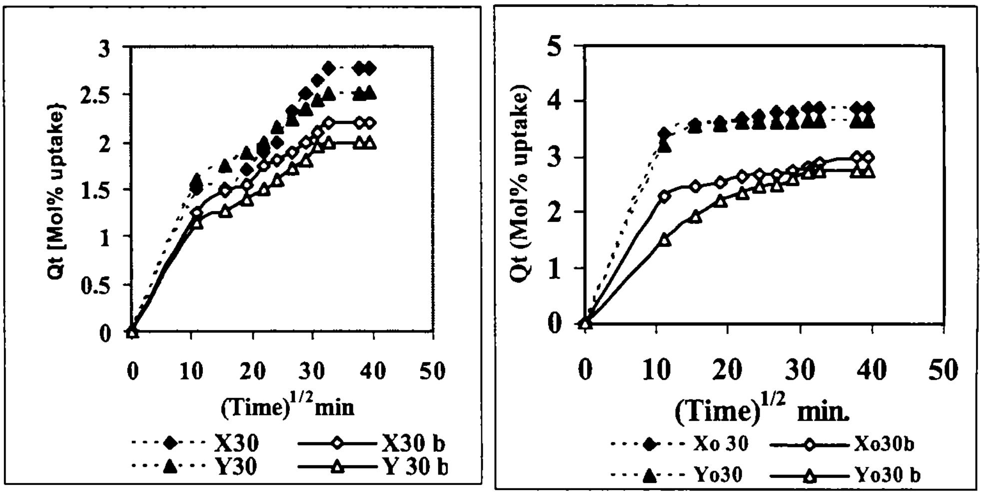
Table 6.2 gives the change in volume fraction of the rubber due to swelling (V_t) for vulcanizates containing different loadings of fibre for both systems. It is evident that the composites containing bonding agent have substantially lower (V_r) values than those without bonding agent. It was reported that the adhesion between rubber and fibres could be evaluated by restricted equilibrium swelling measurements. With the increase in extent of adhesion between rubber and fibre, the factor V_r decreases [11]. A high resistance to swelling indicates superior bonding.

Table 6.2 Change in the volume fraction of rubber due to swelling for the composites cured at 100°C and 150°C

Composites	**Ratio of the change in volume fraction of rubber due to swelling[V_r]**			
Solvents	**Toluene**		**n-Hexane**	
Curing temp	**100°C**	**150°C**	**100°C**	**150°C**
GUM	0.94	1.09	0.70	0.79
X_{10}	0.89	0.93	0.65	0.78
X_{20}	0.83	0.87	0.63	0.76
X_{30}	0.79	0.83	0.61	0.74
X_{40}	0.76	0.80	0.55	0.63
X_{10b}	0.85	0.89	0.59	0.73
X_{20b}	0.73	0.85	0.50	0.69
X_{30b}	0.65	0.73	0.41	0.60
X_{40b}	0.55	0.70	0.38	0.48
Y_{30}	0.69	0.76	0.59	0.64
Y_{30b}	0.55	0.65	0.40	0.50

Figures 6.4 (a) and (b) give the sorption curves obtained by plotting Q_t (the mol% uptake of the solvent) versus square root of time in toluene for a 30 phr loaded fibre

composite cured at 100°C and 150°C respectively. The uptake of the solvent is less in the case of composite cured at 100°C, which shows the better interfacial bonding for low temperature cured samples.



(a) Cured at 100°C **(b) Cured at 150°C**

Figure 6.4 Equilibrium sorption curves of the vulcanizates in toluene at 25°C

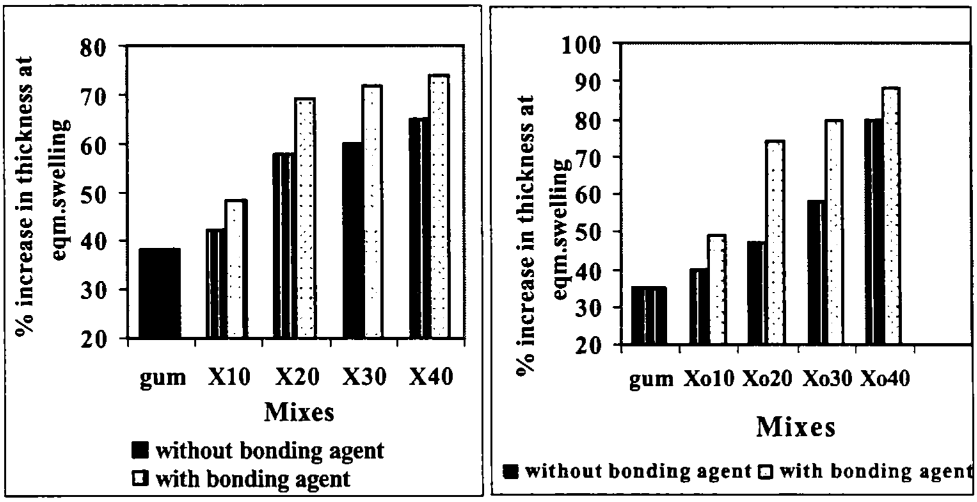
At the same fibre loading, the amount of solvent sorbed by a composite at equilibrium is less for the composite containing bonding agent compared to that without bonding agent. Another interesting observation is that the initial rates of diffusion is fast for the composite without bonding agent which is more pronounced in the case of composite cured at 150°C. This is because of the fact that in unbonded fibre rubber composites the solvent can penetrate into the polymer along the thickness direction and also through the weak interfaces parallel and perpendicular to the fibre orientation. The initial driving force for swelling is higher in unbonded composites as a result of large number of voids at the interface. But in the case of composites with bonding agent the interface is strong and the liquid can penetrate into the polymer only through the space between the fibre ends. As a result, the diffusion rate is slow in composites with good bonding. The same observations have also been reported in the case of sisal rubber composites [4]. The uptake of aliphatic solvent is less than that of aromatic solvent. Normal hexane, which is puckered in nature, avails greater surface area than toluene, which is planar. Hence it is difficult for hexane to penetrate into the composite than toluene with the result that the solvent uptake is less for hexane.

6.3.1.4 Effect of chemical treatment

The effect of chemical treatment of fibre on equilibrium swelling of the composites is given in figures 6.2 and 6.4. It is observed that in composites containing treated fibres, the solvent uptake is reduced further, which is due to the enhanced interfacial bonding between the fibre and rubber. This prevents the transport of solvent to some extent through the interface. The effect of chemical treatment on the fibre surface is evident from SEM studies explained in Chapter 3. The fibrillar nature as well as the porosity of the fibre is revealed in the fibre topography. On alkali treatment due to the dissolution of impurities and waxy materials from the surface, the pores become more significant and fibres become thinner than the untreated fibre. This renders roughness to the fibre thereby enhancing the mechanical interlocking at the interface. Thus it is clear that equilibrium liquid uptake can provide information regarding the efficiency of interfacial bonding. On comparing the equilibrium uptake of composites containing treated and untreated isora fibres it can be seen that the former composites are better than the latter in resisting the uptake of both solvents as evident from the figures 6.2 and 6.4

6.3.1.5 Dimensional changes of the composites

The percentage increase in thickness at equilibrium swelling in toluene is shown in Figures 6.5 (a) and (b) for the composites cured at 100°C and 150°C respectively.



(a) cured at 100°C (b) cured at 150°C

Figure 6.5 Percentage increase in thickness of the composites in toluene.

It is observed that the change in thickness is higher for the composite containing bonding agent and it increases with fibre loading. In a well-bonded, oriented fibre rubber composite, the swelling is anisotropic. It will swell to a greater extent in the direction perpendicular to the fibre orientation. This is because the oriented fibres will prevent the penetration of the liquid in the direction perpendicular to the flat surfaces of the specimen. Hence the solvent can diffuse into the polymer only through a direction parallel to fibre orientation. Thus swelling was considered to be constrained in one direction and as a result the thickness of the specimen increased considerably. The percentage increase in thickness was found to be higher for the composite cured at higher temperature (150°C) as evident from the figure 6.5. This also accounts for the better reinforcement of the composite cured at lower temperature.

The optical photographs of the unswollen and swollen samples of varying fibre loadings cured at 100°C in hexane are shown in Figure 6.6

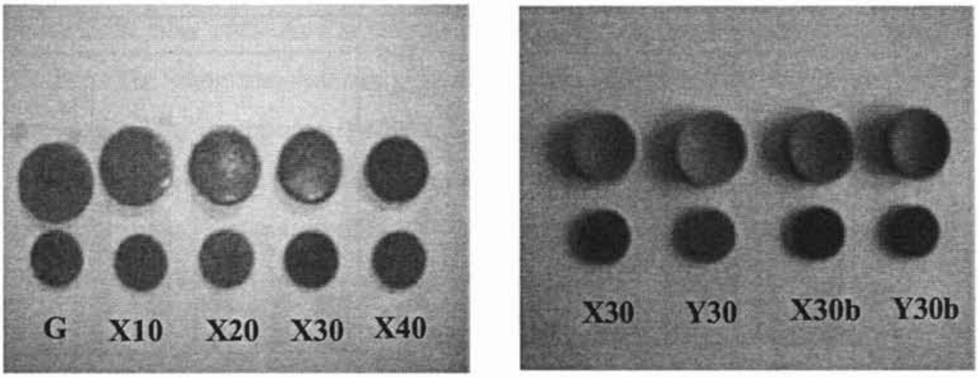


Figure 6.6 Optical photographs of the samples cured at 100°C before and after swelling in n-hexane at 25°C

From the figure it is clear that as fibre loading increases, the diameter of the swollen samples decreases. At the same fibre loading [30phr] the diameter of the bonded composite is lower than that of the unbonded composite as evident from the figure 6.6. From this it is clear that in highly bonded composites swelling occurs predominantly in the thickness direction. Thus the restricted equilibrium swelling can be used to measure the extent of interfacial bonding between the fibre and rubber.

6.3.2 Swelling of isora/NR composites in oils used in automobiles

6.3.2.1 Effect of fibre loading and bonding agent

Figures 6.7 (a) and (b) give the variation of % swelling index with fibre loading for the composites cured at low temperature (100°C) in fuels like petrol and diesel. It is clear that as fibre loading increases, equilibrium solvent uptake decreases. These observations are similar to those obtained in the case of organic solvents like toluene and hexane. Also for the composites containing bonding agent there is a sharp decrease in the uptake of solvents. Here also a highly bonded system would exhibit high resistance to swelling compared to the unbonded systems.

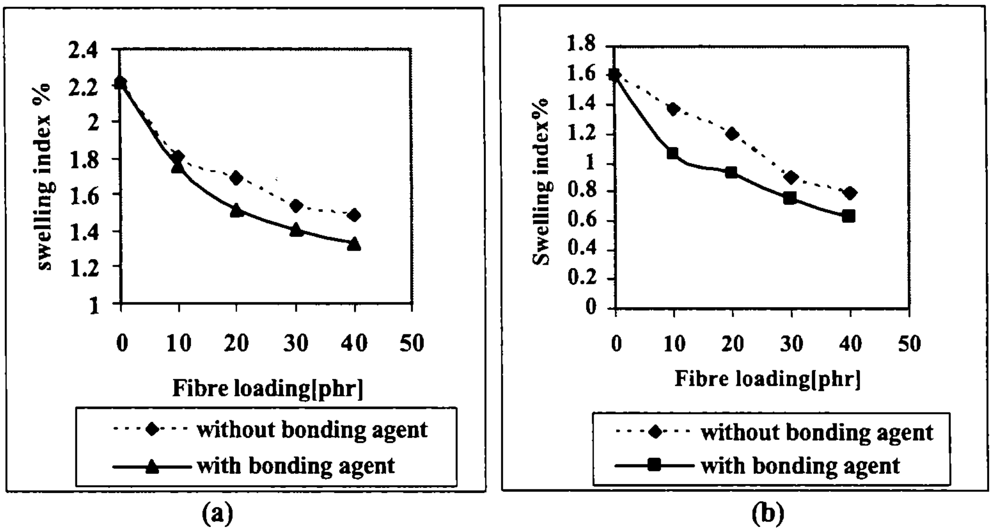


Figure 6.7 Variation of the % swelling index with fibre loading for the composites cured at 100°C in (a) petrol and (b) diesel

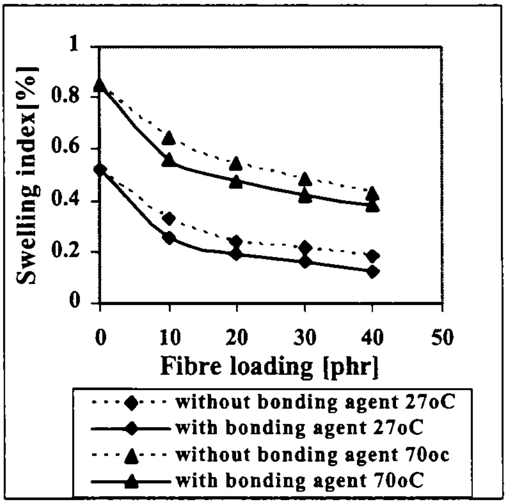


Figure 6.8 Variation of the % swelling index with fibre loading for the composites cured at 100°C in lubricating oil at 27°C and 70°C

The effect of fibre loading and bonding agent on the swelling index of the composites in lubricating oil at different temperatures is given in Figure 6.8. Here also as fibre loading increases the swelling in oil decreases. At room temperature the composites show greater resistance to swelling. As temperature increases the swelling in oil increased. At higher temperature the viscosity of the oil decreases, the molecules are free to move and can very well penetrate into the composite. The presence of bonding agent in the composites restricts the swelling considerably due to the strong interfacial adhesion. Maximum uptake of solvent was observed with petrol followed by diesel and then lubricating oil. The low molecular weight hydrocarbons present in petrol can easily penetrate into the material. As the molecular size increases as in diesel and lubricating oil, the uptake of oil decreases. This may be due to the larger size of solvent molecule that hinders the molecule from entering into the voids or solvent pockets present in the composite.

Table 6.3 Swelling coefficient of the mixes in various oils

Mixes	Petrol	Diesel	Lubricating oil
Gum	**3.46**	**1.93**	**0.808**
X_{10}	**2.71**	**1.65**	**0.626**
X_{10b}	**2.57**	**1.28**	**0.561**
X_{20}	**2.58**	**1.35**	**0.540**
X_{20b}	**2.32**	**1.11**	**0.423**
X_{30}	**2.42**	**1.09**	**0.451**
X_{30b}	**2.31**	**1.02**	**0.387**
X_{40}	**2.41**	**0.96**	**0.41**
X_{40b}	**1.91**	**0.88**	**0.369**
Y_{30}	**2.12**	**1.01**	**0.411**
Y_{30b}	**1.95**	**0.90**	**0.379**

It was reported that the liquid uptake increases as the molecular size increases and reaches a maximum value and then decreases [19].The swelling coefficient of the mixes in various oils is given in table 6.3. It is clear that mixes with bonding agent have comparatively low values than the unbonded ones, which is due to the improved interfacial bonding between fibre and rubber.

6.3.2.2 Effect of chemical treatment

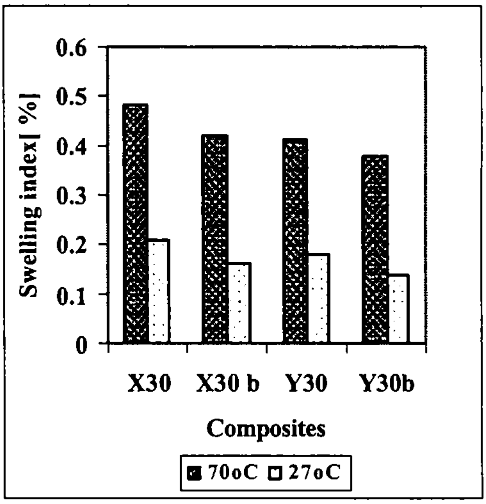
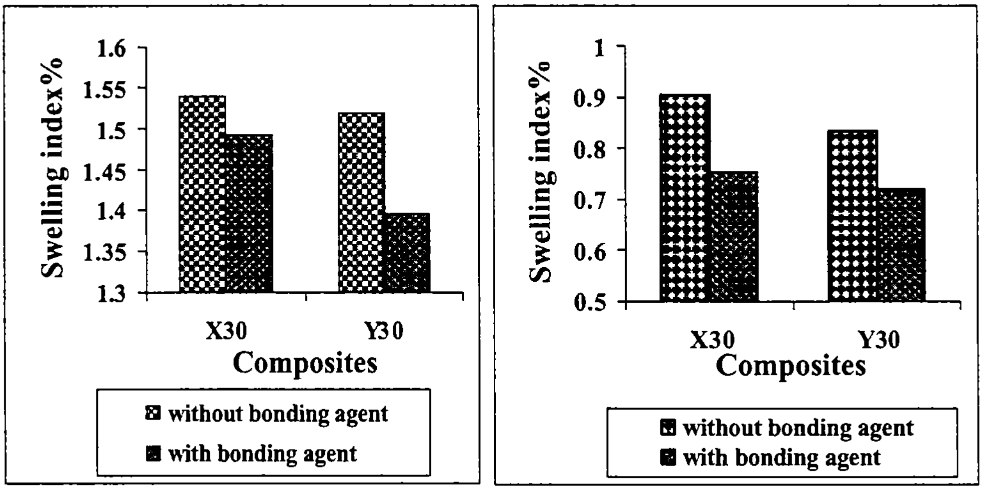


Figure 6.9 Comparison of the % swelling index for the composite containing untreated and alkali treated fibres in lubricating oil

The effect of chemical treatment of fibres on equilibrium swelling of the composites in various oils can also be evident from the figures 6.9 and 6.10. It is observed that in composites containing treated fibre, the solvent uptake is reduced further, which is due to the enhanced interfacial bonding between the fibre and rubber. This prevents the transport of solvent to some extent through the interface.



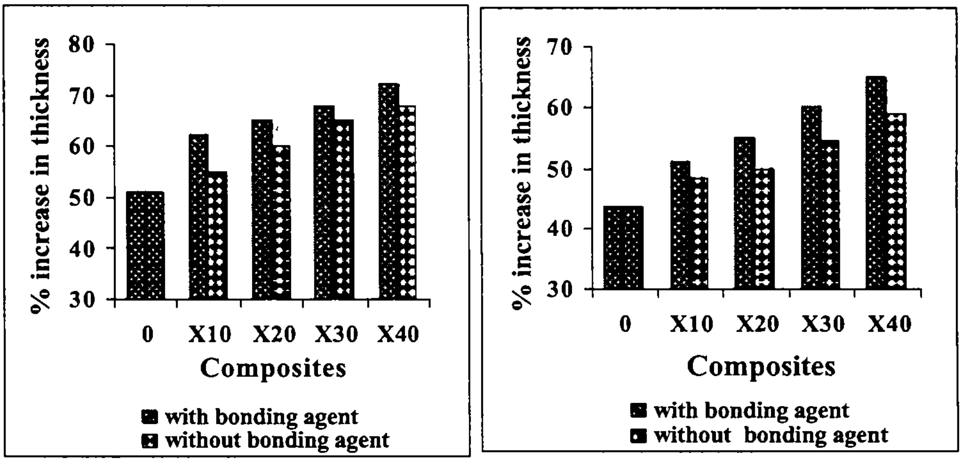
(a) (b)

Figure 6.10 Comparison of the % swelling index for the composite containing untreated and alkali treated fibres in (a) petrol and (b) diesel

Thus it is clear that equilibrium liquid uptake can provide information regarding the efficiency of interfacial bonding. On comparing the solvent uptake of composites containing chemically modified fibres with that of untreated ones it can be seen that the former composites are better than the latter in resisting the uptake of solvents/oils as evident from the figures 6.9 and 6.10.

6.3.2.3 Dimensional changes of composites

The percentage increase in thickness at equilibrium swelling for the composites cured at 100°C in petrol and diesel are shown in figures 6.11(a) and (b). Here also as in the case of toluene the change in thickness is higher for the composite with bonding agent and it increases marginally with fibre loading.



(a) (b)

Figure 6.11 Variation of % increase in thickness with fibre loading for the composite cured at 100°C in (a) petrol and (b) diesel

Gum vulcanizates showed lower swelling in the the thickness direction due to the sharp alignment of molecules in a particular direction during the milling and moulding operations. Anisotropic swelling becomes more pronounced when fibre is incorporated. At higher loadings the increase in thickness in both composites (bonded/unbonded) is comparable. The number of fibres in unit volume increases and penetrant molecule finds it more difficult to diffuse into the polymer and therefore entire swelling will take place in the thickness direction. At low fibre loadings, the penetrant can enter into the matrix both in the direction parallel and perpendicular to the fibre orientation. When bonding is poor, the matrix swells both in diameter and thickness directions. As a result, at low loading and also in the absence of bonding agent, the net swelling took place in the thickness direction is less. Although during swelling dimensional changes are shown by both bonded and unbonded composites, the effect is more pronounced in the case of composite with bonding agent especially at low fibre loadings. In diesel the percentage increase in thickness is less compared to that of petrol. The penetration of large hydrocarbon molecules in diesel is difficult and hence increase in thickness is less.

Optical photographs of samples cured at 100°C for varying fibre loadings before and after swelling in petrol are shown in figure 6.12.

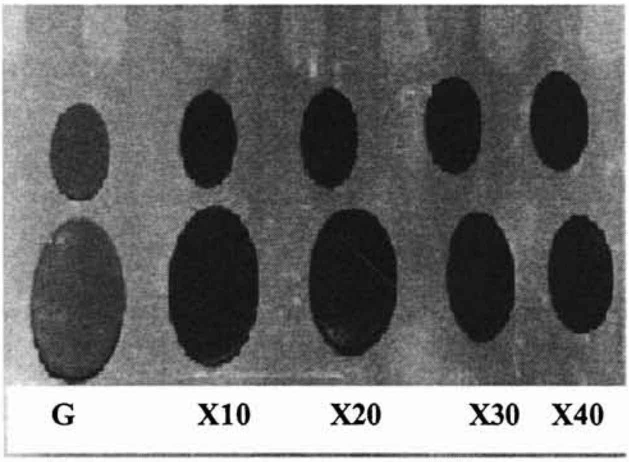


Figure 6.12 Optical photographs of the samples of varying fibre loadings before and after swelling in petrol

From the figure it is clear that as fibre loading increases the diameter of the swollen samples decreases. At the same fibre loading [30phr] the diameter of the bonded composite is lower than that of the unbonded composite as evident from figure 6.13. From this it is evident that in unbonded composites swelling occurs predominantly in the thickness direction.

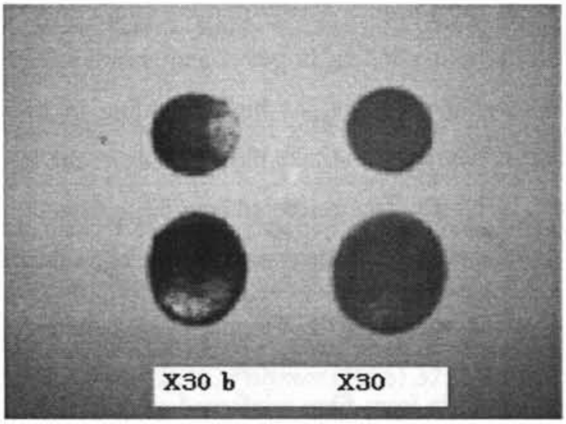


Figure 6.13 Optical photographs of the samples with and without bonding agent before and after swelling in petrol

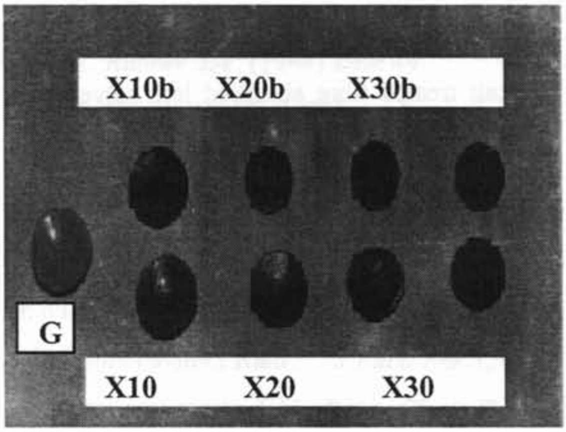


Figure 6.14 Optical photographs of the samples of varying fibre loadings after swelling in diesel.

In diesel, the diameter of the samples at equilibrium swelling is found to be less affected when compared to that swelling in petrol and shows a slight decrease with increase in volume loading of the fibre. At higher loading in the case of bonded composites, the swelling is restricted and take place mostly in the thickness direction as evident from figure 6.11(b). Thus the restricted equilibrium swelling can be used to measure the extent of interfacial bonding between the fibre and rubber.

6.4 CONCLUSIONS

Equilibrium swelling observed in isora fibre reinforced natural rubber is lower for the composite cured at 100°C compared to that cured at 150°C in solvents like toluene and hexane. The uptake of aromatic solvent is higher than aliphatic solvent for the composites. Maximum uptake was observed with petrol followed by diesel and then lubricating oil.

Increased fibre content resulted in reduced swelling. The % swelling index and swelling coefficient are substantially low for composites with bonding agent.

Composites containing alkali treated fibre absorbed less solvent compared to those with untreated fibre indicating that alkali treatment improves the adhesion between fibre and rubber. At higher fibre loadings swelling predominantly took place in the thickness direction.

6.5 REFERENCES

1. Jost W., *Diffussion in solids liquids and gases*, Academic press, Newyork (1952)
2. Kraus G., *Rubb Chem Technol,* (1964) **37**: 6
3. Prasanthkumar R.,Thomas S., *J Adhesion Sci* Technol, (2001) **15(6)**:633
4. Varghese S., Kuriakose B.,Thomas S., *Rubber Chem Technol*, (1995) **68(1)**:37
5. Maya J., Thomas S., Varghese K.T., *Comp Sci Technol*, (2004) **64:** 955
6. George S.C., Ninan K.N., *Polymer,*(1996) **37:** 5839
7. G.,Singh R.P.,Laksminarayan R., *J App Polym Sci,*(1996)**611:** 2035
8. Unnikrishnan G., Thomas S., *Polymer,* (1996) **37(13):** 2687
9. Parks C.R., *Rubb Chem Technol,*(1982) 55: 1170
10. Geethamma V.G., Joseph R., Thomas S., *J App Polym Sci,* (1995) **55:** 583
11. Das B ., *J Appl Polym Sci*, (1973) **17**:1019
12. Coran A. Y., Boustany K., Hamed P., *Rubber Chem Technol*,(1974) **47**:396
13. Dunnom D.D., *Rubber age*, (1968) **100:** 49
14. Lee L.H., *J Polym Sci*, (1967) **5:** 751
15. Hewitt N.L., *Rubber age,* (1972) **104:** 59
16. Noegi P., *Diffussion in Polymers-Transport phenomena in Polymer membranes,* Ch. 4, (1996) Marcel Dekker Inc., Newyork.
17. Aminabhavi T.M., Aithal U.S., *J Chem Educ,*(1990) **67**:82
18. Lovely M., Shiny palatty., Rani J., *J Rubb Res*, (2006) **9(1)**:21
19. Solomon G., Amerongen G. J. V., *Rubb Chem Technol*,(1948) **21:** 67

CHAPTER 7

DYNAMIC MECHANICAL ANALYSIS

7.1 Introduction

7.2 Experimental

7.3 Results and Discussion

  7.3.1 Glass transition temperature

  7.3.2 Effect of fibre loading and bonding agent

  7.3.3 Effect of chemical treatment

  7.3.4 Effect of fibre orientation

7.4 Conculsions

7.5 References

CHAPTER 7

DYNAMIC MECHANICAL ANALYSIS

Abstract

The dynamic mechanical properties of natural rubber filled with untreated and chemically treated isora fibre have been investigated. The effect of fibre matrix interface on visco elastic properties of the composite has been evaluated and it is found that interface adhesion increases the storage modulus and decreases the mechanical loss. The effects of fibre orientation, fibre loading, and temperature on the dynamic mechanical properties have also been investigated. Treated fibre composites offer good interfacial bonding and hence tend to dissipate less energy than those of untreated composites. Presence of bonding agent in the composite strongly influences the visco elastic properties.

Results of this chapter have been communicated to *Composite Science and Technolgy*

7.1 INTRODUCTION

Dynamic mechanical analysis has been widely employed for investigating the structure and viscoelastic behaviour of polymeric /rubber composites for determining their stiffness (modulus) and damping (energy dissipation) characteristics as they are deformed under periodic stress. A large number of rubber articles like automobile tyres, springs and dampers are subjected to cyclic deformation or loading during their service life. Since rubber products generally undergo dynamic loading during service there dynamic mechanical analysis is very important. Under such conditions bonding between fibre and rubber plays an important role in the performance of a short fibre reinforced rubber composite. Thus it is particularly useful for evaluating the mechanical properties of viscoelastic materials like natural rubber composites whose properties exhibit time, temperature and frequency dependence.. Several studies have been reported on the dynamic mechanical properties of various natural/synthetic fibre reinforced rubber composites [1-7]. Modelling of material damping of unidirectional fibre reinforced composites has been done by Kaliske and Rothert [8]. Studies have been conducted on the role of adhesion on the viscoelastic properties of rubber tyre cord composites [9]. DMA of the composites containing short PET (polyethylene terephthalate) fibres with chloroprene rubber and urethane rubber have been reported [10-11]. Interface characterization using DMA was done by several researchers [12-18]. Studies have been made on the effect of diazide as adhesion agent on the composite of SBR and short PET fibres [19]. Thomas and coworkers have reported the dynamic mechanical response of various natural fibre filled polymer composites [20-23].It was observed that addition of natural fibres into the polymer improved the viscoelastic properties to a greater extent. Otaigbe reported that incorporation of solid elastic filler into polymer matrix increases the mechanical damping of the polymer [24]. Nielson observed that incorporation of reinforcing fillers usually decreases damping [25]. Ibarra et al studied loss modulus values increase with loading of short

PET fibres in NR, chloroprene rubber, nitrile rubber and SBR compared to their respective gum compounds [26]. The dynamic viscoelasticty of isoprene rubber reinforced with short cellulose fibres have been investigated by Yano *et al* [27].

Dynamic mechanical studies have considerable practical significance for several reasons, particularly if they are analyzed over a wide range of frequencies and temperatures. They can yield an insight into various aspects of material structure, by providing the convenient measure of T_g. The dynamic properties are also of direct relevance to a range of unique polymer applications, concerned with the isolation of vibrationsor dissipation of vibrational energy in engineering components. The characterization and evaluation of the viscoelastic reponse of fibre filled elastomers for structural applications require an understanding of the following factors. Such as a) fibre composite material is temperature sensitive, b) addition of fibre changes the temperature dependence of the viscoelastic mechanism of the matrix, and c) dewetting and caviation that occur in the composite. Due to these factors much of the research carried out on elastomers was employed on selected filler systems and less attention has been focused on the behaviour of short fibre filled systems. In this chapter we report characteriztion and evaluation of the viscoelastic response of a series of short isora fibre filled natural rubber composites. Specifically this chapter analyses effects of fibre loading, fibre orientation, chemical treatments, incorporation of a bonding agent, and temperature on the dynamic mechanical properties of short isora fibre reinforced natural rubber composites.

7.2 EXPERIMENTAL

The compounds were prepared as per the formulation given in Table 7.1

Table 7.1 Compound Formulation [phr] [a]

Ingredient	X_{10}	X_{20}	X_{30}	X_{40}	X_{10b}	X_{20b}	X_{30b}	X_{40b}	Y_{30b}
RF resin	-	-	-	-	2.5	5.0	7.5	10	7.5
Silica	-	-	-	-	1.0	2.0	3.0	4.0	3.0
Hexa	-	-	-	-	1.6	3.2	4.8	6.4	4.8
Fibre [X]	10	20	30	40	10	20	30	40	
Fibre [Y]	-	-	-	-	-	-	-	-	30

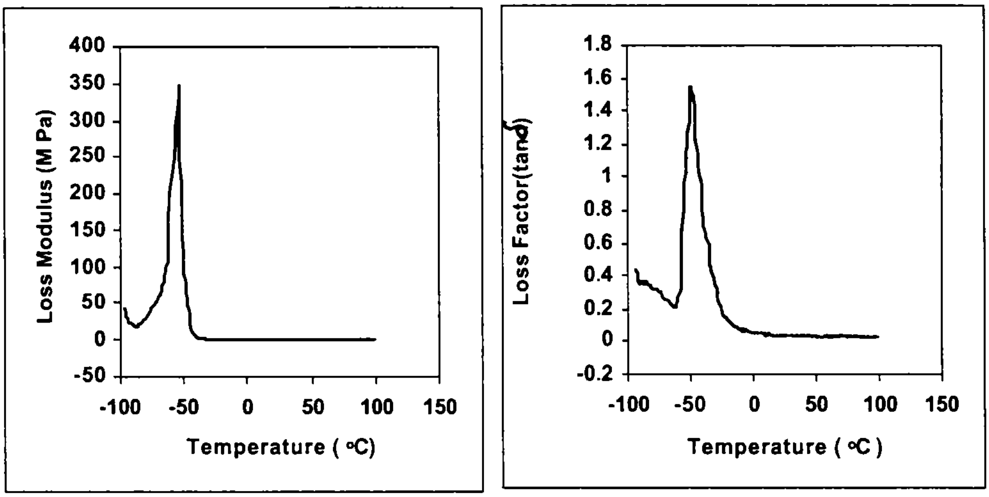
[a] Basic recipe: [Gum] NR-100, ZnO-5.0, Stearic acid-2.0, TDQ-1.0 ,CBS- 0.6,TMTD- 0.1, S-2.5

X -untreated, **Y**- alkali treated, compounds were also prepared using alkali treated, and silane treated fibres [30 phr] represented by $\mathbf{Y_{30}}$ and $\mathbf{Z_{30}}$ respectively

7.3 RESULTS ANS DISCUSSION

7.3.1 Glass transition temperature

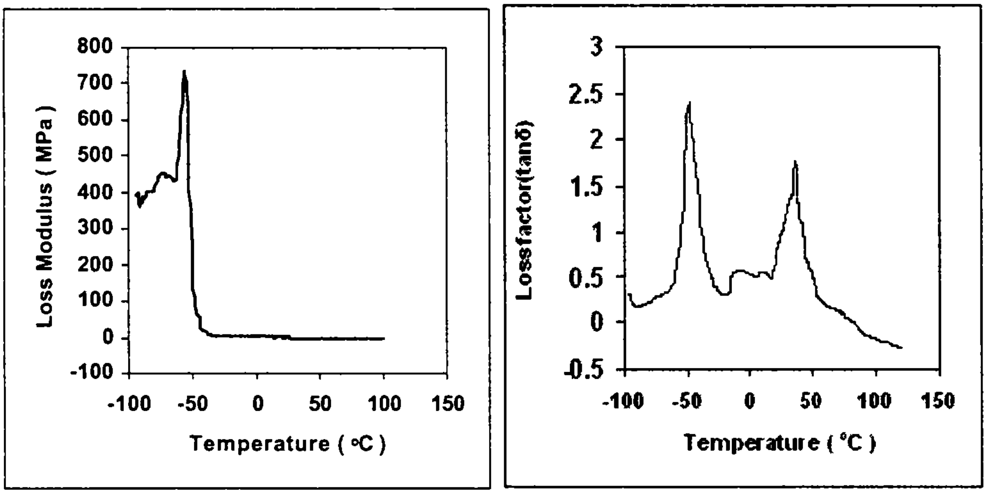
DMA is an effective tool to determine the dynamic glass transition temperature T_g, morphology of crystalline polymers and damping characteristics. The dynamic T_g is defined as the temperature at which 1) the maximum of tan δ and loss modulus E”occurs or the middle point of the storage modulus E’ Vs temperature curve. For a polymer system, the above values should be the same at a specific frequency. Figures 7.1&7.2 give the variation of loss modulus and tan δ with temperature of natural rubber vulcanizate and its composite at a frequency 1 Hz. At low temperature the viscosity of the rubber is very high and strain rate is very low due to the lack of molecular flow and hence energy dissipated is negligible. With the increase of temperature viscosity decreases, the strain rate becomes more pronounced so that energy dissipation or loss modulus and loss factor is comparatively high in the transition region.



(a) (b)

Figure 7.1 Variation of (a) Loss modulus (b) tan δ with temperature of natural rubber compound measured at a frequency of 1 Hz

The effective straining rate of the polymer segments continue to increase with temperature above T_g. But at the same time viscosity of the rubber decreased further. The net result is a decrease in damping and so a decrease in E" and tan δ at higher temperatures. It can be seen from figure 7.1 that the maxima in tan δ and E" curves of the gum vulcanizate almost coincide with one another. But it can be observed in figure 7. 2 that the behaviour of DMA curve of the isora fibre reinforced NR composite is some what different from that of the gum vulcanizate. The maxima in tan δ and E" do not coincide in the case of composites as that observed for gum vulcanizate. Thus is due to the complexity of the dynamic mechanical behaviour of these composites which depend mainly on the relaxation properties of the NR matrix, isora fibre and the interface between these two.

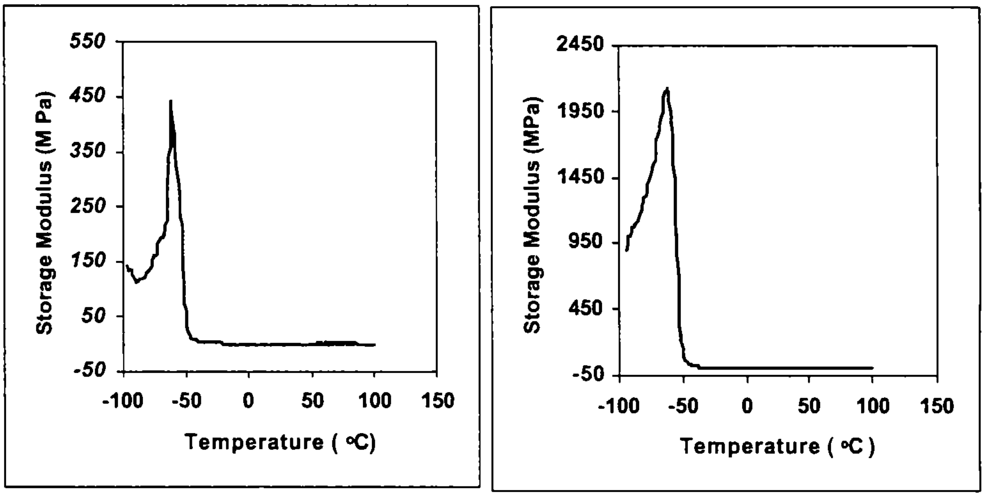


(a) (b)

Figure 7.2 Variation of (a) Loss modulus (b) tan δ with temperature of natural rubber composite X30 measured at a frequency of 1 Hz

Dynamic viscoelastic properties of PET fibre reinforced styrene-isoprene and styrene-butadiene copolymers have been studied by Guo and Ashida [28]. They have reported that the tan δ Vs. temperature curve of a two phase systems show two peaks characteristic of the T_g of each component. Similarly in the present study also two peaks were observed for tan δ Vs temperature curve for the composites as shown in figure 7.2(b), one at a lower temperature corresponding to the main relaxation of the rubber matrix where the damping effect is the greatest and it gives the dynamic T_g of the matrix and the other at a higher temperature due to the relaxation of isora fibre. In addition to these two peaks a small peak was observed between them which are considered to be due to the interface region in the composite. But from figure 7.2(b) it is clear that in contrary to the tan δ curve, only one peak is observed for E" Vs temperature curve of these composites (Fig 7.2a). Hence T_g obtained from E" peak gives a more consistent and appropriate index than one based on tan δ peak.

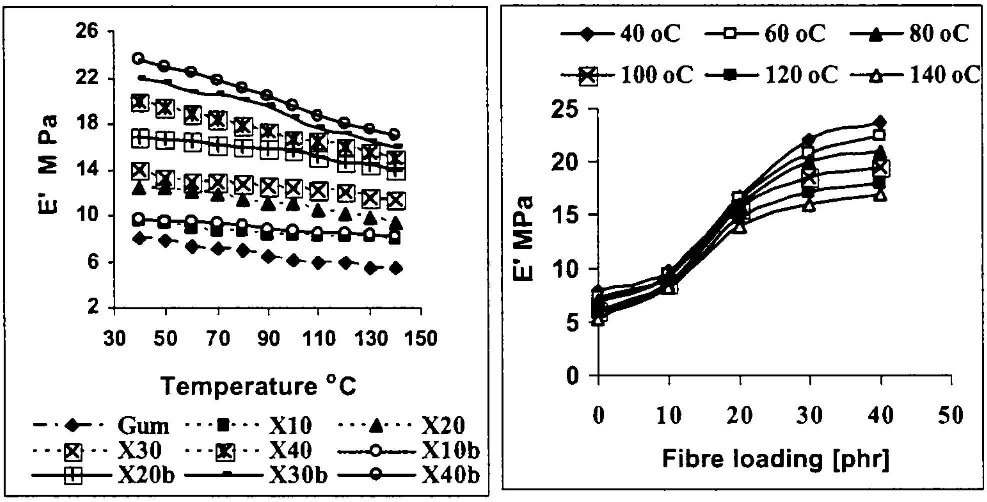
7. 3. 2 Effect of fibre loading and bonding agent



(a) (b)

Figure 7.3 Variation of storage modulus with temperature of the (a) natural rubber compound (b) rubber composite (X30) measured at a frequency of 1 Hz

Variation of storage modulus with temperature for the gum vulcanizate and the rubber composite[X_{30}] are given in figures 7.3 (a) and (b). It can be seen that the storage modulus of the composite is increased in the low temperature region for the composite by the introduction of high modulus fibres compared to that of the gum vulcanizate. The damping mechanism in composites mainly results from the viscoelastic nature of the matrix and fibre, the coulomb friction damping due to slip between the unbonded, debonded and bonded region of the fibre matrix interface and the energy dissipation occurring at cracks or delaminations [29]. Figure 7.4(a) show the effect of temperature in the range (30-140°C) on the storage modulus (E') of the composites as a function of fibre loading measured at a frequency of 10Hz. It is observed that E' increases with increase in the fibre content. The increase in E' is more pronounced at low temperatures. The increase in E' is due to the reinforcement imparted by fibre allowing uniform stress transfer from matrix to strong fibres.



(a) (b)

Figure 7.4 Variation of storage modulus [E'] with (a) temperature (b) fibre loading measured at a frequency of 10Hz

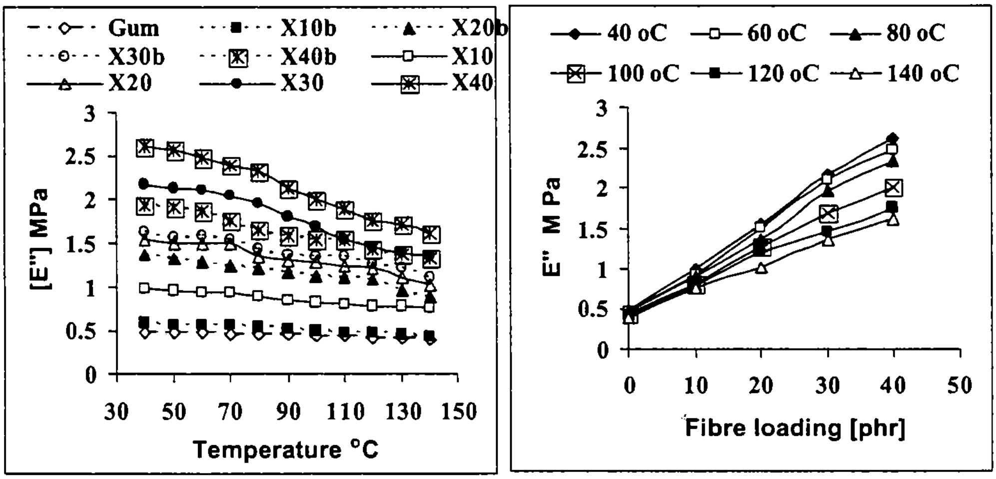
Effect of fibre loading on storage modulus as a function of temperature is given in figure 7.4 (b). The E' is found to decrease with the increase of temperature. It is reported that the decrease of modulus with increase of temperature is associated with the deterioration of rubber matrix at higher temperatures and also due to the thermal expansion occurring in the matrix resulting in reduced intermolecular forces [30]. From figure 7.4 (a) it is clear that composites containing bonding agent show enhancement in the storage modulus as the matrix get stiffened by the addition of bonding agent when the fibres get firmly bonded to the matrix. This indicates the importance of a strong fibre matrix adhesion in improving the viscoelastic properties of short fibre reinforced polymer composites. Table 7.2 shows the storage modulus[E'] and relative or normalized storage modulus[E_r'] values of isora/NR composites at different temperatures -100°C [below T_g], -50°C [around T_g], and 100°C [above T_g].

Table 7. 2 Variation of storage modulus and normalized storage modulus with fibre loading at different temperatures

Material	**Storage modulus (MPa)**			**Normalized storage modulus(MPa)**		
	-100°C	**-50°C**	**100°C**	**-100°C**	**-50°C**	**100°C**
Gum	142	251	1.72	1	1	1
X_{10b}	171	323	5.29	1.20	1.28	3.07
X_{20b}	438	549	6.75	3.08	2.18	3.92
X_{30b}	871	896	12.4	6.13	3.56	7.21
X_{40b}	905	914	9.28	6.37	3.64	5.4

The E' and E_r' of the composite increases with increase in fibre loading below and around T_g. But above T_g [100°C] though E' and E_r' values increases with increase in fibre loading, there is a decrease in the modulus at higher loading [40%]. From the normalized modulus values it is clear that E_r' is not showing considerable variation around T_g ie, at -50°C. But at very low and high temperature [-100°C and 100°C] comparatively high E_r' values are obtained for composites with higher loading [>20%] compared to that of gum vulcanizate. Also from Table 7.2 and figure 7.4(a) it can be seen that E' varied marginally with fibre loading in the rubbery state whereas a notable variation was observed in the glassy state.

From figures 7.1(a) and 7.2(a) it is observed that E" of the composite at any temperature is greater than that of the gum vulcanizate. Fibre incorporation increases the E'' values which indicate the higher heat dissipation of short isora/NR composites compared to that of gum vulcanizate. Also E" of the composite exhibits a significant drop in the transition region and this region is narrower than that of the gum compound. The peak intensity and position of E" peak of the composite also vary with fibre incorporation. The variation of loss modulus [E"] of the composites with fibre loading as a function of temperature is given in figure 7.5b.



(a) (b)

Figure 7.5 Variation of loss modulus [E"] with (a) temperature (b) fibre loading measured at a frequency of 10Hz

The variation of loss modulus with temperature also shows the same trend as that of storage modulus. As in the case of storage modulus, the loss modulus of the composite also increases with increase of fibre content and the effect was more noticeable in the case of composites with bonding agent which is due to the improved fibre matrix adhesion [Figure 7.5(a)]. With the improved interfacial bonding between fibre and rubber the heat dissipation is minimized. Bonded composites show relatively lower E" values than that of unbonded composites.

The damping properties of the composites can be understood from the plot of tan δ Vs temperature [Figures 7.2(b) and 7.6]. It is seen that damping behaviour of these composite increases with the incorporation of short isora fibres into the rubber matrix. Tan δ_{max} value of the gum vulcanizate is much less than that of the composite (Figures 7.1(b) &7.2(b).

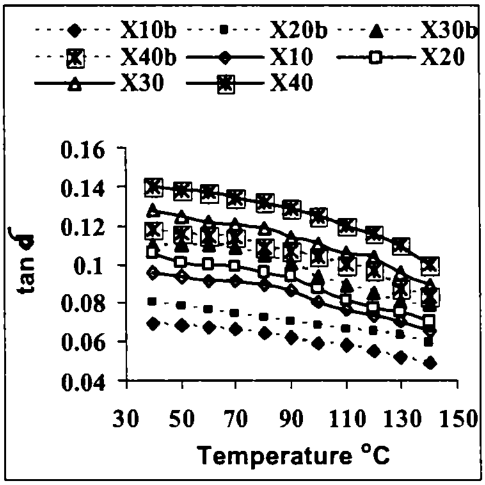


Figure 7.6 Variation of tanδ with temperature as a function of fibre loading at a frequency of 10Hz

As in the case of E'&E", tan δ also increases with the increase in fibre loading (Figure 7.6). Similar behaviour of natural rubber composites was already reported [4]. As the fibre loading increased, the interfacial area increases and the frictional loses are high leading to higher damping of the composites. Larger the interfacial area, the more is the energy loss at the interface. The higher interfacial bonding between the fibres and the rubber matrix in presence of bonding agent is further evident from the lower tan δ values of the composites with bonding agent. Also tan δ values decreased with increase of temperature and the decrease was sharper at higher loadings (>20%)

From figures 7.4, 7.5& 7.6 it can be concluded that fibre matrix adhesion influences the viscoelastic properties of the composites. When there is no bonding between the fibre and the matrix, the fibre can slip past from the matrix under tension, but when there is bonding between the fibre and the matrix there will be shear at the interface between fibre and the matrix which leads to a decrease in mechanical loss. The high storage modulus of the well bonded composite supports the fact the load transfer between the fibre and the matrix occurred through the rubber fibre interface

It is reported that in the case of cord rubber composite, the cord do not contribute to the mechanical loss in the absence of adhesion and therefore the mechanical loss of the unbonded cord rubber composite will be lower than the rubber [31]. But in the case of short fibre reinforced rubber composites, when the bonding between the fibre and the rubber is poor, the fibre ends will be free and act as stress raisers and contribute to mechanical loss [3]. However the extent of mechanical loss will decrease with the increase in the adhesion level.

7. 3. 3 Effect of chemical treatment

The effect of chemical treatments on the damping ratio (tan δ) of isora/NR composites as a function of temperature measured at a frequency of 1 Hz is shown in Figure 7.8

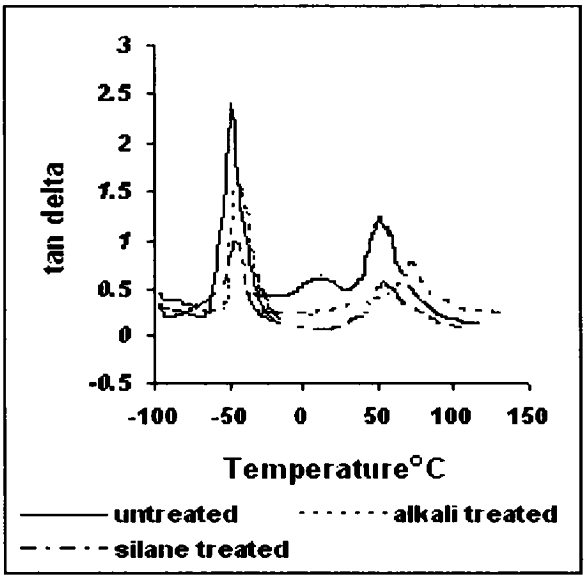


Figure 7.8 Effect of chemical treatment of isora fibre on the tan δ of the composite (30phr) measured at a frequency of 1 Hz.

The tan δ is a damping term that can be related to the impact resistance of the material. Since the damping peak occurs in the region of glass transition where the material changes from a rubbery to a rigid state, it is associated with the segmental mobility of the chains. The higher the peak tan d value, the greater is the degree of molecular mobility. It was reported that in the case of carbon fibre epoxy composite materials higher the damping at the interface, poorer the interfacial adhesion [32]. From figure 7.8 it is revealed that composite with poor interfacial bonding tends to dissipate more energy than that with good interfacial bonding. It was observed that composite Z_{30} contains fibres subjected to silane treatment exhibited low tan δ values both at high and in the glassy region. This indicates that composite Z_{30} possesses low damping and so good interfacial bonding characteristics. But composite X_{30} contains untreated fibres exhibit some what higher tan δ_{max} values both at low and high temperature regions. Hence these composites are better candidates for high damping applications compared to silane treated fibre composites. Composite Y30 contains alkali treated fibres whose tan δvalues is in between the untreated and silane treated composites. Variation of E' and E" with temperature of alkali treated and untreated composites measured at a frequency of 10 Hz is given in figures 7.9 (a) & (b).

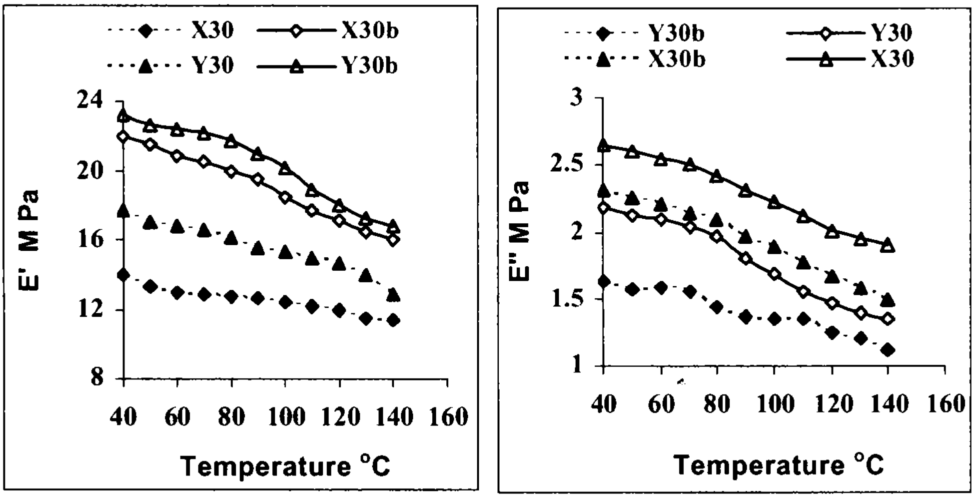
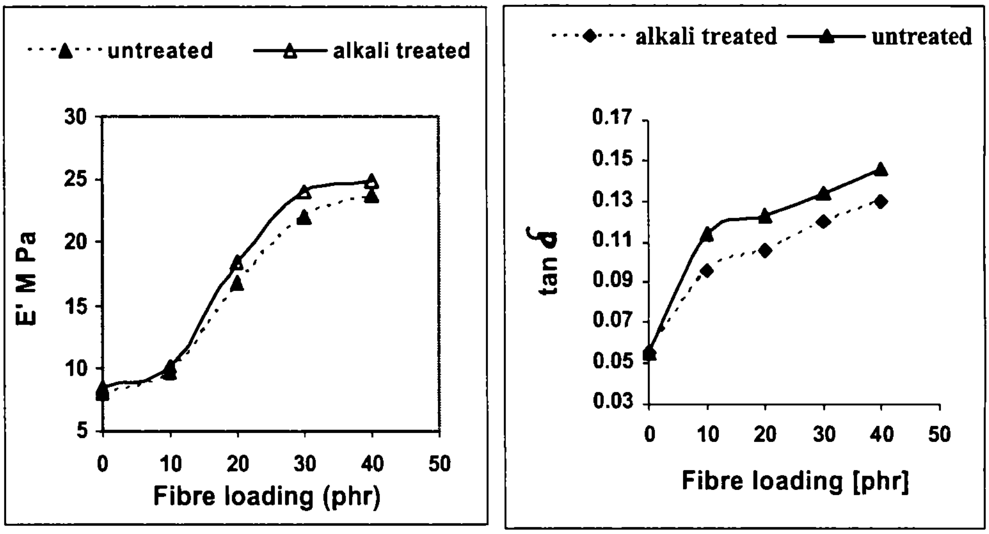


Figure 7.9 Effect of chemical treatment and bonding agent on (a) storage modulus and (b) loss modulus of the composites measured at frequency of 10Hz

It is seen that significant improvement in the storage modulus is attained for the alkali treated fibre composites, which is attributed to the increase in stiffness achieved through more fibre matrix interaction. Due to the improved interfacial adhesion of the alkali treated fibre composites lesser is the damping at the interface or less energy is dissipated and hence a decrease in loss modulus is registered when compared to the untreated fibre composites. Figures 7.10 (a) and (b) shows the variation of storage modulus and tan δ measured at a frequency of 10Hz with fibre loading at a temperature of 40°C of alkali treated and untreated fibre composites.

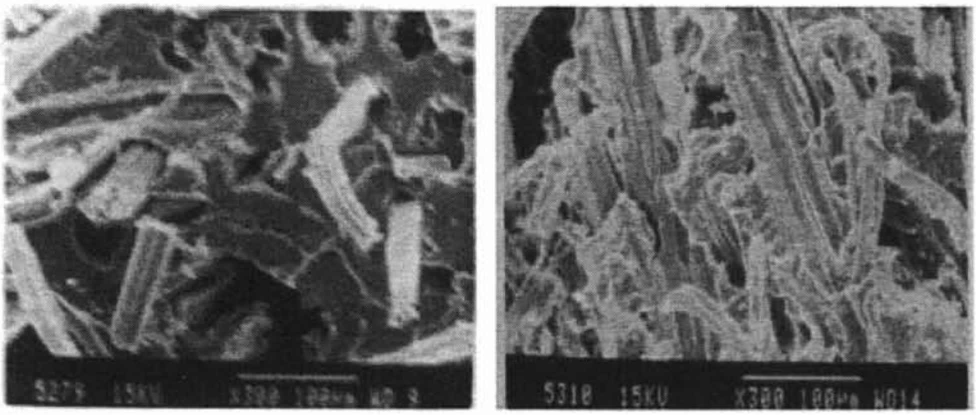


(a) (b)

Figure 7.10 Variation of (a) storage modulus and (b) loss factor with fibre loading for the untreated and alkali treated fibre composites at 40°C measured at a frequency of 10Hz.

A higher modulus and a low tan δ value is always showed by the composite containing treated fibre this again is associated with strong fibre rubber adhesion in the treated fibre composites.

Figures 7.11(a) and (b) shows the tensile fracture surfaces of the composite X_{30} and Y_{30b} which contains untreated and alkali treated fibres without and with bonding agent. It can be seen that there are few holes on the surface after the fibres are pulled out from the matrix indicating poor wetting between fibres and matrix. But in the fracture surface of the composite Y_{30b} broken fibres are seen which indicate that the fibres are well bonded to the matrix. Careful examination of the fracture surface reveals that the failure is brittle type in composite Y_{30b} which is evident from the presence of fracture lines from different planes. The brittle nature of the composite is associated with the strong matrix fibre interactions



(a) (b)

Figure 7.11 SEM photograph of the composite (a) (X_{30}) containing untreated fibre without bonding agent (b) (Y_{30b}) containing treated fibre with bonding agent

Tan δ_{max} values and T_g of isora /NR composites with varying fibre loading are given in Table 7.4. The tan δ_{max} value is the lowest for the gum vulcanizate and the value increase with increase in fibre loading. The highest glass transition temperature is obtained for the gum vulcanizate and the value is decreased by the addition of fibres. This decrease in T_g by the fibre incorporation is associated with the cross link nature of the rubber compound.

Table 7. 4 T_g and tan δ_{max} of the composites at different fibre loadings at a frequency 1 Hz

Material	T_g	tan δ_{max}
Gum	-49.1	1.483
X_{10}	-49.9	1.516
X_{20}	-50.7	1.685
X_{30}	-51.3	2.409
X_{40}	-53.2	2.962

At high loadings due to the interaction between fibres and rubber and also due to the over crowding of fibres, the extent of cross linking in the rubber compound decreases and hence chain mobility is easier in presence of fibres with the result that there is a decrease in T_g in the case of composites. Similarly from figure 7.8 it is clear that the peak temperatures of the tan δ curves of composites with untreated and various treated fibres at low temperatures are shifted to higher temperature range in comparison to that of gum (-51.1°C) as evidenced from figure 7.1(b) This shifting is due to the immobilization of the polymer matrix in the vicinity of the fibre due to the interfacial bonding between the two phases. Hence higher shifts are observed for the composite with higher interfacial bonding, which contains modified fibres. Thus the highest shifting in T_g of the composite Z_{30} (-48.1°C) indicates its higher interfacial bonding.

7. 3. 4 Effect of fibre orientation

Figure 7.12 shows the effect of fibre orientation on the storage modulus of the composite containing untreated and alkali treated fibres as a function of temperature. It is observed that the longitudinally oriented fibre composite exhibit higher storage modulus than the transversely oriented ones at the same fibre loading. When the fibres are in the direction of the applied load, the load will be effectively transferred by the fibres and hence a higher modulus is obtained. This is not with the case of transversely oriented fibre composites, where the fibres are aligned in a direction perpendicular to the direction of applied load and the stress transference is not effective hence have a decreased modulus value.

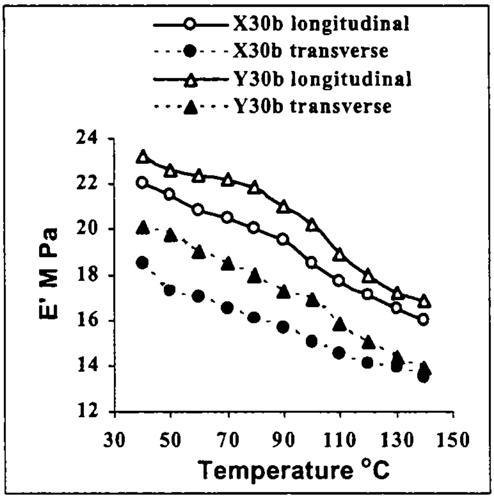


Figure 7.12 Variation of E' with temperature at a frequency of 10Hz of the composite X30 in the longitudinal and transverse directions.

7. 4 CONCLUSIONS

Addition of short isora fibre to natural rubber increased the storage modulus, loss modulus and tan d of rubber vulcanizate.

Composites with poor interfacial bonding tends to dissipate more energy than that with good interfacial bonding both at low and high temperature.

Composite containing silane treated fibres exhibited a very low tan δ values in the low temperature region than with composites containing alkali treated and untreated fibres.

Decrease in Tg at higher loading is due to the decrease in the extent of cross linking of rubber as a result of the overcrowding of fibres.The anisotropy of the composites is well established which also affects the viscoelastic properties.

7.5 REFERENCES

1. Akay M., *Comp Sci Technol,* (1993) **47:** 419.
2. Ashida M., Noguchi T., *J Appl Polym Sci,* (1984) **29:** 661.
3. Murthy V.M., De S.K., *J Appl Polym Sci*, (1983) **28:** 3485.
4. Varghese S., Thomas S. , Kuriakose B. *Ind J Nat Rubb Res*,(1992) **5:**18
5. Ashida M., Noguchi T., *J Appl Polym Sci,* (1985) **30:**1011
6. Prasanth kumar R., Thomas S., *Polym International,* (1995) **38(2):** 173.
7. Bhagawan S S., Tripathy D.K., De S.K.,*J Appl Polym Sci,* (1987) **34:**1581
8. Kaliske M., Rothert H., *Comp Engg,* (1995) **5:** 551.
9. Prevosek D.C., Sharma R.K., *Rubb Chem Technol,* (1981) **54:** 72.
10. Ashida M., Noguchi T., Mashimo S., *Comp Polym,* (1989) **2:** 339
11. Foley M.E., Obaid A.A, Huang X., *Compos, Part A* ,(2002) **33:** 1345.
12. Khatibi A.A, Mai Y., *Compos, Part A,* (2002) **33:** 1585

13. Kumnuanti C., Sombatsompop N., Materials *Letters,* (2003) **7:** 3167.
14. Manchado L.M.A., Biagiotti J., Kenny J.M., *Polym Engg Sci,* (2003) 43: 1018.
15. Hashmi S.A.R., Chand N., Kitano T., Polym *Comp,* (2003) 24: 149.
16. Joseph P.V., Joseph K., Thomas S., *Compos, Part A,* (2003) 34: 275.
17. Naskar A., Bhowmick A.K., De S.K., *J App Polym Sci* ,(2002)**84:** 622
18. Sarasua J.R., Pouyet J. J ., *Thermoplast Comp Mater,*(1998) **11:** 2
19. Ibarra L., *J Appl Polym Sci,* (1993) 49: 1595.
20. George J., Bhagawan S.S., Thomas S., *J Thermal Analysis,*(1996) **47:**1121
21. Varghese S., Kuriakose B., Thomas S., *J Adh Sci Technol,* (1994) **8:** 235
22. Sreekala M.S., Bhagawan S.S., Thomas S., *J Reinf Plast Comp,* (1998) **17:** 1471
23. Pothan L.A., Oommen Z, Thomas S., *Comp Sci Technol,*(2003) **63:** 283
24. Otaigbe J.U., Polym *Engg Sci,* (1991) **31:** 100.
25. Nielson L.E., Mech *Prop Polym and Comp, Marcel Dekkar,* (1974) **2:** 114.
26. Ibarra L, Macias M., *J Appl Polym Sci,* (1995) **57:** 831.
27. Yano S., Hirose S., Hatakeyama H., *J Appl Polym Sci,* (1990) **40:** 657
28. Guo W., Ashida M., *J Appl Polym Sci,*(1993) **50:** 1435.
29. Rozman H.D., Ismail H, Tay G.S., *Euro Polym J,*(2001) **37:** 12831
30. George J., Bhagawan S. S., Thomas S., *J Thermoplastic Comp Mat,* (1999) **12:** 443.
31. Ashida M., Noguchi T., *J Appl Polym Sci,* (1984) **29:** 631.
32. Dong S., Gauvin R., *Polym Comp,* (1993) **14:** 414.

CHAPTER 8

SUMMARY AND CONCLUSIONS

Abstract

The major findings of the study are summarized in this chapter. The scope for future work is also outlined.

A. SUMMARY AND CONCLUSIONS

The summary and conclusions of the work carried out on the isolation and charactrisation of isora fibre, and on the use of this fibre as reinforcement in natural rubber are outlined in this chapter.

In recent years there has been a tremendous advancement in the field of science and technology of short fibre reinforced polymer composites. The low density, high strength, high stiffness to weight ratio, excellent durability and design flexibility are the primary reasons for their use in many diversified fields such as air crafts, automobiles, marine industry etc. Compared to the various natural and synthetic fibres used as reinforcement for elastomer composites isora fibre is superior in many aspects. 'Isora' is a natural lignocellulosic fibre which is easily available in South India especially in Kerala. The fibre is separated from the bark of the Helicteres isora plant by retting process. This fibre has excellent mechanical properties and is easily amenable to physical and chemical modifications.

A literature survey on short fibre polymer composites, a brief discussion on the classification of composites, advantages and disadvantages of natural fibres, factors influencing the performance of short fibre elastomer composites are outlined in ***Chapter 1.*** The various experimental techniques used in the investigation are briefly discussed in ***Chapter 2.***

Studies on chemical composition, surface modifications, morphology, mechanical and thermal properties are explained in ***Chapter 3.*** The major constituent of the fibre is found to be cellulose. The lignin content is comparatively low. Chemical modifications by alkali, silane and gamma irradiation can be carried out on the fibre to improve the hydrophobicity, thermal stability and reinforcing ability of the fibre. Morphological studies revealed that fibre surfaces are modified by chemical treatment. Fine structural changes of the fibre could be seen from the respective scanning electron and atomic force micographs respectively. Thermal stability and degradation characteristics of the fibres were investigated by thermgravimetry and differential thermal analysis. It is found that alkali and silane treatments improve the thermal stability of the fibres. Fibres are stable upto 300°C without any considerable weight loss. Chemical treatment marginally decresed the tensile strength but enhanced the young's modulus of the fibre. Microfibrillar angle and strength of the fibre were theoritcally evaluated. The theoretical strength (525 MPa) is found to be close with the experimentall value (560 MPa). The properties of isora fibre are found to be comparable to other natural fibres and hence it may have a great potential as reinforcing agent for polymer matrices.

The mechanical and processing behviour of the unmodified and chemically modified short isora fibre reinforced natural rubber composites have been studied and are outlined in ***Chapter 4.*** The mechanical properties of the composites have been analysed as a function of fibre length, fibre orientation, and fibre concentration. A fibre length of 10mm is found to be optimum for best balance of properties. Compsites containing longitudinally oriented fibres show superior mechanical performance than that of transverse orientation. The addition of short fibres upto 30 phr loading to natural rubber offers good reinforcement and causes improvement in mechanical properties. The adhesion between fibre and rubber can be enhanced by chemical treatment and by the use of a tricomponent bonding system [RF rein-Hexa-Silica]. The improvement in the interfacial interaction between the fibre and rubber can be confirmed by SEM studies. From green strength measurements, the extent of fibre orientation was analysed and found that the mix containing about 25 to 30 phr of fibre has better fibre orientation due to the better dispersion of fibres during mixing. The effect of different chemical treatments on the tensile properties of the composites was investigated. Alkali and silane treated fibre composites showed better tensile properties compared to untreated fibre composites due to their rough surface topography and increased aspect ratio. SEM photographs also support the strong fibre- matrix adhesion in isora/NR composites. The effect of low temperature curing by ZDC/Xanthate system on the mechanical performance has also been investigated. Low temperature curing system can be advantageously used in these composites since at high temperature fibre and matrix show a tendency to degrade.

Chapter 5 gives a detailed description about the degradation behaviour of short isora fibre reinforced natural rubber composites due to thermal, ozone and radiation ageing. On thermal ageing, the percentage retention of tensile and tear strength of the composites increases progressively with fibre loading for both modified and unmodified systems. Ozone resistance of the composites increases with increase in fibre loading especially in presence of bonding agent. The longitudinally oriented fibre composites offer better resistance to ozone attack. The treated fibre composites offer good resistance to crack propagation than the untreated composites. On exposure to gamma radiations the retention in tensile properties gradually increases with increase in fibre loading up to a loading of 30% fibre and there after remains almost constant for systems with and without bonding agent. On prolonged irradiation (15Mrad) polymer degradation takes place at low fibre loadings but at higher fibre loading retention in tensile properties are slightly improved.

The restricted equilibrium swelling behaviour of short isora fibre reinforced natural rubber composites in organic solvents has been analysed in order to evaluate the interfacial bonding and is dealt with in ***Chapter 6***. The results are reported with special reference to the effect of fibre loading, chemical treatment and bonding agent. The restriction to swelling of natural rubber composites by short isora fibres as well as anisotropy of swelling of the composites is evident from the results of this study. The resistance to swelling is progressively increases with volume loading of fibres.

Chemicl treatment and use of bonding agent further enhances the resistance. In well bonded composites swelling take place mainly in the thickness direction due to the capillary action of the fibres and by presence of voids at the interface of the composite. SEM and optical studies also support the effect of interfacial adhesion on improving resistance to swelling. Swelling parameters like swelling index and swelling coiefficient were evaluated in order to study the effect of isora fibres on the swelling behaviour of the rubber composites in fuels like petrol, diesel, and lubricating oil etc,.

The dynamic mechanical properties of short isora fibre reinforced natural rubber composites are reported in **Chapter 7.** These properties were studied with special reference to the effect of fibre loading, orientation, chemical treatment and bonding agent as a function of temperature. It is observed that storage modulus, loss modulus and loss factor are greatly influenced by the incorporation of fibres. The study shows that composites with poor interfacial bonding tend to dissipate more energy than that with good interfacial bonding. The mechanical loss also can be related to interfacial bonding. The effect of chemical treatment of isora fibre on damping was also studied. It is observed that composites with silane treated fibres exhibit some what lower tan δ_{max} both in the low and high temperature region which indicates that this composite posseses low damping and hence good interfacial bonding characteristics. Untreated fibre composites exhibit high tan δ_{max} both at high and low temperature region. Hence these composites are better candidates for high damping applications. Composites with longitudinally oriented fibres showed high storage modulus than transversely oriented ones due to the effective stress transfer between fibre and matrix.

B. FUTURE OUT LOOK

i. Analysis to study the eco friendly nature of the composites.

It is known that petroleum based polymers cause harm to our environment due to the lack of biodegradability. One method to overcome this hazard is to use biodegradable polymers such as poly (a hydroxy lactic acid, poly (ß hydroxyl alkonates) etc. but these polymers are not widely because are expensive and have inferior mechanical properties. Both the constituents of the composite developed in the study are of natural orgin and hence the composite is likely to be biodegradable. A comprehensive idea about the biodegradability can be obtained only from a systematic study. Hence the biodegradation characteristics of these composites have to be analysed.

iii. Preparation of isora microfibril composites.

Another potential research area is the development of advanced composite based on natural rubber by extracting microfibrils from isora fibre. Hence separation of micro fibrils by a novel enzymatic method has to be done and characterized before the preparation of composites.

iv. Other polymer composites

Isora, being identified as a very useful natural fibre can be tried with other thermoplastic and thermoset matrices for developing value added engineering composites. Based on the specific utility the best composite can be chosen. Properties of isora fibre composites could be improved by hybridizing with synthetic fibres like glass, nylon etc. To explore the possibility of manufacturing high strength materials, maximum reinforcing action of the fibre should be achieved.

ii. Product manufacturing and testing.

Isora fibre reinforced natural rubber composites can be advantageously used in many engineering products such as V belts, oil seals, gaskets etc. Preparation of tyical products and the evaluation of their performance is another future area of work resulting from this study.

LIST OF ABBREVIATIONS

A	*Area of cross section*
ASTM	*American standards and testing methods manual*
AFM	*Atomic Force microscopy*
CBS	*N-cyclohexyl-2-benzothiazyl sulphenamide*
DMA	*Dynamic mechanical analysis*
DSC	*Differential scanning calorimetry*
DTA	*Differential thermal analysis*
E'	*Storage modulus*
E"	*Loss modulus*
EB	*Elongation at break*
FTIR	*Fourier transform infrared*
FRC	*Fibre reinforced composite*
GS	*Green strength*
Gum	*Rubber compound without fibre/filler*
hrs	*Hours*
Hexa	*Hexa methylene tetramine*
Hz	*Hertz*
HRH	*Hydrated silica-resorcinol-hexa*
I_c	*Crystallinty* index
ISNR	*Indian Standard Natural Rubber*
ICP-AES	*Integrated coupled plasma -Atomic emission spectrometer*
L	*Longitudinal*
min	*Minutes*
mol	*Mole*
M_H	*Maximum torque*

M_L	*Minimum torque*
MPa	*Mega Pascal*
NaOH	*Sodium hydroxide*
NR	*Natural rubber*
O	*Orientation*
phr	*Parts per hundred rubber*
PF	*Phenol formaldehyde resin*
Q_t	*Mole% uptake*
RF	*Resorcinol formaldehyde resin*
SEM	*Scanning Electron Microscope*
T	*Transverse*
TDQ	*Polymerized 2,2,4-trimethyl-1,2-diydroxy quinoline*
t_{90}	*Optimum cure time*
t_{10}	*Scorch time*
$\tan \delta$	*Loss factor*
T_g	*Glass transition temperature*
TMTD	*Tetramethyl thiuram disulphide*
TGA	*Thermo gravimetric analysis*
UTM	*Universal testing machine*
V_f	*Volume fraction of rubber in swollen sample*
V_i	*Volume fraction of rubber in unswollen sample*
V_τ	*Change in volume fraction of rubber due to swelling*
WAXRD	*Wide angle X ray diffractometer*

SCIENTIFIC PUBLICATIONS

A. International/National journals

1. *Isora fibre and its composites with natural rubber: Progresses in Rubber Plastics and Recycling Technology* **(2004); 20(4): 337**
2. *Isora fibre- a potential natural reinforcement for ecofriendly composites: Advances in Eco materials Stallion press, Singapore,* **(2005); 2: 44.**
3. *Effect of gamma radiations on the mechanical, chemical and morphological properties of isora fibre: Indian Journal of multidisciplinary research* **(2005); 1(2): 213**
4. *Swelling behaviour of short isora fibre reinforced natural rubber composites in oils used in Automobiles: Bulletin of Materials Science* **(2006); 29: 91**
5. *Isora fibre: Morphology, Chemical composition, Surface modification, Mechanical and Thermal properties Journal of Natural fibres* **(2006); 3(4): 110.**
6. *Low temperature curing studies of short isora fibre reinforced natural rubber Composites: Journal of Rubber Research,***(2006); 9(1):21**
7. *Effect of curing temperature, fibre loading and bonding agent on the swelling behaviour of short isora fibre reinforced natural rubber composites: Composite interfaces,* **(2006) ;13 (4-6): 391**
8. *Studies on short isora fibre reinforced polyester composites: Composite interfaces* **(2006) ;13 (4-6): 377**
9. *Mechanical properties of short isora fibre reinforced natural rubber Composites, Journal of Applied Polymer Science (in press)*

10. *Ageing behaviour of short isora fibre reinforced natural rubber composites: gamma irradiation, ozone and thermal ageing: Journal of Natural fibres (in press)*
11. *Short isora fibre reinforced natural rubber composites: Rubber, Plastics and Composites (Communicated)*
12. *Dynamic Mechanical Analysis of short isora fibre reinforced natural rubber Composites: Composite Science and Technology (Communicated)*

B. International/National Conference papers

1. *."Cure characteristics and mechanical properties of short isora fibre reinforced natural rubber composites" presented at the International Conference APT 2002 Jointly organized by Eindhovan University, Netherlands, and Department of Polymer Science and Rubber Technology, Cochin University held at Ernakulam on December 2002*
2. *"Effect of different chemical treatments on the fibre properties and on the mechanical performance of short isora fibre reinforced natural rubber composites" presented at the National conference organized by the Material Research Society of India held at BARC, Bombay on February 9-11, 2003*
3. *"Effect of high energy radiations, ozone, and heat on the degradation behavior of short isora fibre reinforced natural rubber composites" Presented at the International Conference ECO COMP 2003 held at Queen Mary, University of London on September 1-3, 2003.*
4. *"Effect of different bonding / coupling agents on the mechanical properties of short isora fibre reinforced natural rubber composites" Presented at the International Conference APT 2004 jointly organized by*

Eindhovan University, The Netherlands, and Department of Polymer Science and Rubber Technology, Cochin University held at Cochin University on January 15-16, 2004

5. *"Effect of Interfacial adhesion on the swelling behavior of short isora fibre reinforced natural rubber composites" Presented at the national conference organized by the Material Research Society of India held at Banaras Hindu University, Varanasi on February 10-12, 2004.*

6. *"Effect of low temperature curing of short isora fibre reinforced natural rubber composites" Presented at the International Conference MACRO 2004 organized by SPSI held at Trivandrum on December 15-17, 2004.*

7. *"Effect of Curing temperature and fibre loading on the swelling behavior of NR/ ISORA composites in oils used in automobiles" Presented at the National conference organized by the Material Research Society of India held at National Chemical Laboratory, Pune on February 10-12, 2005*

8. *"Effect of Curing temperature and fibre loading on the equilibrium swelling of NR/ ISORA composites" Presented at the international conference organized by the School of chemical sciences of M.G University Kottayam on March 21- 23, 2005*

9. *"Effect of alkali treatment on the mechanical properties of short isora fibre reinforced polyester composites" Presented at the international conference organized by the School of chemical sciences of M.G University Kottayam on March 21-23, 2005*

10. *"Isora fibres; an effective reinforcement for eco friendly composite materials" Presented at the 'ICMAT 2005' conference held at Suntec international convention and exhibition centre Singapore organized by Material Research Society Singapore on July 3-8, 2005*

11. *"Studies on mechanical properties of unidirectional isora fibre reinforced* *polyester composites " Presented at the 17th Kerala Science congress held at Trivandrum from January 29-31, 2006*

12. *"Dynamic mechanical properties of short isora fibre reinforced natural rubber composites" Presented at the 'Polymer 2006' National conference held at IACS, Kolkatta, Jointly organized by SPSI Kolkatta Chapter and IACS on February 10-13, 2006*

13. *"Effect of Gamma radiation on isora fibre and fibre reinforced natural rubber composites " Presented at the National conference organized by the Material Research Society of India held at CMS Conventional centre, Lucknow on February 13-15, 2006*

14. *"Studies on mechanical properties of unidirectional isora fibre reinforced epoxy resin composites" Presented at the National conference organized by the Material Research Society of India held at CMS Conventional centre, Lucknow on February 13-15, 2006*

15. *"Mechanical properties of unidirectional isora fibre reinforced polyester and epoxy composites" Presented at the 'Polymer 2006' National conference held at IACS Calcutta jointly organized by SPSI Kolkatta chapter and IACS on February 10-13, 2006*

16. *Natural fibres for product design and development of engineering materials Presented at the National conference on 'Women scientists/technocrats –challenges and opportunities' held at Ernakulam organized by Shakti a National movement for women on June 23-25, 2006.*