ISORA FIBRE REINFORCED POLYESTER AND EPOXY COMPOSITES

Thesis submitted to the

Cochin University of Science and Technology

in partial fulfilment of the requirements

for the award of the degree of

DOCTOR OF PHILOSOPHY

under the

Faculty of Technology

by

JOSHY M. K.

DEPARTMENT OF POLYMER SCIENCE AND RUBBER TECHNOLOGY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022, INDIA.

October 2007

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

Dr. Rani Joseph
Professor

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

CERTIFICATE

This is to certify that the thesis entitled **"Isora Fibre Reinforced Polyester and Epoxy Composites"** which is being submitted by Mr. Joshy M. K., in partial fulfilment 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 him under my guidance and supervision, in the Department of Polymer Science and Rubber Technology, Kochi-682 022, and no part of the work reported in the thesis has been presented for the award of any degree from any other institution.

Rani Joseph

Dr. RANI JOSEPH
(Supervising Teacher)

Kochi-22
15th October 2007

DECLARATION

I hereby declare that the work presented in this thesis entitled **"Isora Fibre Reinforced Polyester and Epoxy Composites"** is based on the original research work carried out by me under the guidance and supervision of **Dr. Rani Joseph,** Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi-682 022 and no part of the work reported in this thesis has been presented for the award of any degree from any other institution.

Kochi-22
15th October 2007

Joshy M. K.

ACKNOWLEDGEMENT

I gratefully acknowledge my deep sense of gratitude to my supervising teacher Prof. Dr. Rani Joseph, Department of Polymer Science and Rubber Technology, CUSAT, for her inspiration, guidance and constant encouragement throughout this research work.

I am greatly indebted to Dr. C. Pavithran, Scientist/Deputy Director, RRL, Thiruvananthapuram, for his valuable suggestions and advice, gave me a turning point in my research work.

I wish to express my sincere gratitude to Prof. K. E. George, former Head of the Department, for his valuable help and guidance during the period of my research work. I sincerely acknowledge the valuable suggestions and encouragement rendered by Dr. Eby Thomas Thachil of the Department. I am extremely thankful to Dr. Thomas Kurian, Head of the Department, for his support and the keen interest he has shown in my research and for allowing me to freely avail the facilities of the Department. I am also happy to express my whole-hearted thanks to other faculty members of the Department, Dr. Philip Kurian and Dr. Sunil Narayanankutty for their advice and cooperation during my research work.

I remain very much indebted to Dr. Lovely Mathew, Newman College, Thodupuzha, for her constant encouragement, help and guidance throughout my work and I sincerely acknowledge it.

I am extremely thankful to Prof. Sabu Thomas, School of Chemical Sciences Kottayam, for his support during my research.

I gratefully acknowledge the valuable help extended to me by Dr. Thomas N. Abraham during the initial stages of my research work. I am very much thankful to Mr. Bipinbal for his selfless help during the course of my work. I also sincerely acknowledge the help and advice from Dr. Benny Cherian and Dr. K. P. Unnikrishnan, U. C. College Aluva.

Let me take this opportunity to thank my dear FIP colleagues, Sreenivasn P. V., Raju P, Jude Martin Mendez, Maya K. S., Bhuvaneswary M. G., Prema, Parameswaran, Suma and Mary Alexander, who made my research tenure, a pleasant and memorable experience.

I extend my deep gratitude to the young research scholars of the Department, Sinto, Ansu Jacob, Saritha, Dhanya, Vijayalakshmi, Abhilash, Priya, Sreekanth and Rajesh, for their co-operation and help.

I am also thankful to Dr. Anoop Anand, Dr. Ushamani, Dr. Honey, Dr. Soney, Miss Lity Alen, Dr. Nisha and Dr. M.S. Sreekala for their advice and help.

I earnestly thank Mr. Gurulinga, IISc. Bangalore for his support in analytical studies and Mr. Jiju, Sree Chitra Tirunal Institute for Medical Sciences, Thiruvananthapuram for his help in conducting impact tests.

I should also mention with gatitude the help extended by the Libraian and staff members of IISc. Bangalore, Mahatma Gandhi University, Kottayam and my home Institution, Cochin University of Science and Technology.

The help rendered by the technical and administrative staff of CUSAT is thankfully acknowledged.

I thank Mr. M. K. Preman, Poochinnipadam and Mr. Ajayan, Mak Tools, Ernakulam for their help in making moulds.

The help received from Sri. P. Rishikumar, SNM College, Maliankara is also sincerely acknowledged. I gratefully remember the help received from Mr. Binoop M.R, Indu Photos, in the page setting and the cover designing of the thesis.

I take this opportunity to acknowledge with thanks the help and support received from the Management, Principal and colleagues of SNM College, Maliankara.

The financial support in the form of Teacher fellowship from UGC is also gratefully acknowledged.

I bow my head with respect and honour before my beloved teacher Dr. M. M. Chandy who was the Head of the Department of Chemistry, Christ College Irinjalakuda, during my college days and who inspired me as a teacher and instilled research interest in me.

I thank my parents, all other family members, friends and relatives for their help, concern and prayers.

The help rendered by Sri. E. K. Balan, Vettilapara in procuring Isora fibre and Sri. Thumbarathy Koru, to ret the fibres, is gratefully acknowledged.

I owe a lot to my wife Linda and my beloved children Akhil and Ankita for the love, consideration and patience they have shown at all times.

Above all, I thank God Almighty who showered on me all His blessings.

Joshy M. K.

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PREFACE

Isora is a lignocellulosic fibre separated from the bark of Helicteres isora plant. It is an effective reinforcement material for natural rubber. The aim of this investigation is to study the effectiveness of isora fibre as reinforcement material in short and long forms, for unsaturated polyester and epoxy resins.

A review on the recent developments on natural fibres and natural fibre reinforced composites is given in Chapter 1. The materials and various experimental techniques used in the investigation are briefly discussed in Chapter 2. Studies on the optimization of fibre length and fibre loading of randomly oriented isora-polyester composite are described in Chapter 3. The salient features of the alkali treatment of short isora fibre on the properties of randomly oriented isora-polyester composite are outlined in Chapter 4. The effect of surface modification of the hydrophilic isora fibre by different chemical treatments on the properties of randomly oriented isora-polyester composite is outlined in Chapter 5. The properties of oriented long isora fibre reinforced polyester composites are presented in Chapter 6. The properties of oriented and randomly oriented isora fibre reinforced epoxy composites with special reference to the effect of fibre loading are reported in Chapter 7. The dynamic mechanical properties of the oriented and randomly oriented isora-polyester and isora-epoxy composites are presented in Chapter 8. In Chapter 9 the water absorption kinetics of oriented and randomly oriented isora-polyester composites and oriented isora-epoxy composites are given. The effect of hot air oven aging on the tensile and flexural properties of oriented isora-polyester and isora-epoxy composites are also reported in this chapter. Finally the thesis concludes by giving the summary of the results obtained in the present work and an outline of the future prospects in this topic.

Chapter 1

INTRODUCTION

1.1. General Introduction

In recent years, composites made of natural fibres have received increasing attention in light of the growing environmental awareness. Also because of their low density, good mechanical performance, unlimited availability and problem-free disposal, natural fibres offer a real alternative to the technical reinforcing fibres presently available. Natural fibres can compete with glass fibres especially with respect to the specific strength and specific stiffness.

Composites were a need in the evolution of engineering materials because by a combination of materials it is possible to overcome, for instance, brittleness and poor processability of stiff and hard polymers. The developments in composite material after meeting the challenges of aerospace sector have cascaded down for catering to domestic and industrial applications. Composites, the wonder material with light weight, high strength-to-weight ratio and stiffness properties have come a long way in replacing the conventional materials like metals, wood etc. The material scientists all over the world focused their attention on natural composites reinforced with jute, sisal, coir, pineapple etc. primarily to cut down the cost of raw materials.

The relative importance of the structural materials most commonly used, ie. metals, polymers, composites, and ceramics, to various societies throughout history has fluctuated. Ashby presents a chronological variation of the relative importance of each group from 10,000 B.C. and extrapolates their importance through the year 2020. The information contained in Ashby's article has been partially reproduced in Figure 1.1. The importance of composites has experienced steady growth since about 1960 and is projected to continue to increase through the next several decades.

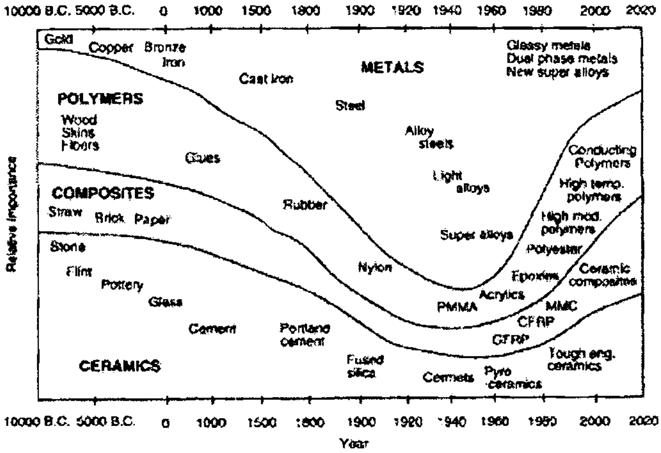


Figure 1.1. Relative importance of material development through history

[Ref: Ashby, M. F. Philosophical Transactions of the Royal Society of London, (1987) A322: 393-407.]

The fibre-reinforced plastics market is estimated at almost 1.04 million metric tonnes (2.3 billion lbs) in 2002, and is expected to increase by 15% in volume by 2007. These figures are forecast in a study released from Business Communications Co, Inc, *Composites: Resins, Fillers, Reinforcements, Natural Fibers and Nanocomposites* (report number RP-178). According to the report, the market for fibre-reinforced plastics will grow at an average annual growth rate (AAGR) of 3.0% through the next five years, increasing to 1.2 million tonnes per year by 2007.

A composite material is defined [1-2] as any substance which is made by physically combining two or more materials differing in composition or form to produce a multiphase material which possesses superior properties that are not obtainable with any of the constituent materials acting alone. These constituents remain bonded together but retain their identity and properties. The constituent that is continuous and is often but not always, present in the greater quantity in the composite is termed the *matrix* [3]. The second constituent is referred to as the *reinforcement,* as it enhances or reinforces the mechanical properties of the matrix. In principle, any isotropic material can be reinforced; the reinforcing material is usually stiffer, stronger or tougher than the matrix and there has to be a good adhesion between the components. At least one of the dimensions of the reinforcement is small, say less than 500μm and sometimes only of the order of a micron. The geometry of the reinforced phase is one of the major parameters in determining the effectiveness of the reinforcement. In other words, the mechanical properties of composites are function of the shape and dimensions of the reinforcement.

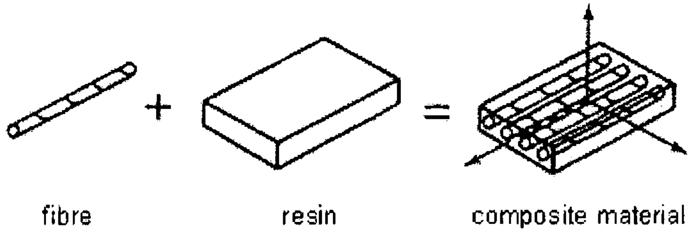


Figure 1.2. Formation of composite material

Although composite materials are widely perceived as being a modern development, composites have in fact been around for over 5000 years-since the construction of Babylon with bitumen reinforced with straw and horse hair. Indeed, composites can theoretically be called the oldest engineering concept, as nature has been exploiting them since the dawn of time. Modern and ancient applications all make use of the fact that composites can possess enhanced strength, stiffness and fracture toughness whilst not exhibiting an increase in weight.

Composites prepared from plastic materials with fibre reinforcement are called fibre-reinforced plastics (FRP). Fibres can be either discontinuous (chopped) or continuous. In FRP, the polymer or plastics possessing the properties like durability and easy modality is combined with reinforcements like synthetic or natural fibres having characteristics like light weight, non-corrosiveness, adequate strength, stiffness and load bearing capacities. The combination of these properties provides synergism to the composite making it more suitable for the desired end users. The unprecedented growth of FRP now-a- days is due to their great versatility and high performance [4,5].

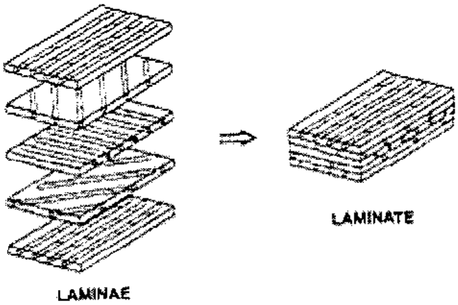


Figure 1.3. Tailored composite (Laminar)

In recent years, polymer composites containing vegetable fibres have received considerable attention both in the literature and industry. The interest in natural fibre reinforced polymer composites is growing rapidly due to the high performance in mechanical properties, significant processing advantages, low cost and low density. Natural fibres are renewable resources in many developing countries of the world; they are cheaper, pose no health hazards and finally, provide a solution to environmental pollution by finding new uses for waste materials. Furthermore, natural fibre reinforced polymer composites form a new class of materials, which seem to have good potential in the future as a substitute for scarce wood and wood based materials in structural applications. The structure, properties and applications of various composites have been investigated worldwide by several researchers [6-12]

1.2. Classification of Composites

Composites can be classified in different ways depending on

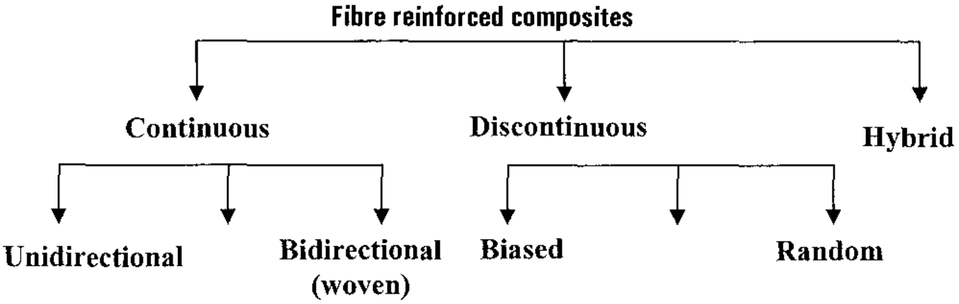
a. The size of the constituents-macro ($>10^{-6}$m), micro (10^{-8}-10^{-6}m) and nano (10^{-8}-10^{-9}m)

b. The occurrence of the composites-natural, synthetic

c. The form of their structural components- fibrous (composed of fibres in a matrix), laminar (composed of layers of materials-Fig. 1.3) and particulate (composed of particles in a matrix)

d. The matrix material- metal (MMC), ceramics (CMC), polymer (PMC)

Fibrous composite can be subdivided into - continuous fibre (large aspect ratio), discontinuous (short) fibre (low aspect ratio) and hybrid (combination of more than one type of fibre)



Schematic representation of fibrous composites is given in Figure 1.4.

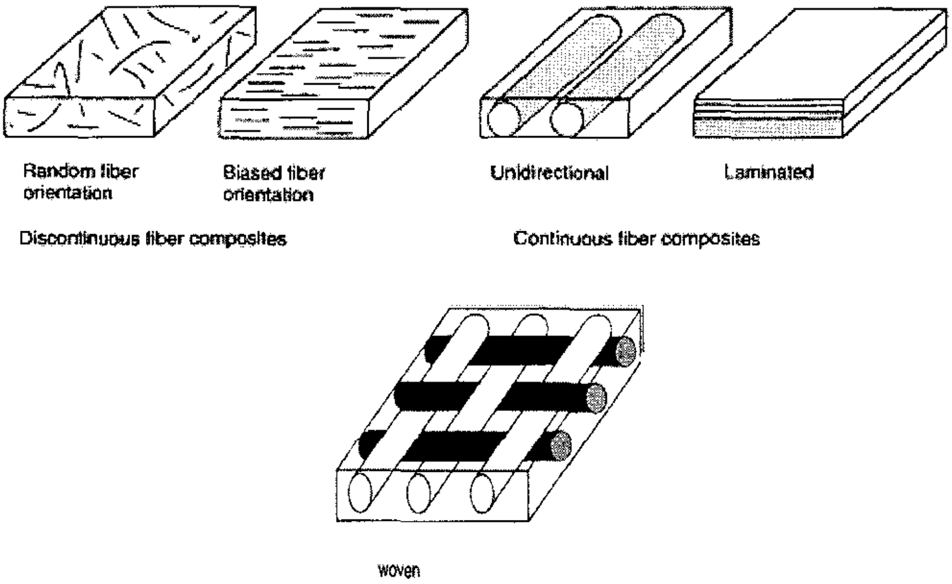


Figure 1.4. Schematic representation of fibrous composites.

The particulate class can be further sub divided into flake (flat flakes in a matrix) or skeletal (composed of a continuous skeletal matrix filled by a second material)

Composites in which the reinforcements are discontinuous fibres or whiskers can be produced so that the reinforcements have either random or biased orientation. Material systems composed of discontinuous reinforcements are considered single layer composites. The discontinuities can produce a material response that is anisotropic, but in many instances the random reinforcements produce nearly isotropic composites. Continuous fibre composites can be either single layer or multilayered. The single layer continuous fibre composites can be either unidirectional or woven, and multilayered composites are generally referred to as laminates. The material response of a continuous fibre composite is generally orthotropic. Schematics of both types of fibrous composites are shown in Figure 1.4.

A particulate composite is characterized as being composed of particles suspended in a matrix. Particles can have virtually any shape, size or configuration. There are two subclasses of particulates: flake and filled skeletal: A flake composite is generally composed of flakes with large ratios of platform area to thickness, suspended in a matrix material. A filled/skeletal composite is composed of a continuous skeletal matrix filled by a second material (Figure 1.5).

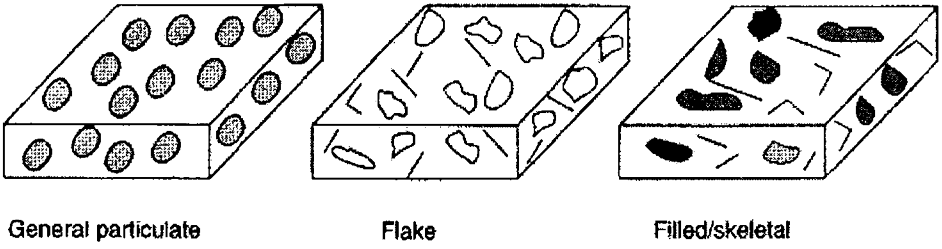


Figure 1.5. Schematic representation of particulate composites.

1.3. Role of matrix materials in composites

In a composite the matrix is required to fulfil the following functions:

- To bind together the fibres by virtue of its cohesive and adhesive characteristics
- To protect them from environments and handling.
- To disperse the fibres and maintain the desired fibre orientation and spacing.
- To transfer stresses to the fibres by adhesion and/or friction across the fibre-matrix interface when the composite is under load, and thus to avoid any catastrophic propagation of cracks and subsequent failure of the composites.
- To be chemically and thermally compatible with the reinforcing fibres.
- To be compatible with the manufacturing methods which are available to fabricate the desired composite components.

The matrices are of three types. They are:

1.3.1. Thermoset polymer matrices

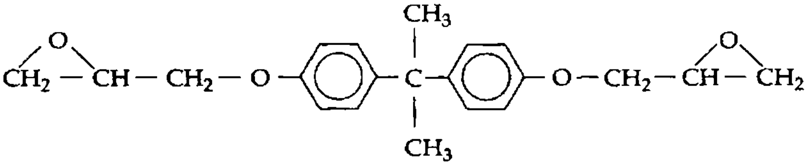
Thermosetting polymers or thermosets are resins which change irreversibly under the influence of heat into an infusible and insoluble material by the formation of covalently cross-linked, thermally stable networks. Such polymers are prepared in two stages. The first step is the formation of long chain molecules, which are capable of further reaction with each other. The second stage is the application of heat and / or the addition of curatives, which causes a reaction to occur between the chains, thus producing a complex cross-linked polymer. Sometimes irradiation is employed to achieve cross-linking [13]. Important thermosetting resins are unsaturated polyesters, epoxy resins, alkyds, vinyl esters and allyl resins, phenolics, amino plastics, urethanes, silicones, furfural etc. [14]

The thermosetting category is dominated by polyester resins which accounts for 88% of this category and 74% of all matrix resins. Epoxy resins (5% of the total) come next, followed by other phenolic resins (7% of the total). The popularity of polyester resins is due to their ease of handling, good curing properties and for the fact that they are the cheapest among all the thermoset resins.

The structure of epoxy resin and unsaturated polyester resin are given below.

1.3.1.1. Epoxy resins

Epoxy resins are characterized by the presence of more than one 1, 2- epoxide groups per molecule. It has the general structure shown below.

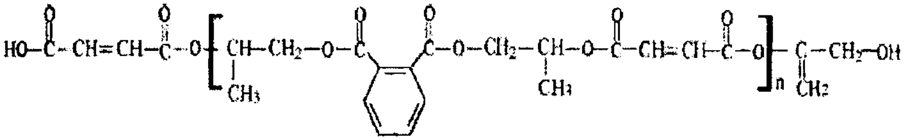


Cross-linking is achieved by introducing curatives that react with epoxy and hydroxyl groups situated on adjacent chains. Epoxy resins can be cured at room temperature but quite often heat is applied to accelerate and improve curing. Hardeners include anhydrides (acids), amines, polyamides, dicyandiamide etc. Where mechanical properties and temperature tolerance of unsaturated polyesters are no longer suffice, epoxies are often used due to their significant superiority in these respects. Significance of epoxies are low viscosity, low shrinkage and the fact that they adhere well to the reinforcement fibres make them a unique matrix. The major drawbacks of epoxies are high price, toxicity and complex processing requirements, which often include elevated temperature and consolidation pressure, thus translating into costly manufacturing operations.

1.3.1.2. Unsaturated Polyester resin (UPR)

A large number of thermoset resins are commercially available and these can be classified into alkyds, unsaturated polyesters, vinyl esters, allyl resins etc. It has been reported that USP represents about 70% of the total use while the other thermoset and thermoplastics evenly share the remaining part.

General-purpose (GP) grade USP is prepared by the condensation of propylene glycol with a mixture of maleic anhydride and phthalic anhydride. The condensate is then dissolved in an unsaturated co-reactant diluent, styrene to get a resin formulation. It has the following typical structure.



When cross-linking is initiated with the help of a catalyst and an accelerator, styrene facilitates cross-linking at the sites of unsaturation in the polyester chains. The saturated acid reduces the number of cross-linking sites and consequently the cross-link density and brittleness of the cured resin. Since cross-linking occurs via free radical addition mechanism across the double bonds in the polyester chain and the reactive diluent, no volatiles are given off during cure.

In addition to the above-mentioned thermosets, there are several other thermoset matrices used in composite applications. Some of them are: Polyurethanes, Aminoplasts, silicones etc.

1.3.2. Thermoplastic matrices

Thermoplastic matrices were developed to provide cheaper alternative to thermosets and to improve the upper use temperature of polymer matrix composites. Thermoplastics readily flow under stress at elevated temperatures, so allowing them to be fabricated into the required component, and become solid and retain their shape when cooled to room temperature [3]. These polymers may be repeatedly heated, fabricated and cooled and consequently scrap may be recycled. Unlike thermosets, thermoplastics are not cross-linked, and can therefore melt. They derive their strength and stiffness from the inherent properties of the monomer units and the very high molecular weight. They are semi crystalline or amorphous in nature. Thermoplastics have superior toughness to thermosets. Some of the thermoplastic polymers in common use are: Polyethylene (PE), Polypropylene (PP), Polyamides (PA), Poly(ethylene terephthalate) (PET), poly (butylene terephthalate) (PBT), poly (ether ketone) (PEK), poly (ether ether ketone) (PEEK), polysulphone (PSU), polyether sulphone (PES) and poly(arylsulphone) (PAS), poly (ether imide) (PEI) and poly (amide imide) (PAI), Poly(phenylene suphide) PPS.

1.3.3. Elastomers

These are macromolecular materials that return rapidly to their initial dimension and shape (approximately) at room temperature, after substantial deformation by a weak stress and subsequent release of the stress. Rubber is a versatile and adaptable material that has been successfully used as matrix for composite preparation. There are different types of rubbers including Natural rubber (NR) which is a high molecular weight polymer of isoprene in which essentially all the isoprenes have the cis 1-4 configuration and a variety of synthetic rubbers like Styrene butadiene rubber (SBR), Polybutadiene rubber (BR), nitrile-butadiene rubber (NBR), Ethylene propylene co polymer (EPM), Ethylene propylene diene monomers (EPDM), Poly isoprene rubber (IR), Butyl rubber (IIR) etc.

1.4. Reinforcements used in composites

The structural load applied to the composite is primarily carried by the reinforcement. Thus the strength and stiffness of the composite is mainly determined by the reinforcement. Composite reinforcement may be in the form of fibres, particles or whiskers. Particles have no preferred directions and are mainly a means to improve properties or lower the cost of isotropic material. The aspect ratio (length to diameter ratio) of the particles is of the order of unity and dimension that range from that of a fibre diameter to several millimeters. Whiskers have aspect ratios of order 1000 and diameter of order 0.1-1μm. Whiskers are pure single crystals manufactured through chemical vapour deposition and thus have preferred directions. Whiskers are more or less randomly arranged in the matrix, whisker reinforced composites are likely to be considered as macroscopically isotropic. Reinforcements are of two types- synthetic and natural.

1.4.1. Synthetic fibres

1.4.1.1. Glass fibres

Glass fibre is the best known reinforcement in high performance composite applications due to its appealing combination of good properties and low cost. The major ingredient of glass fibre is silica which is mixed with varying amounts of other oxides. The different types of glass fibres commercially available are E and S glass. The letter 'E' stands for 'electrical' as the composition has a high electrical resistance and 'S' stands for strength.

1.4.1.2. Carbon fibres

Carbon fibres are commercially manufactured from three different precursors-rayon, polyacrylonitrile (PAN) and petroleum pitch. They are mainly used in aerospace industry due to its outstanding mechanical properties combined with low weight.

1.4.1.3. Aramid fibres

'Aramid' is a generic term for aromatic polyamide fibres. eg. Kevlar.

1.4.1.4. Polyolefins

The most common example of high strength polyolefin fibre is ultra high molecular weight polyethylene (UHMWPE). The potential applications of polyolefin fibres include ballistic protection and sporting goods.

Table 1.1. Mechanical properties of some mineral and synthetic fibres

[Ref: Bledzki A. K.and Gassan J., Prog. Polym. Sci. (1999) 24: 221]

Fibre	Sp. Gravity	Tensile strength(GPa)	Young's 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
Aramid	1.40	3-3.15	6.3-6.7	3.3-3.7

1.4.2. 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. Jute, sisal, banana and coir, the major source of natural fibres, are grown in many parts of India. Some of them have aspect ratios >1000 and can be woven easily. Recent reports indicate that plant-based natural fibres can very well be used as reinforcement in polymer composites, replacing to some extent more expensive and non-renewable synthetic fibres such as glass.

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.

Natural fibres can be divided into three types- bast fibres, leaf fibres and seed hair fibres - based on their origin within the plant, as given below.

1.4.2.1. Bast fibres

Bast consists of a wood core surrounded by a stem. Within the stem, there are a number of fibre bundles, each containing individual fibre cells or filaments. The filaments are made of cellulose and hemicellulose, bonded together by a matrix, which can be lignin or pectin. The pectin surrounds the bundle thus holding them on to the stem. The pectin is removed during the retting process. This enables separation of the bundles from the rest of the stem (scutching). Stronger composites are obtained if the bundles are pre-treated in a way that removes the lignin between the cells. Boiling in alkali is one of the ways to separate cells. Bast fibres are usually grown in warm climates. eg. Bagasse, flax, hemp, jute, kenaf, ramie.

a) Bagasse

Bagasse is a by-product from the sugarcane industry and it consists of the sheath and pith of the cane stalks. It grows abundantly in tropical countries like Brazil, India, Pakistan, Indonesia, Philippines and Jamaica. Bagasse fibre reinforced composites have been used as materials for structural components.

b) Flax

This fibre is extracted from the plant *Linum usitatissimum L.* that is grown chiefly in the USSR, Poland, France, Belgium and Ireland. Flax is an annual plant with a slender, grayish green stem growing to a height of 90-120 cm. After deseeding, the straw is retted. i.e. the fibres are liberated through enzymatic action on pectinous binding material in the stem. The fibre is then hackled for alignment and final cleaning.

c) Hemp

The hemp fibre is extracted from the plant *Cannabis sativa.* The plant is grown for commercial production of fibre, mainly in China and Eastern Europe. The hemp plant is grown for fibre from the stem, for oil from the seeds or for drugs from the flowers or leaves. The retted and dried stem is further treated by either hand breaking and hackling to remove the woody stem portion by mechanical breaking

d) Jute

The jute fibre is obtained from two species of the annual herbaceous plant *Corchorus capsularis* of Indo-Burma origin and *C. olitorius* from Africa. The major jute production areas are India and Bangladesh. The plants are harvested by hand at an early seed stage using knives and the stems are left on the ground for several days to promote defoliation. The defoliated stems are bundled and taken for wet retting in canals, ditches or ponds for periods of 10-20 days.

e) Kenaf

The kenaf fibre is extracted from the plant *Hibiscus cannabinus.* The plant is native to Egypt and USSR. The plant is a herbaceous annual growing in single stem heights of 1-4 m. Kenaf is is often stem-retted followed by hand or mechanical stripping and washing.

f) Ramie

This fibre also known as China grass is produced from the stems of *Bochmeria nivea*, growing in regions varying from temperate to tropical including China, Brazil, Taiwan and Japan. The plant grows 1-2 m high or higher with stems 8-16 mm in diameter. The ramie fibre is contained in the bark and is usually extracted by hand stripping and scrapping. The plant is cut green and defoliated manually and bast ribbons are stripped from the woody stem.

1.4.2.2. Leaf fibres

In general, the leaf fibres are coarser than the bast fibres. eg. sisal, abaca, banana and henequen. Within the total production of leaf fibres, sisal is the most important which is obtained from the agave plant. The stiffness is relatively high and it is often applied as binder twines. The abaca fibre that is from the banana plant is durable and resistant to sea water.

a) Banana

Banana fibre is extracted from the plant *Musa sapientum*. Each of the stalks is 2.7-6.7 m tall with a trunk 10-20 cm wide at the base. The sheaths before expanding are 2-4 m long, 13-20 cm wide and about 10 mm thick at the centre. The fibres run lengthwise in the sheaths. The mature stalks are cut off at the roots and at a point just below where they begin to expand. The main countries of origin are India, Indonesia and Philippines.

b) Sisal

Sisal is extracted from the leaves of the plant *Agave sisalana* that is widely cultivated in the Western hemisphere, Africa and Asia. The agaves have rosettes of fleshy leaves, usually long and narrow, which grow out from a central bud. As the leaves mature, they gradually spread out horizontally and are 1-2 m long, 10-15 cm wide and about 6 mm thick at the centre. The fibres are embedded longitudinally in the leaves and are most abundant near the leaf surfaces. The fibre is removed when the leaves are cut because dry fibres adhere to the pulp. The fibre is removed by scraping away the pulpy material, generally by a mechanical decortication process.

c) Pineapple

The fibres are extracted from the leaves of the plant *Ananus cosomus* belonging to the Bromeliaceae family. The fibre is extracted by hand scraping after beating the leaves to break up the pulpy tissue or after a retting process that partially ferments and softens the leaves.

1.4.2.3. Seed fibres

Cotton is the most common seed fibre and is used for textile all over the world. Other seed fibres are applied in less demanding applications such as stuffing of upholstery. Coir is an exception to this and is used to make mats and ropes. Other examples are kapok and oil palm.

a) Coir

The fibre is contained in the husk of coconut tree *(Cocos nucifera)* Sri Lanka and India are important producers of coir. The extraction of the fibre involves retting of husks in water. The retted husks are beaten with sticks to remove extraneous matter and the dried fibre is suitable for spinning.

b) Oil palm

It belongs to the species *Elaeis guineensis* and is commonly found in the tropical forests of West Africa. Its major industrial cultivation is in the Southeast Asian countries such as Malaysia and Indonesia. Oil palm empty fruit bunch (OPEFB) fibre and oil palm mesocarp fibre are two important types of fibrous materials left in the palm-oil mill. OPEFB is obtained after the removal of oil seeds from fruit bunch for oil extraction. The fibres are extracted by retting followed by cleaning and drying.

1.5. Microstructure of natural cellulose fibres

All vegetable fibres predominantly contain cellulose, along with varying amounts of substances like hemicellulose, lignin, pectins and waxes. Cellulose resists alkalis 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 micro fibrils of 5 nm diameter; each composed of 30 to 100 cellulose molecules in extended chain conformation and provides mechanical strength to the fibre. A good orientation of micro fibrils 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 (Fig.1.6). 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.

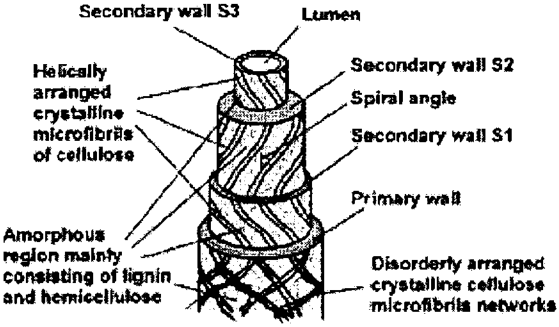
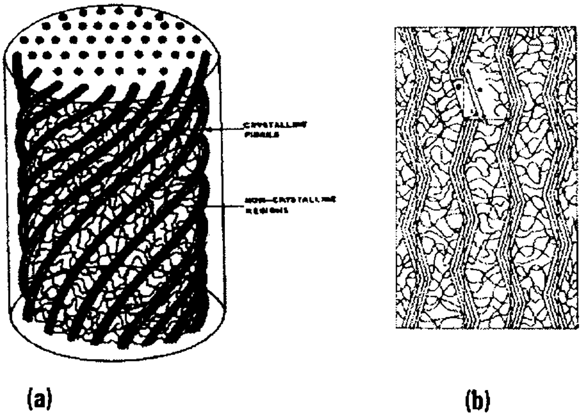


Figure 1.6. Structural constitution of natural vegetable fibre cell, in which the secondary wall S_2 makes up ~80% of the total thickness and then act as the main load bearing component

[Ref: Xun Lu, Comp. Sci. and Technol. (2003) 63: 177-186]

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.



(a) (b)

Fig. 1.7. Model for the description of the stiffness of the fibre

(a) layers in a 3D view, (b) layers in a 2D view

[Ref: Bledzki A. K.and Gassan J., Prog. Polym. Sci. (1999) 24: 221]

The spiral angle of the fibrils and the content of cellulose, determines generally the mechanical properties of the cellulose based natural fibres. The model for the description of the stiffness of the cellulose fibres developed by Hearle *et al.* [15] is shown in Figure.1.7. 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 1.2.

Table 1.2. Mechanical properties of some natural fibres

[Ref: Bledzki A. K.and Gassan J., Prog. Polym. Sci. (1999) 24: 221]

Fibre	Density (g/cm^3)	Elongation (%)	Tensile strength (MPa)	Young's Modulus (GPa)
Cotton	1.5-1.6	7.0-8.0	287-597	5.5-12.6
Jute	1.3	1.5-1.8	393-773	26.5
Flax	1.5	2.7-3.2	345-1035	27.6
Hemp	-	1.6	690	-
Ramie	-	3.6-3.8	400-938	61.4-128
Sisal	1.5	2.0-2.5	511-635	9.4-22.0
Coir	1.2	30.0	175	4.0-6.0
Viscose (cord)	-	11.4	593	11.0
Softwood kraft	1.5	-	1000	40
Oil Palm OPEFB[a]	1.4	14	248	2
Mesocarp[b] fibre	-	17	80	0.5

a-obtained from fruit bunch after removal of oil seeds

b- obtained from oil seeds after oil extraction

1.6. 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. With the exception of cotton, the components of natural fibres are cellulose, hemicellulose, lignin, pectin, waxes and water soluble substances. Cellulose, hemicellulose and lignin are the basic components responsible for the physical properties of the fibres.

a) Cellulose

Cellulose is a linear condensation polymer consisting of D-anhydro glucopyranose units joined together by β-1,4-glycosidic bonds. The structure of cellulose is given in figure 1.8.

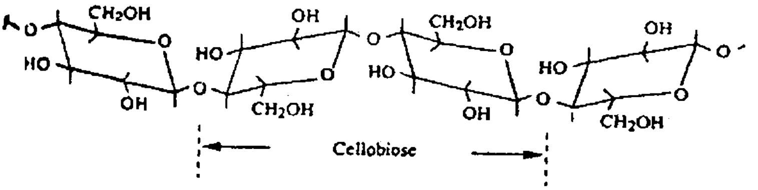


Figure 1.8. Structure of cellulose

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.

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 [17] while they have anti parallel configuration [18] in cellulose-II.

b) Hemicellulose

Hemicellulose consists of a group of polysaccharides that remain associated with the cellulose after lignin has been removed. The hemi cellulose differs from cellulose in that they contain several sugar units whereas cellulose contains only glucopyranose units. Hemi cellulose 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 hemi cellulose. Unlike cellulose, the constituents of hemicellulose differs from plant to plant [19].

c) Lignin

Lignins are complex hydrocarbon with aliphatic and aromatic components. The monomer units present in lignin are various ring substituted phenyl propanes linked together in ways which are still not fully understood and the detailed structure differ from source to source. The mechanical properties are lower than those of cellulose [20].

d) Pectin

Pectin is a collective name for hetero polysaccharides which consists essentially of polygalacturon acid and is soluble in water only after partial neutralization with alkali or ammonium hydroxide [12].

e) Waxes

Waxes make up the part of the fibres, which can be extracted with organic solvents and consists of different types of alcohols which are insoluble in water as well as in acids.

Table1.3. Composition of different cellulose based natural fibres

[Ref: Wright J.R., Mathias L.J., J Appl Polym Sci, (1993) 48: 2241]

	Cotton	**Jute**	**Flax**	**Ramie**	**Sisal**
Cellulose	82.7	64.4	64.1	68.6	65.8
Hemi-cellulose	5.7	12.0	16.7	13.1	12.0
Pectin	5.7	0.2	1.8	1.9	0.8
Lignin	-	11.8	2.0	0.6	9.9
Water Soluble	1.0	1.1	3.9	5.5	1.2
Wax	0.6	0.5	1.5	0.3	0.3
Water	10.0	10.0	10.0	10.0	10.0

1.7. 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. Nowadays 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 [21]. The vegetable fibres 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 gives good opportunities for the effective utilization of agricultural products. Physical, chemical and mechanical properties of some important natural fibres are given in Table 1.2. 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 [22]. Investigations have been carried out by Hedenberg and Gatenholm in recycling the plastic and cellulose waste into composite [23]. Systematic investigations on wood flour reinforced polystyrene composites have been carried out by Maldas and Kokta [24]. 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 [25]. 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 [26]. Yamini *et al.* [27] investigated the effect of board density on the properties of particle board from oil palm fibre and urea formaldehyde resin.

In recent years, considerable interest has been shown in the potential of bast fibres such as flax and hemp to act as reinforcement in polymer matrix composites (PMCs). Interest in natural fibre reinforced PMCs has been driven by a number of factors including cost, environmental issues and the wish to diversify agricultural practice. This has led to some limited commercialisation of natural fibre reinforced PMCs, most notably in the automotive sector [1].

Nevertheless, uptake in other areas has been minimal, but despite this, there is good potential for bast fibre reinforced composites in many sectors ranging from consumer goods to construction. There are a number of reasons why there has been so little commercial attention paid to these composites, outside the automotive sector, but perhaps the most significant is that the performance of current materials is simply inadequate for most structural applications. Increasing the performance of these materials is therefore essential, if they are to gain widespread acceptance.

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.

1.8. Major drawbacks of Natural fibres

1.8.1. 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. Bio fibres 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 [28]. The hemicelluloses are mainly responsible for moisture absorption. Water penetration through natural fibres can be explained by capillary action [29]. 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, hemi cellulose 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 [30]. The schematic representation of swelling process in cellulose is given in figure 1.9.

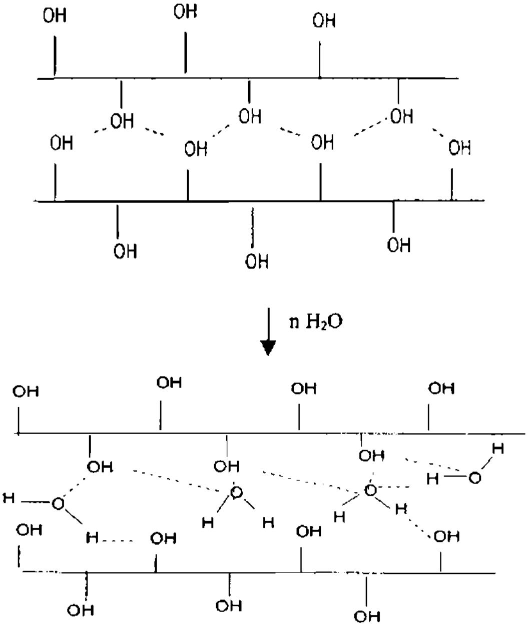


Fig. 1.9. Schematic representation of water absorption of cellulosic fibres

[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.

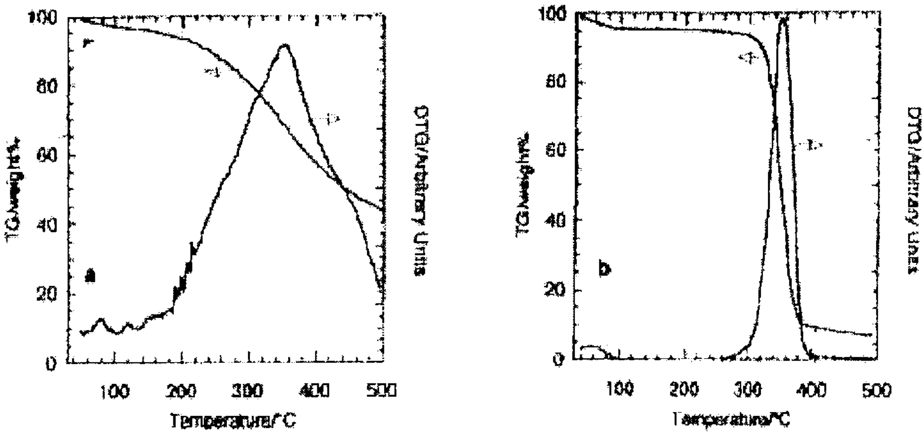
1.8.2. Thermal stability of natural fibres

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, hemi cellulose 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 [31].

Lignin, specifically the low molecular weight protolignin, degrades first and at a slower rate than the other constituents. This is shown in Figure 1.10(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, as shown in Figure 1.10(b).

This process has been described by Shurky and Girgis [32] who also presented an analysis of the products of degradation. From Figure 1.10(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 [33] 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 [34, 35]. 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.



(a) (b)

Fig. 1.10. 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]

Gassan and Bledzki [36] 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 scissions, 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 [37-42]. 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 [43, 44].

1.8.3. 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 [45]. Lignocellulosics 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 [46]. The surface becomes richer in cellulose content as the lignin degrades. In comparison to lignin, cellulose is much less susceptible to ultraviolet degradation.

1.9. Fibre reinforced composites

Fibre reinforced composites consist of fibres of high strength and modulus embedded in a matrix with distinct interfaces between them. Fibre reinforcement improves the stiffness and the strength of the matrix. In the case of polymers that are not tough in the non-reinforced form, the toughness may also increase [47]. The fibre reinforced composites exhibit anisotropy in properties. The maximum improvement in properties is obtained with continuous fibre reinforcement. However, short fibre reinforced composites offer many advantages like ease of fabrication, low production cost and possibility of making complex shaped articles, over continuous fibre reinforcement. The performance of the composite is controlled by the fibres and depends on factors like aspect ratio, orientation of fibres and fibre-matrix adhesion. Discontinuous fibre reinforced composite form an important category of materials used in engineering applications. The use of fibre reinforced plastics (FRP) composites for the production of rebars and pre stressing tendons in civil engineering and transportation applications are becoming increasingly important in recent years [48].

Major constituents in a fibre reinforced composite material are the reinforcing fibres and a matrix, which act as a binder for the fibres. Coupling agents and coatings used to improve the wettability of the fibre with the matrix and fillers used to reduce the cost and improve the dimensional stability are the other commonly found constituents in a composite.

1.10. Factors influencing the properties of fibre reinforced composites

1.10.1. Strength, modulus and chemical stability of fibre and matrix

In fibre reinforced composites fibres are the main load carrying members and the matrix keeps them in the desired orientation and location. The final properties of fibre-reinforced composite depend on the strength and modulus of the reinforcing fibre [49-51]. Choice of the matrix depends on the final requirements of the product and other factors like cost, fabrication process, environmental conditions and chemical resistance of the matrix. The function of the matrix will vary depending on how the composite is stressed [52]. For compressive loading, the matrix prevents the fibres from buckling and provides a stress transfer medium, so that when an individual fibre breaks, it does not lose its load carrying capacity. The physical properties of the matrix that influence the behaviour of the composites are shrinkage during cure, modulus of elasticity, ultimate elongation, tensile and flexural strength and compression and fracture toughness.

1.10.2. Fibre length, loading and orientation

Fibre length, loading and orientation play important roles in determining the ultimate properties of the fibre reinforced composites. There are several studies on the effect of fibre length and fibre orientation on the tensile strength of the short fibre composites [53]. In the case of short fibre reinforced composites, there exists a critical aspect ratio at which the properties are maximised. The critical aspect ratio depends on the volume fraction of the fibre and also on the ratio of the modulus of the fibre and matrix [54]. At low volume fraction, the fibres play no major role and the strength of the composite is matrix dominated. Above a critical volume fraction of the fibre, the strength of the composite increases. The critical volume fraction depends on the fibre aspect ratio and found to decrease with increase in aspect ratio. At low fibre content, the critical aspect ratio remains almost constant and show sharp decrease at higher volume fraction. The critical aspect ratio is given by the equation

$$\left(\frac{L}{D}\right)_C = \frac{\sigma_f}{2\tau_i}$$

where,

L - length of fibre

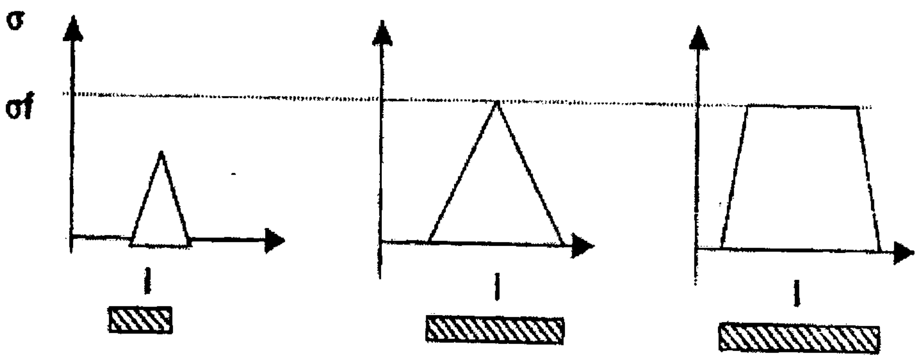
D - diameter of fibre

$(L/D)_c$ - critical aspect ratio

σ_f - tensile strength of fibre

τ_i - fibre-matrix interfacial shear strength.

A critical fibre length may be defined as the minimum fibre length at which the maximum allowable fibre stress can be achieved. Fig. 1.11 shows the variation of fibre stress along the fibre length in a fibre-matrix composite.



$l < (l/d)_c$ $l = (l/d)_c$ $l > (l/d)_c$

Fig. 1.11. Variations in fibre stress at a fibre/matrix interface along the fibre length

The increase in fibre length above critical fibre length does not contribute to the increase in composite strength. However a decrease in fibre length below the critical fibre length results in a decrease in composite strength. When all the fibres are below critical length, the fibre act only as filler and the strength of the composite decreases. As the critical aspect ratio depends on the efficiency of stress transfer from the matrix to fibre the critical aspect ratio decreases with improvement in fibre-matrix adhesion.

In the case of fibre reinforced composites there is an optimum spacing between the fibres at which the fibre tensile strength is fully exploited [55] and below which the structure starts to disintegrate under loading before the tensile failure. The spacing between the fibres is controlled by the volume fraction of the fibre and fibre dispersion in the composite.

Orientation of the fibre also affects the composite strength and other properties of the composites. The reinforcement provided by each individual fibre depends on the orientation with respect to the loading axis. Longitudinally oriented fibre composites in which the fibres are oriented in the direction of applied forces, the composites are inherently anisotropic, and the maximum stress and reinforcement are achieved in the direction of fibre orientation. In the case of transversely oriented fibre composite, fibre reinforcement is virtually absent and fracture occurs at a very low tensile stress, which is usually lower than the strength of the matrix. In the case of randomly oriented composites the strength lies between these two extremes.

Although the tensile strength of longitudinally oriented fibre composites are very high, the compressive strength shows lower values due to the buckling of the fibre [4, 56,]. In Table 1.4 the mechanical properties of unidirectionally aligned continuous fibre with polyester matrix are compared with randomly oriented short fibre composites.

Table1. 4. Mechanical properties of unidirectionally aligned continuous fibre with polyester matrix v/s randomly oriented short fibre composites

[Ref: C. Pavithran, M. Brahmakumar, K. G. Satyanarayana, K. Sukumaran, S. G. K. Pillai, K. K. Ravikumar, Metals, Materials and Processes, (2001) 13 (2-4)]

Fibre (wt%)	Tensile Strength MPa	Young's Modulus GPa	Flexural Strength MPa	Flexural Modulus GPa	Impact Strength KJm^{-2}
Unidirectional					
Sisal (40)	129	8.5	192	7.5	98*
Banana (30)	121	8.0	-	-	52*
Coir (30)	45	4	56	4	44*
Chopped random					
Sisal (25)	34.5	1.9	86.4	-	30
Banana (25)	43.5	2.3	92	-	10
Coir (25)	14.0	1.4	31.2	-	11
Fabric					
Banana-cotton	27.9-35.9**	3.3	50.6-64*	-	3.1-7.5**

* Impact Strength (Charpy) for $0.5V_f$

** Depending on type of fibre in the test direction.

1.10.3. Presence of voids

During the incorporation of fibres into the matrix or manufacture of laminates, air or other volatiles may be trapped in the material. The trapped air or volatiles exist in the cured laminates as micro voids and may significantly affect the mechanical properties of the composites. There are two types of voids in composite materials (a) voids formed along individual fibres and (b) voids formed between lamina and in resin-rich regions. Shrinkages during cure of the resin and the cooling rate play important role in void formation. A high void content (over 20% by volume) usually leads to lower fatigue resistance, greater susceptibility to water diffusion and increased scattering in mechanical properties. The volatiles produced during the curing cycle in thermosetting resins and during melt processing operation in thermoplastic polymers may also result in the production of voids.

1.10.4. Fibre-matrix interface

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 [57], fibre 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 fibre aspect ratio, strength of interactions, fibre orientation and aggregation etc.[58-60]. Extensive research has been done to evaluate the interfacial shear strength (ISS) of man made fibres [61-64] and natural fibres [65-68] by using methods such as fibre pull out tests, critical fibre length and micro bond tests.

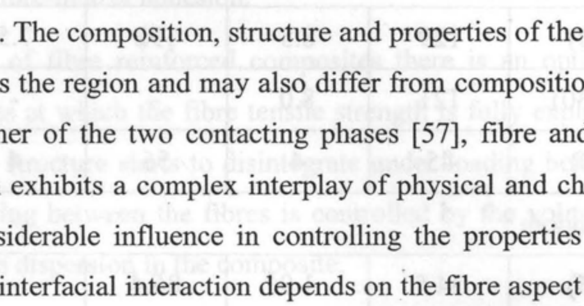


Figure 1.12. Interface/Interphase in a fibre reinforced composite

[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 1.12 [69]. 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.

1.11. Mechanisms of fibre-matrix adhesion

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

a) Adsorption and wetting

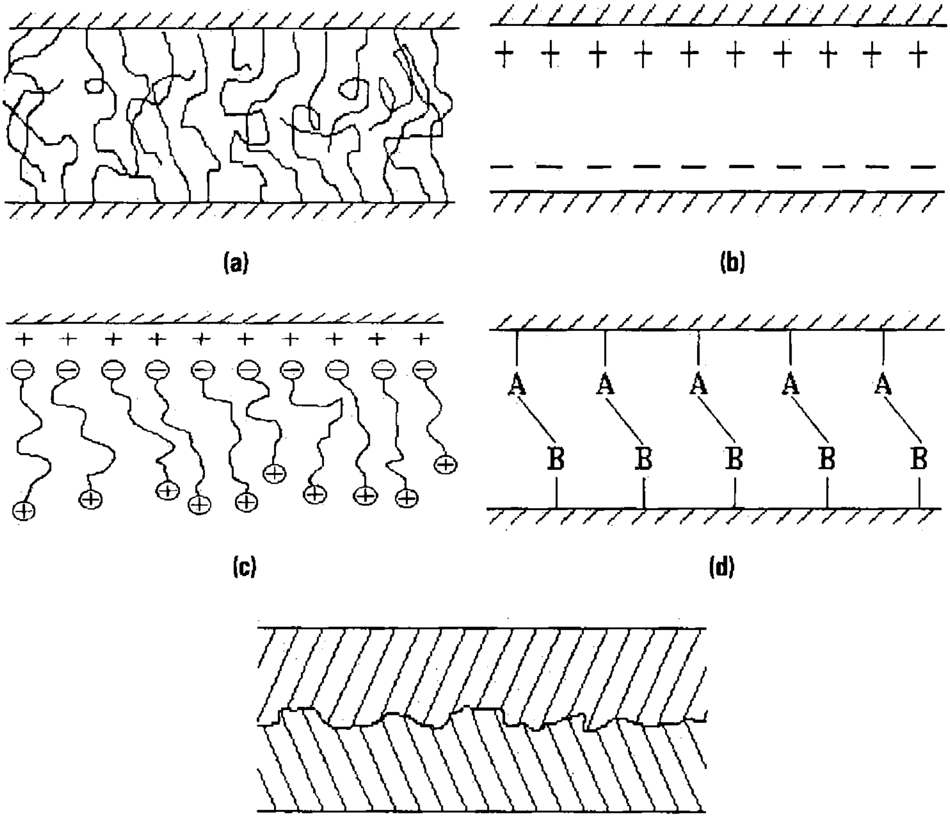
This is due to the physical attraction between the surfaces, which is better understood by considering the wetting of solid surfaces by liquids. Between two solids, the surface roughness prevents the wetting except at isolated points. When the fibre surface is contaminated, the effective surface energy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

b) Interdiffusion

Polymer molecules can be diffused into the molecular network of the other surface, say fibre, as shown in Figure 1.13(a). The bond strength will depend on the amount of molecular conformation, constituents involved and the ease of molecular motion.

c) 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 1.13 (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 1.13. Schematic representations of various fibre-matrix adhesions.

d) 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 1.13 (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.

e) Mechanical adhesion

Mechanical interlocking at the fibre-matrix interface is possible as given in Figure 1.13 (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.

1.12. Fibre-matrix interface modifications

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 [70-80]. 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 [81-86]. The compatibilizer can be a polymer with functional groups grafted into the chain of the polymer. The coupling agents are generally tetra functional organometallic compounds based on silicon, called silanes [87]. 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 [88]. Ishak *et al.* [89] 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. 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 [90]. The increase in the percentage crystallinity 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 [91]. 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 of the fibre surface thereby producing a rough surface morphology [92]. 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 [93].

Cao *et al.* [94] found that the mechanical properties of biodegradable composites reinforced with bagasse fibre were found to be superior after alkali treatment of the fibre.

The study by Van de Weyenberg *et al.* [95] on improving the properties of UD flax fibre reinforced composites by applying an alkaline treatment proved that it is a simple and effective method to enhance the fibre/matrix bonding with an epoxy resin.

Boynard *et al.* [96] analyzed the effect of mercerization treatment to improve the strength of fibre/polyester interface. They found that although the surface analysis showed the treatments promote a clear removal of outer surface layer of fibres with exposition of the inner fibrillar structure and the consequent increase of the fibre surface area, only a secondary increase on the mechanical properties was obtained. The slight increase observed was attributed only to mechanical interlock. Samal *et al.* [97] 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.* [98] 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 resulted in the increase in the interfacial shear strength (ISS) between the fibre and the matrix and increase in the mechanical properties of the composites. The ISS between acetylated fibres and various polymer matrices-polyesters, epoxy and polystyrene showed that improvements in the ISS were observed upon acetylation of the fibres. Whilst those with thermoset systems show the highest magnitude in ISS, the greater improvement upon acetylation was shown by polystyrene [67]. Increased hydrophobicity of fibres has also increased the ISS values. The introduction of the acetyl group on the fibre surface has increased the ISS of the composites with polystyrene (as compared to the unmodified) significantly than those of epoxies and polyesters. This resulted in improved wetting of polystyrene on to the unmodified fibre surface thereby increasing the work of adhesion. The work of adhesion is increased by an increase in the surface tensions.

Bessadok *et al.* [99] studied the effect of chemical treatments of Alfa *(Stipa tenacissima)* fibres on water sorption properties. The chemical treatments were acetylation, treatments with styrene, acrylic acid and maleic anhydride. It was found that chemical treatments, especially styrene treatment, reduced water uptake of Alfa fibre.

A study of the effect of acetylation and propionylation surface treatments on flax, hemp and wood fibres was done by Tserki *et al.* [100]. The highest extent of esterification was achieved for the wood fibres due to their high lignin/hemicellulose content. It was also shown that the fibre crystallinity decreased slightly as a result of esterification.

The work carried out by Bairdo *et al.* [101] showed that acetylation of the fibre surface remarkably increased the strength of a Bionelle/flax fibre composite, by improving the interfacial strength of natural fibres. George *et al.* [102] 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.* [103].

Cyanoethylation of jute fibres using acrylonitrile monomer was done by Saha *et al.* [104] using acrylonitrile monomer, which reacts with hydroxyl group of fibre constituents. The degree of cyanoethylation to different extents was varied by the reaction time. The moisture regain, water absorption and thickness swelling of jute fibre based composites were significantly reduced by cyanoethylation of fibre. The dimensional stability of composite was also improved by the cyanoethylation of jute fibre. A significant improvement on the tensile and the flexural properties of jute-PP composite was also observed which is associated with improved bonding at the interface between jute fibre and polyester. The improved mechanical properties of cyanoethylated jute polyester amide composites may be due to bonding of β-cyanoethyl group of fibre with the polyester matrix thereby improving the fibre-matrix interaction [105]. Reddy and Bhaduri modified cellulose fibre by cyanoethylation [106]. The moisture regain, water absorption and thickness swelling of jute fibre based polyester composites were significantly reduced when cyanoethylated fibre was used [107].

Surface modification of coir fibre was done by Rout *et al.* [108] by dewaxing, using an alkali treatment, vinyl grafting with methyl methacrylate and cyanoethylation. The morphology studies showed the removal of tyloses from the surface of coir as a result of alkali treatment, resulting in a rough fibre surface with regularly spaced parts. At a lower percentage of grafting (PMMA) the surface became more or less uniform, while the surface of the coir fibres with a higher percentage of grafting were increasingly covered with grafted material, resulting in canal-like cavities between the overgrowths of grafted material on the unit cells. Cyanoethylated coir fibre surfaces showed an insufficient deposit of cyanoethyl groups. The morphological features correlated with the mechanical properties of modified fibres.

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.* [109]. 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 [110]. 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.* [111] employed lignin as compatibilizer in coconut fibre polypropylene composites. Since lignin contains both polar hydroxyl groups and non polar 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 reduced water absorption and thickness swelling of the composites.

Development, optimization and characterization of two treatments; acetylation and stearation of flax fibres were done by Zafeiropoulos *et al.* [112]. The two treatments were applied on two grades of flax fibres (green and dew retted flax). Three characterization techniques were applied on the treated and untreated fibres; X-ray diffraction, Scanning electron microscopy and inverse gas chromatography. It was found that both treatments resulted in removal of non-crystalline constituents of the fibres and alter the characteristics of the surface topography. It was also found that both treatments changed the fibre surface free energy, with acetylation increasing it and stearation decreasing it. Butyrated kraft lignin was added to an unsaturated thermosetting resin, consisting of a mixture of acrylated epoxidized soybean oil (AESO) and styrene. Composites were made by the vacuum assisted transfer moulding process with varying amounts of butyrated kraft lignin dissolved in the unsaturated resin system. These results suggest that addition of lignin-BA to the AESO/styrene resin results in the natural fibre-AESO/styrene interface, by compatibilizing the resin and the natural fibre [113].

Conventional compatibilization techniques involve wet chemical methods for the modification of lignocellulosic components and involve mainly the primary and secondary hydroxyl groups of the polysaccharide chain [114-116]. Cold plasma chemistry opens up a new way for the surface modification of materials for composites and other applications [117-1119]. The energies of neutral and charged plasma species, including electrons, ions of either polarity, free radicals, excited species, atoms, molecules and photons are comparable to bond energies involved in all organic compounds and as a consequence, both the gas phase and surface molecular fragmentation and recombination processes can be controlled by selecting the proper plasma parameters [116,120].

Cold plasma enhanced functionalisation reactions will only be adequate for the modification of components for melt processing compounding if the surface area of the substrate is very large relative to its volume, which is crucial for the development of interaction between the fibre and matrix [121,122]. Interfacial properties and micro failure degradation mechanisms of the oxygen plasma treated biodegradable poly (p-dioxanone) (PPDO) fibre/poly (l-lactide) (PLLA) composites were investigated for the orthopaedic applications as implant materials using micromechanical technique and nondestructive acoustic emission (AE). PLLA oriented in melt state was brittle and their mechanical strength was not high, whereas PPDO fibre appeared to have high mechanical strength and flexibility [123].

Thomas and coworkers [124-129] have carried out systematic studies on the chemical modification of various natural fibres like sisal, coir, oil palm, banana and pineapple and its reinforcing effect on various thermosets, thermoplastics and rubbers. 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.

1.13. Fabrication of composites

The fabrication and shaping of composites into finished products are often combined with the formation of the material itself during the fabrication process. The formation of the composite involves the combination of the matrix and fibre such that the matrix impregnates, surrounds and wets the fibres. The important processing methods for thermosetting polymers involve Hand lay-up, Bag moulding process, Filament winding, Pultrusion, Bulk moulding, Sheet moulding, Resin Transfer Moulding etc.

1.13.1. Hand lay-up

The hand lay-up technique (Fig.1.14) is the oldest, simplest and most commonly used method for the manufacture of both small and large fibre reinforced plastic products. A flat surface, a cavity or a positive shaped mould, made from wood, metal, plastics or a combination of these materials may be used. Fibre reinforcements and resin are placed manually against the mould surface. The quality of the product depends on the skill of the personnel in removing air bubbles and voids. The hand lay-up method is labour intensive and is suitable for low rate of production.

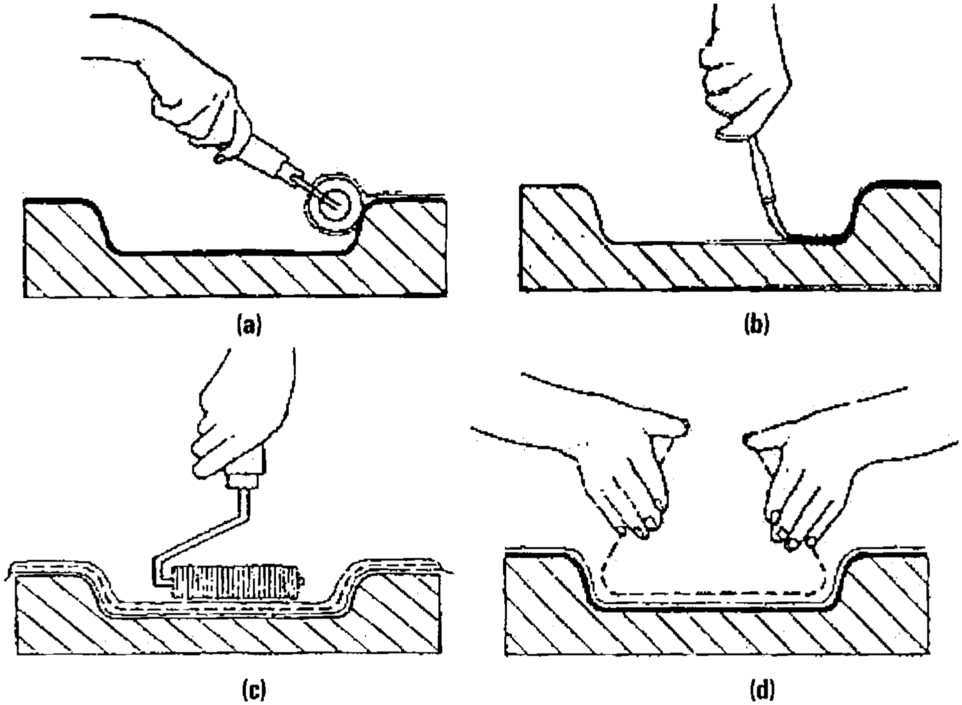


Fig. 1. 14. Hand laminating (a) apply gel-coat with brush (b) apply laminating resin with roller (c) cut and fit reinforcement layer (d) consolidate with ribbed roller

1.13.2. Spray-up technique

Spray-up technique is the principal fabrication process used by the FRP industry. The catalysed resin and chopped fibre are laid down simultaneously on the mould surface with specialised spray equipment. The chopped fibre, 3.8-5.0 cm long is produced by feeding continuous fibre roving into a rotating chopper at the head of the spray gun. The technique requires skilled operators to get uniform products and to prevent excessive scrap by overspraying.

1.13.3. Bag moulding process

Bag moulding is one of the oldest and most versatile of the processes used in manufacturing composite parts. The lamina is laid up in a mould and resin is spread or coated, covered with a flexible diaphragm or bag and cured with heat and pressure. After the required curing cycle, the materials become an integrated moulded part shaped to the desired configuration. The general process of bag moulding can be divided into three basic moulding methods: pressure bag, vacuum bag, and autoclave. Vacuum bag and autoclave methods are used to produce most bag-moulded parts. Their main advantages are that the tooling is relatively inexpensive and the basic curing equipment can be used for an unlimited variety of shaped parts. The disadvantage of the pressure bag system is that the tooling is relatively expensive because it is combined with the curing pressure system and can be used only for the specific part for which it is designed.

1.13.4. Filament winding

Filament winding is a technique used for the manufacture of surfaces of revolution such as pipes, tubes, cylinders and spheres and is frequently used for the construction of large tanks and pipe work for the chemical industry. High-speed precise lay down of continuous reinforcement in prescribed patterns is the basis of the filament winding method. Continuous reinforcements in the form of roving are fed from a multiplicity of creels. A creel is a metallic shelf holding roving packages at desired intervals and designed for pulling roving from the inside of the package.

1.13.6. Pultrusion

Pultrusion is an automated process for manufacturing composite materials into continuous, constant-cross-section profiles. In pultrusion the product is pulled from the die rather than forced out by pressure. A large number of profiles such as rods, tubes and various structural shapes can be produced using appropriate dies. Profiles may have high strength and stiffness in the length direction, with fibre content as high as 60-65% by volume.

1.13.7. Compression moulding

Compression moulding offers a method for large volume production of components with excellent dimensional accuracy and good finish on both surfaces. Compression moulding is done by pressing and shaping the moulding charge in a matched die and curing the products by fast curing methods. The products take the shape of the cavity.

1.13.8. Resin transfer moulding (RTM)

RTM [130,131] is unique in that it permits the manufacture of high performance composite parts of essentially unrestricted geometry with fast cycle times. A dry reinforcement preform is placed in the mould and the mould is closed. The preform is impregnated with a thermoset liquid resin which is injected into the mould. The injection is done by an applied pressure difference created by an external source of elevated pressure. During the infiltration process, the resin wets out the reinforcement and polymerises. Once the composite develops sufficient green strength it can be removed from the tool and post cured.

1.13.9. Modern developments using thermosets

A series of processes have emerged in which the reinforcement is placed in the mould and the resin matrix is injected. These are called collectively Liquid Composite Moulding (LCM). At its simplest, this involves placing the glass (usually) in the mould in a prescribed pattern, followed by injection of resin. Manual placement of glass is slow and skill-dependent, and preforms are widely used. The glass is prepared to shape in a separate operation, and is lightly bonded with a thermoplastic binder which softens when warmed to accommodate to the mould. It is simply dropped into place at the moulding stage.

1.14. Short fibre reinforced thermosets

A discontinuous fibre composite is one that contains relatively short discrete lengths of the fibre dispersed within the matrix. The fibres may be aligned in one direction but are more usually in a random, or semi random configuration. Unlike continuous fibre composites, the mechanical behaviour of short fibre reinforced thermosets is often dominated by complex stress distributions due to the fibre discontinuity, in particular the stress concentration at the fibre ends. A number of different approaches have been used to predict the mechanical properties of short fibre thermosets, including modification of the 'rule of mixture' theory originally developed for continuous fibre composites, and the probabilistic theory. When an external load is applied to the composite, the fibres are loaded as a result of stress transfer from the mixture to the fibre across the fibre/matrix interface. The degree of reinforcement that may be attained is a function of the fibre fraction (V_f), the fibre orientation distribution (FOD), the fibre length distribution (FLD) and the efficiency of stress transfer at the interface. In general, the reinforcement is more effective when V_f is high, the fibres are long, the fibres are aligned in the principal stress direction and the interface is strong.

There are two well accepted but simplistic, models for stress transfer [132]. Cox models the composite as a pair of concentric cylinders. The representative element used in the Cox analysis is shown in Figure 1.15.

The central cylinder represents the fibre and the annular outer region, the matrix. The ratio of the diameters (r/R) is adjusted to the required V_f. Both fibre and matrix are assumed to be elastic and the cylindrical bond between them is considered to be perfect. It is also assumed that there is no stress transfer across the ends of the fibre. If, as is usually the case, the fibre much stiffer than the matrix, an axial load applied to the system will tend to induce more strain in the matrix than in the fibre and leads to the development of shear stresses along the cylindrical interface. The tensile stress in the fibre rises from zero at the end of the fibre to a plateau region along the middle portion. The tensile (a) and shear (b) stress profiles in the fibre and the interface according to Cox model is shown in Figure 1.16.

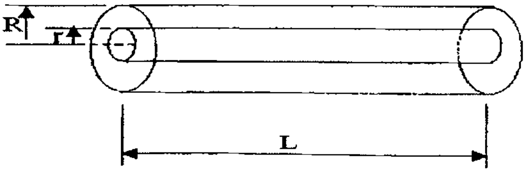


Figure 1.15. The representative element used in the Cox analysis.

[Ref: F. R. Jones, Hand Book of Polymer-Fibre Composites, Longman Scientific, (1994)]

One shortcoming of the Cox model is that a maximum shear stress is predicted at the end of the fibre; in fact, this is where the shear stress must be zero. The other problem is that the interface strength is not considered at all, as the model assumes a perfect bond and only elastic interactions.

The alternative model due to Kelly and Tyson [133] is based on the concept of frictional stress transfer at the interface. It is considered that a constant shear stress is induced from the fibre ends; these results in a linear stress build up. The frictional stress may be regarded as the interface shear strength (τ_i). This concept is often used for the experimental estimation of interface shear strength by the fragmentation or pull out test.

In general, theoretical strength and stiffness are not achieved in real mouldings because of the complexities of load transfer. However, for longer fibres, the low strain properties approach those for continuous fibre with appropriate corrections for fibre orientation and length. Matrix cracking and fibre debonding contribute to non-linear stress-strain curves and the ultimate strength.

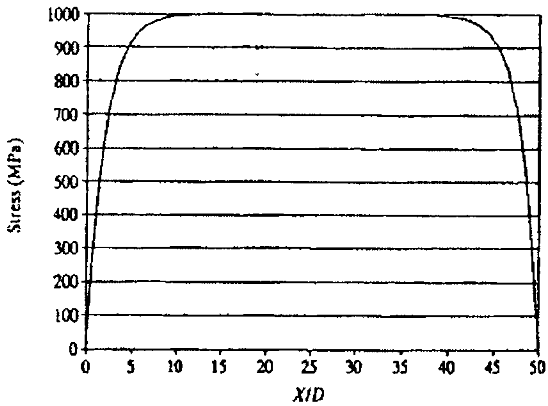


Figure 1.16. (a) The tensile stress profiles in the fibre and interface according to the Cox model

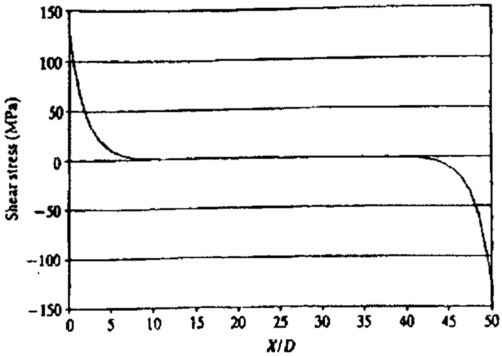


Figure 1.16. (b) The shear stress profiles in the fibre and interface according to the Cox model

[Ref: F. R. Jones, Hand Book of Polymer-Fibre Composites, Longman Scientific, (1994)]

The values used in the equations are typical of those for an E-glass fibre in an epoxy resin. The transfer length is of the order of 10 fibre diameters. The parameter X/D is the distance from the end of the fibre in units of diameter.

1.15. 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 favourable balance between the advantages and disadvantages inherent in any composite material [134]. 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 [135,136]. Sisal and glass fibres are good examples of hybrid composites possessing very good combined properties [137]. 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.* [136] 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 [138] 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.* [139] 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.* [140] 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.*[141]. Hybrid composites containing surface modified coir fibres showed significant improvement in flexural strength and reduced water absorption. Sreekala *et al.* [142] 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.*[143] and Haseena *et al.* [144] 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. Burgueno *et al.* [145] studied on Cellular biocomposite cores made from industrial hemp or flax fibres with unsaturated polyester were hybridized with woven jute, chopped glass and unidirectional carbon fabrics and found that the composite possessed improved stiffness, strength, moisture absorption ability and enhanced structural behaviour. Clark *et al.* [146] have reported on the jute and glass fibre hybrid laminates and optimum ply conditions are identified which offer respectable mechanical properties at an attractively low cost. Pavithran *et al.* [147] established that hybridization of sisal fibre with glass in polyester composites, in view of improving the impact performance of the former, can be better utilized in glass core-sisal shell laminates than in sisal core-glass shell laminates.

1.16. Applications of composites:

Reinforced plastics have gained popularity over conventional materials because of the following advantages:

1. High strength to weight ratio and rigidity.
2. Unlimited moulding size used.
3. Wide range of manufacturing techniques.
4. Ease of fabrication.
5. Versatility in design.
6. Low capital outlay (low cost) as has been visualised for hand-lay-up technique.
7. Resistance to water, weathering and corrosion.
8. Resistance to various chemical reagents.
9. Can be made fibre retardant, electrically and thermally resistant.
10. If needed, good degree of transparency can be achieved.

Due to these overwhelming advantages of composites, there is wide range of applications of fibre reinforced plastics. Some important applications are given below:

1. *Transportation:* Manufacture of vehicle bodies, cooling system components and farm equipments.
2. *Marine:* Fuel and water tanks in ships, submarine and ship hulls for recreation.

3. *Material handling:* Pharmaceutical trays and boxes,storage tanks etc.
4. *Sporting goods:* Fishing rods, Tennis racquets, Hockey sticks etc.
5. *Construction:* Structured shapes, panelling, sliding etc.
6. *Electrical applications:* In transformers, motors, generators, switch gears and electronics equipments.
7. *Corrosion applications:* Fuel and chemical tanks, fertiliser storage hoppers etc.
8. *Aerospace and Military:* Rocket motor cases, nozzles, nose cones, blades, pressure bottles, assault boat and rifle stocks, bullet proof helmet, bridge sections, ladders etc.
9. *Railways:* Window frames, window guides, axle box cover, battery box, flooring for toilets, Laboratory Chula, roof ventilator, sliding doors, rotary switch panels, emergency lead terminals, fan blade assembly etc.

1.17. Isora fibre

Various natural fibres like sisal, coir, jute, oil palm, bamboo etc. have been proved to be a better reinforcement in thermoset matrix. Incorporation of natural fibres resulted in better long term mechanical performance of thermosets. 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 [148]. 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. 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. Fruits disperse during April to June, and about 620 dried seeds weigh 1 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. Certain quantity of seed collected from forest areas might have also gone to the general market, on which there is no quantified data available.

1.17.1. Characterisation of Isora fibres

*[**Ref:** Ph. D. Thesis, Dr. Lovely Mathew, Cochin University of Science and Technology, Kochi.]*

The photograph of isora fibre is shown in Figure 1.17 and that of stem, leaves, fruits and the dried seeds are given in Figures 1.18 (a-d).

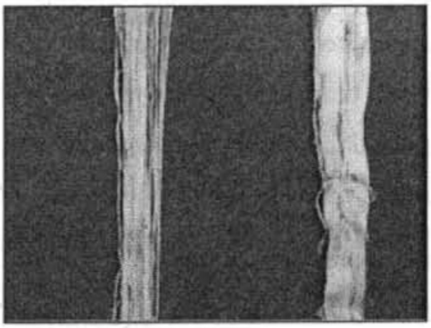
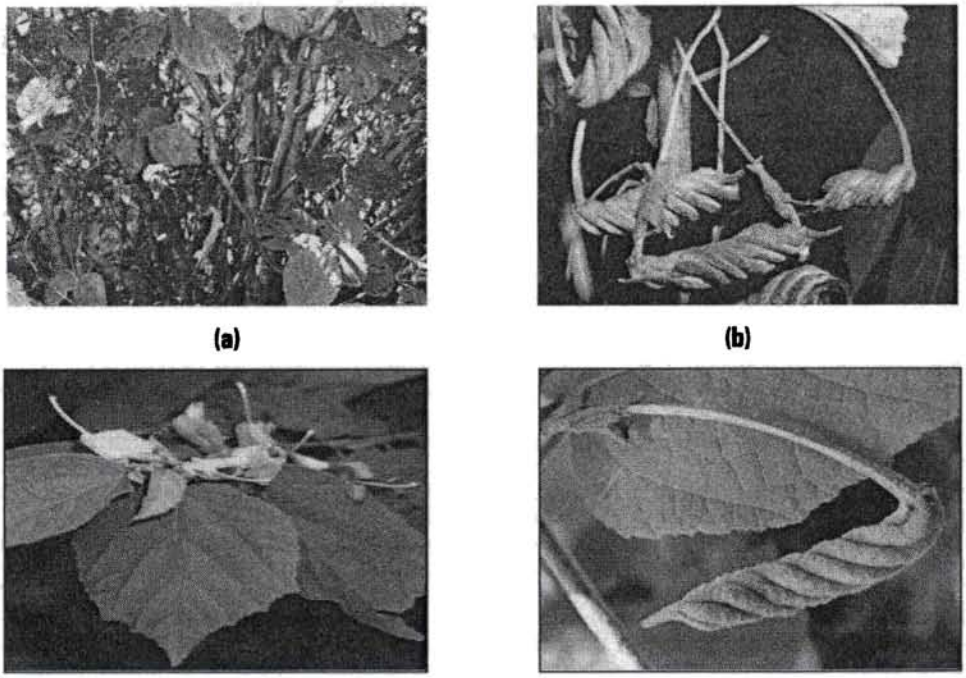


Figure 1.17. Photograph of isora fibre



(a)

(b)

(c)

(d)

(a) stem (b) dried seed (c) leaves (d) fruit

Figure 1.18. Helicteres isora plant

a) Chemical analysis: The chemical components present in the isora fibre and the solubility of the fibre in different solvents are given in Table 1.5.

Table 1.5. 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		

It is clear from Table 1.5 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 fibre is hygroscopic and its moisture content is found to be 5-6%. From the Table it is clear that the fibre contains about 12% water soluble materials.

The physical and mechanical properties of the fibre are given in the Table 1.6. After chemical treatment there is a slight positive change in the density which normally signifies cell wall densification.

Table 1.6. Physical and Mechanical properties of isora fibre

Properties	U	A	Si	γ 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^{-1})	0.987	-	-	-
Length to diameter ratio	99	-	-	-
Diameter (μm)	10	<10	<10	10

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

The tensile stress strain curves of the raw and modified isora fibres are given in Figure 1.19. Fibre modifications lead to major changes on the fibrillar structure of the fibre. Brittleness of the fibre is substantially reduced upon treatments.

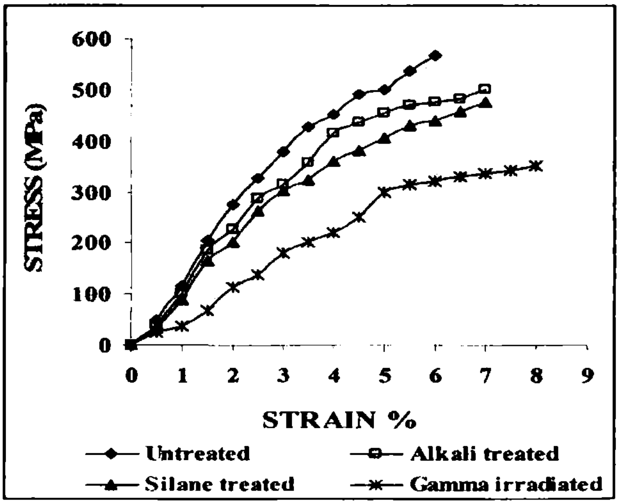


Figure 1.19. Stress-strain curves of raw and modified fibres.

Important tensile properties like tensile strength, Young's modulus and elongation at break of the raw and modified fibres are given in Table 1.16. Chemical modifications of the fibre surface decreased the tensile strength. Tensile strength of the treated fibre is less than that of the untreated fibre (Figure 1.19). Elongation at break shows a slight increase after chemical treatment. 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. These factors control the interfacial interaction.

b) Morphological analysis of fibre

i. Scanning Electron Microscopic studies

The SEM photograph of a single fibril of isora fibre is given in Figure 1.20. The diameter of the fibre was found to be 10μm.

Figure 1.20. SEM photograph of a single fibril of isora fibre

Isora fibres are composed 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. Isora fibre is a composite material with fibrous reinforcement and a mixture of hemi cellulose and lignin as matrix.

ii. 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 Figure 1.21. 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.

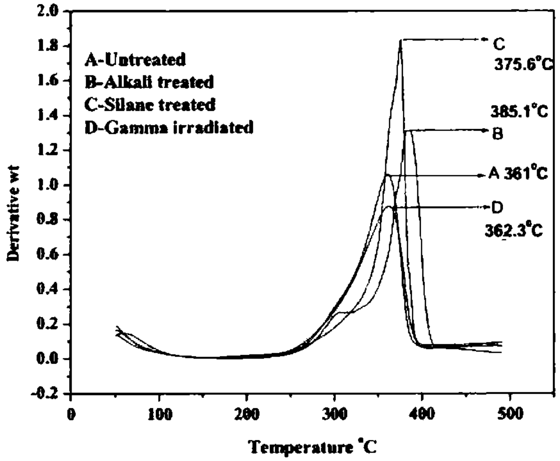


Figure 1.21. Derivative thermograms (DTG) of untreated and chemically modified fibres in Nitrogen atmosphere

From the DTG curves shown in Figure 1.21, it was observed that the thermal stability of the fibres increased in the following order: Untreated < Gamma irradiated < Silane treated <Alkali treated.

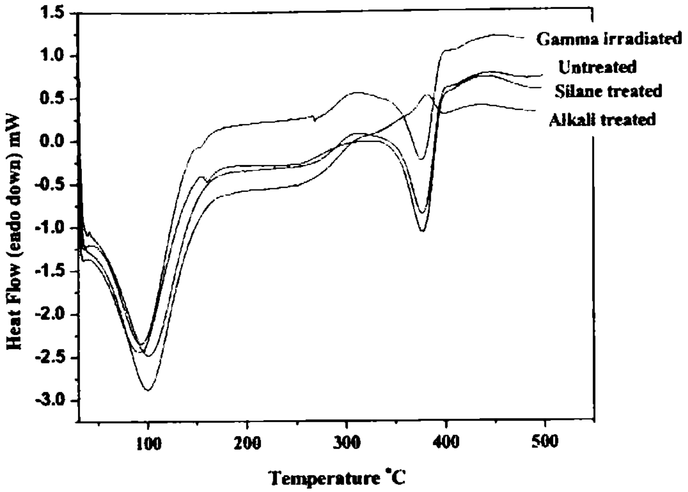


Figure 1.22. DSC curves of untreated and chemically modified fibres in Nitrogen atmosphere

The DSC studies in nitrogen also show a similar trend (Figure 1.22). A broad endotherm in the temperature range of 75-120°C was observed which may be due to the dehydration of fibres. 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 (Figure 1.22) which is an indication of the increase in the crystalline cellulose, which is known to have good thermal resistance.

iii. WAXRD studies

From Table 1.6 and Figure 1.23 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 crystallinity index and the minimum between 101 and 002 peaks (Figure 1.23) is an indication of the reflection intensity of the amorphous material. Alkali and silane treatments increase the crystallite packing order. Crystallinity index is a measure of the order of the crystallites rather than the crystallinity of the crystallites. Alkali treatment is reported to reduce the proportion of crystalline material present in plant fibres.

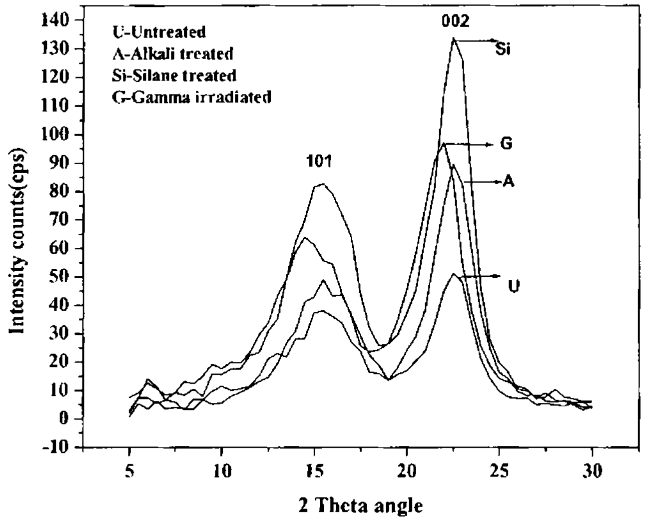


Figure 1.23. WAXRD Spectra of untreated, alkali treated, silane treated and gamma irradiated fibres

1.18. Scope and objectives of the present work

The aim of the present work is to investigate the prospect of using isora fibre as reinforcement in polyester and epoxy matrix. 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 micro fibrillar angle. Isora fibre has relatively high cellulose content and a low micro fibrillar angle. 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 polyester / epoxy matrix, several parameters like fibre length, fibre loading, fibre surface modification, fibre-matrix adhesion etc. have 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.

In the present study it is proposed to focus on the following aspects:

1.18.1. Characterization of the properties of randomly oriented isora fibre-polyester composites

The properties of randomly oriented isora fibre-polyester composites are proposed to be studied as a function of fibre length and fibre loading. A comparison is also proposed to be made between theoretical and experimental tensile properties.

1.18.2. Alkalization of isora fibre surface

The polar natural fibre and non polar polymer matrix are likely to end up in relatively weak bonding. The bonding can be improved to a great extent by varying the polarity of the fibre surface. In view of this, it is proposed to modify short isora fibre with alkali and to investigate the effect of alkalization on the surface morphology by Infra red (IR) Spectroscopy and Scanning electron microscopy (SEM) studies. The effect of concentration of alkali and duration of alkali treatment of fibre on the properties of the composite will also be evaluated.

1.18.3. Chemical modification of isora fibre surface

As a further step to change the surface polarity and thereby improve the fibre-matrix interaction short isora fibre is also proposed to be subjected to various chemical treatments like acetylation, benzoylation, silane and triton. SEM and IR spectroscopy will be used to characterize the untreated and treated fibre surface. The effect of fibre modification on the properties of the composites also will be evaluated.

1.18.4. Characterization of the properties of oriented long isora fibre-polyester composites

The properties of untreated long oriented isora fibre-polyester composites are proposed to be studied as a function of fibre loading. The fibre/matrix interface is proposed to be modified by various fibre treatments and the role of improved fibre/matrix interactions on the properties of the composites will be evaluated. The untreated and treated fibre surface will be characterized by SEM. The effect of fibre modification on the properties of the composites will also be evaluated. A comparison is proposed to be made between theoretical and experimental tensile properties.

1.18.5. Characterization of the properties of isora fibre-epoxy composites

The properties of untreated and alkali treated randomly oriented isora fibre-epoxy composites are proposed to be studied. The properties of untreated oriented long isora fibre-epoxy composites will be studied as a function of fibre loading. The fibre/matrix interface is proposed to be modified by various fibre treatments and the role of improved fibre/matrix interactions on the properties of the composites will be evaluated. SEM will be used to characterize the untreated and treated fibre surface. The effect of fibre modification on the properties of the composites will be evaluated. A comparison is proposed to be made between theoretical and experimental tensile properties.

1.18.6. Dynamic mechanical properties of the composites.

The dynamic mechanical properties of the untreated and chemically modified randomly oriented isora-polyester, isora-epoxy; oriented long isora-polyester and isora-epoxy composites are proposed to be analyzed. The dependence of storage modulus, loss modulus and damping factor of the composites on the temperature will also be studied.

1.18.7. Water absorption and thermal aging studies of isora fibre reinforced polyester and epoxy composites

The water absorption behaviour of and the effect of thermal aging on the tensile and flexural properties of the composites will be investigated as a function of fibre loading and fibre modification.

References

[1] Herakovich C T, *Mechanics of Fibre Composites* (John Wiley & Sons Inc., New York), 1998, 1.

[2] *Dictionary of Composite Materials,* edited by S M Lee (Technomic Publishing Co., Lancaster, PA, USA), 1989, 32.

[3] *Engineering Composites,* Mathews F L & Rawlings R D, 1st ed. Chapman and Hall, London, (1994).

[4] Nielsen L E., Landel R. F., *Mechanical Properties of Polymers and composites,* 2nd ed., Marcel Dekker; New York, 1994.

[5] Weatherhead RG., *FRP Technology: Fibre reinforced Resin systems* Applied Science Publishers Ltd.; London, 1980.

[6] Tjong S C, Meng Y Z, *J Apply Polym Sci,* (1999) **72**: 501.

[7] Zheng Q, Song Y H, Yi X S, *J Mater Sci Lett,* (1999) **18**: 35.

[8] Srivastava V. K. , Hogg P. J., *J Mater Sci,* (1998) **33**: 1119.

[9] Raghavan J., Wool R. P. , *J Apply Polym Sci,* (1999) **71**: 775.

[10] Amash A., Zugenmaier P., *Polymer Bulletin,* (1998) **40**: 251.

[11] Bai S. L. , Wu C. M. L., Mai Y. W. , Zeng H. M., *Advanced Composite Letters,* Letchworth, (1999) **8**: 13.

[12] Bledzki A.K., Gassan J., *Prog Polym Sci* ,(1999) **24**: 221.

[13] Zuo-Guang Zhang, Yu-Bin Li, Yan Wu and Feng-Mei Li., *J Apply Polym Sci,* (2004) **94**(5): 2217.

[14] Brydson J. A., Plastics materials, Butterworths Heinemann, Oxford (1999).

[15] Hearle J.W.S., Sparrow J.T. *J Appl Polym Sci* (1979) **24:**1857-74.

[16] Cook J.G., *Hand book of Textile fibres and Natural fibres,* 4th Edn. Morrow Publishing, England. (1968).

[17] Woodcock C., Sarko A., *Macromolecules,*(1980) **13**: 1183.

[18] Sarko A., Muggli R., *ibid,* (1974) **7**: 480.

[19] Kritschewsky G.E.,*Chemische Technology Von Textilmaterialien,* Moskau, Legprombitisdat(1985).

[20] Xiao B., Sun X.F., Sun R.C., *Polym Deg Stab,*(2001) **74**: 307.

[21] Hill S., *New Scientist* (1997) p. 36.

[22] Wright J.R., Mathias L.J., *J Appl Polym Sci,* (1993) **48:** 2241.

[23] Hedenberg P., Gateholm P., *J Appl Polym Sci,* (1995)**56:** 641.

[24] Maldas D., Kokta B.V., *J Comp Mater,* (1991) **25:** 375.

[25] Maldas D.,Kokta B.V., *Polym Plast Technol, Eng,*(1990) **29**: 419.

[26] Harikumar K.R., Joseph K., Thomas S.,*J Reinf plast Comp,* (1999) **18**: 346.

[27] 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.

[28] Rowel R.M., Banks W.B., *Gen.Tech.Rep.FPL-GTR-50; USDA Forest service,* Forest Products Laboratory, Madison, WI (1985) 24.

[29] Feughelman M., Nordan P.J., *J Appl Polym Sci,* (1962) **6**: 670.

[30] Joly C., Gauthier R., Coubles E.S., *J Appl Polym Sci,* (1996) **61:** 57.

[31] Schniewind A.P., Wood and fire, M.B. Bever (ed), *Encyclopedia of Materials Science and Engineering,* Vol.7, 1st edition, Pergamon Press,Oxford (1986).

[32] Shukry N., Girgis B.S., *Polym Plast Technol Eng,* (1992) **31**: 541.

[33] 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).

[34] Tinh N., Eugene Z., Edward M.B., *J Macromol Sci* (1981) **C20**: 1.

[35] Tinh N., Eugene Z., Edward M.B., *J Macromol Sci* (1981) **C21**: 1.

[36] Gassan J., Bledzki A.K., *J Appl Polym Sci,* (2001) **82**; 1417.

[37] Sreekala M.S., Thomas S., *J Reinf Plast Comp,* (1998) **17**: 579.

[38] Pothen L.A, Thomas S., Oommen Z., *Polimetry,* (1999) **44**: 750.

[39] Prasanthkumar R., Thomas S., *Polym Int,* (1995) **38**: 173.

[40] Geethamma V.G.,Joseph R., Thomas S, *J Appl Polym Sci*(1995) **55**: 583.

[41] Baiardo M., Frisoni G., Scandola M., *J Appl Polym Sci,* (2002) **83**: 38.

[42] Ansell M.P.,Eichhorn S.J.,Baillie C.A., *J Mater Sci* ,(2001) **36**; 2107.

[43] Ge X. C., Li X.H., Meng Y.Z., *J Appl Polym Sci*, (2005) **93**: 1804.

[44] Alvarez V.A., Vazquez A., *Polym Deg Stability*, (2004) **84**:13.

[45] Hatakeyama H., Nakayachi A., *Comp Part A*, (2005) **36**: 698.

[46] Rowell R.M., The *Chemistry of Solid Wood,* Adv. Chem. Ser 207: American Chemical Society, Washington.DC (1985).

[47] De S. K. and White J. R., *Short fibre polymer composites,* Woodhead Publishing Ltd., Cambridge, England, 1996.

[48] Kalamkrov A.L., Liu H.Q., MacDonald D.O., *Composites Part B,* (1998) **29B:** 21.

[49] Theocaris P.S., *Acta Mechanica,* (1992) **95:** 69.

[50] Naik N. K., editor, *Woven fabric composites,* Technomic Publishing Co. Inc., Lancaster, 1994.

[51] Broutman L.J. and Krock R.H., *Composite Materials,* Vol. 16, Academic Press, New York, 1974.

[52] Meilewski J.V. and Katz H.S., *Hand Book of reinforcements for Plastics,* Van Nostrand reinhold Company, Inc., New York, 1987.

[53] Rosen B.W., *Fibre Composite Materials,* Am. Soc. for Metals, Metal Park, Ohio, 1965.

[54] Termonia Y., *J. Mater. Sci.* (1990) **25:** 4644.

[55] Pan N., *Polym Comp*, (1993) **14:** 85.

[56] Rose B.W., *Fibre Composite Materials,* Am. Soc. for Metals, Metal Park, Ohio, 1965.

[57] Schwartz M.M.,*Composite Materials Hand book,* Newyork, McGraw Hill (1984)

[58] Sreekala M.S., Thomas S., Neelakandan N.R., *J Polym Eng*, (1997) **16**: 265.

[59] Brahmakumar M., Pavithran C., Pillai R.M., *Comp Sci Technol* (2005) **65**: 563.

[60] Ivarez P., Blanco C., Santamary'a R., Granda M., *Comp Part A*, (2005) **36**: 649.

[61] Wong S., Shanks R., Hodzic A., *Comp Sci Technol,* (2004) **64**: 1321.

[62] Hristov V.N., Lach R., Grellmann W., *Polym Testing*, (2004) **23**: 581.

[63] Cheng T.H., Jones F.R., Wang D., *Comp Sci Technol,* (1993) **48**: 89.

[64] Drazal L.T., Madukar M., *J Mater Sci*, (1993) **28**: 569.

[65] Felix G.M., Gatenholm P., *J Appl Polym Sci*, (1991) **42**: 609.

[66] Felix G.M., Gatenholm P., *J Appl Polym Sci*, (1993) **50**: 699.

[67] Khalil H.P., Ismail H., Rozman H.D., *Europ Polym J*, (2001) **37**: 1037.

[68] Mani P., Satyanarayan K.G., *J Adhesion Sci Technol*, (1990) **4**: 17.

[69] Liao B., Huang Y., Cong G., *J Appl Polym Sci*, (1997) **66**: 1561.

[70] Rowell R.M., ACS Proceedings, *Polym Mater Sci Eng*, (1992) **67**: 461.

[71] Rowell R.M., Clemson C.M, *Proceedings of the 26th International particle board/Composites Symposium*, WA, (1992) 251.

[72] Bledzki A.K., Gassan J., *J Appl Polym Sci*, (1996) **59**: 1329.

[73] Mohanty A.K., Singh B.C., *J Appl Polym Sci, (*1987) **34**: 1325.

[74] Muzumdar P., Sanyal S., Dasgupta b., *Indial J Fibre Technol*, (1994) **18**: 286.

[75] Anderson M., Tillman A.M., *J Appl Polym Sci*, (1989) **37**: 3437.

[76] Sahoo P.K., Samantaray H.S., Samal R.K., *J Appl Polym Sci*, (1986) **32**: 5693

[77] Samantaray H.S., Samal R.K., *J Appl Polym Sci*, (1986) **37**: 3085.

[78] Mannan-Kh M.,Latifa B., *Polymer*, (1980) **21**: 777.

[79] Huque M.M., Habibuddowla M.D., Mohamood A.J., *J Polym Sci, Polym Chem Ed*, (1980) **18**:1447.

[80] Samantaray H.S., Samal R.K., *J Macromol Sci, Macromol Chem Phy*, (1986) C26:81.

[81] Lu J.Z., Wu Q., Negulescu I.I., *J Appl Polym Sci*, (2005) **96**: 93.

[82] Thielemans W., Wool R.P., *Comp Part A*, (2004) **35**: 327.

[83] Harper D., Wolcott M., *Comp Part A*, (2004) **35**: 385.

[84] Abdulmouleh M., Bou S., Duarte A.P., *Inter J Adhesion*, (2004) **24**: 43.

[85] Hernandez E.G., Claverie A.L., *Polym Comp*, (2004) **25(2)**: 34.

[86] Lu J.Z., Wu Q., Negulescu I.I., *Comp Interfaces*, (2005) **12(1)**:125.

[87] Saheb D.N., Jog J.P., *Advances in Polym Technol*, (1999) **18**: 351

[88] Pedro J., Manuel De H.F., Vega J.A., *J Appl Polym Sci*,(1997) **21**: 197

[89] Mohd Ishak Z.A., Aminullah A., IsmailH, Rozman H.D., *J Appl Polym Sci*, (1998) 68:2189.

[90] Mwaikambo L.Y., Ansell M.P., *J Appl Polym Sci*, (2002) **84**:2168.

[91] Gassan J., Bledzki A.K., *Comp Sci Technol*, (1999)**59**:1303.

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

[93] Aziz S.H., Ansell M.P., *Comp Sci Technol*, (2004) **64**:1219.

[94] Cao Y., Shibata S., Fukumoto I. *Composites: Part A* (2006) **37**: 423-429.

[95] Van de Weyenberg, T. Chi Truong, B. Vangrimde, I. Verpoest: *Composites: Part A.*, (2006) **37(9):** 1368-1376.

[96] Boynard C.A., MonteiroS.N., d'Almeida JRM., *J Appl Polym Sci*,(2003) **87**: 1927.

[97] Samal R.K., Rout S.K., Mohanty M., *J Polym Mater,* (1995) **12**: 229.

[98] Hill C.A.S., Akhalil H.P., *J Polym Sci,* (2000) **78**: 1685.

[99] Bessadok A., Marais S., Gouanve F., Colasse, L., Zimmerlin I., Roudesli S., Metayer M. *Comp Sci Technol.*,(2007) **67: (3-4)** 685-697.

[100] Tserki V., Zafeiropoulos N. E., Simon F., Panayiotou. *Comp. Part A:* (2005) **36:** 1110.

[101] Baiardo M., Zini E., Scandola M., *Comp Part A*, (2004) **35**: 703.

[102] George J., Bhagawan S.S., Thomas S., *Comp Interfaces*, (1998) **5**: 201.

[103] Sreekala M.S.,Joseph R., Thomas S., *App Comp Mater,* (2000) **7**: 29.

[104] Saha A.K., Das S., Basak R. K., Bhatta D., Mitra B.C., *J Appl Polym Sci*,(2003) **87**: 1927.

[105] Mohanty A.K., Khan M.A., Hinrichsen G., *Comp Part A*, (2000) **31**: 143.

[106] Reddy S.S., Bhaduri S. K., *J Appl Polym Sci*,(1990) **39**: 533.

[107] Saha A.K., Das S., Basak R. K., Bhatta D., Mitra B.C., *J Appl Polym Sci*,(2000) **78**: 498.

[108] Rout J. Misra M., Tripathy S. S., Nayak S. K., Mohanty A. K., *J Appl Polym Sci*,(2001) **59**: 1169.

[109] Mohanty A.K., Khan M.A., *Comp Sci Technol,* (2000) **60**: 1115.

[110] Calado V., Barreto D.W., Almeida J.R.M., *Polym Comp*, (2003) **2**:1.

[111] Rozman H.D., Kumar R.N., Ismail H., *Euro Polym J* ,(2000) **36**: 1483.

[112] Zafeiropoulos N. E., Baillie C. A., HodgkinsonJ. M.,*Comp. Part A:* (2002) **33:** 1185.

[113] Thielemans W., Wool R.P., *Comp. Part A:* (2004) **35:** 327.

[114] Denes F., Young R.A., In polysaccharides structural diversity and functional versatility, S. Dumitriu, Ed. Marcel Decker, New York (1998) 1087.

[115] Joseph K., Mattaso L.H.C., Toledo R.D., Thomas S., Carvalho L.H., In Natural polymers and Agrobased Composites, Frolini E., Leao A. Mattaso, LHC Eds, UNESP, Sao Paulo Brazil (2000) 159.

[116] Denes F., Young R.A., In proceedings of wood adhesive ChritiansenA. A., Conner A.H., Eds. Forest Products Society, Portland (1995) 61.

[117] Rowel J., Manolache S., Mattaso L.H.C., Sarfaty M., Young R.A., Denes F.S., In Anais do Second International symposium on Natural polymers and

Composites, Mattoso L.H.C., Frolini E., Leao A., Eds. UNESP, Sao Paulo Brazil (1998) 45.

[118] Hua Z.Q., Sitaru R., Denes F.S., Young r., Plasmas Polym. (1997) **2:** 199.

[119] Tserki V., Zafeiropoulos N.E., Simon F., Panayiotou *Comp. Part A:* (2005) **36:** 1110.

[120] Denes F., *Trip,* (1997) **5:** 23.

[121] Martin A.R., Manolache S., Matasso L.H.C., Rowel R.M., Denes F.S., In In Third International symposium on Natural polymers and Composites, (ISNAPOL) Proceedings, Brazil (2000) 431.

[122] Martin A.R., Manolache S., Matasso L.H.C., Rowel R.M., Denes F.S., *J Appl Polym Sci,*(2002) **85**: 2145.

[123] Park J.M., Sikkim D., Kim S.R., *Comp Sci Technol,* (2004) **64**: 847.

[124] Prasanth kumar R, Thomas S., *Polym International,* (1995) **38(2)**: 173.

[125] Geethamma V.G, Thomas S., *Int J Polym Mater,* (1996) **32**: 147.

[126] Sreekala M.S., Thomas S., *Comp Sci Technol,* (2003) **63**: 861.

[127] Joseph P.V., Joseph K., Thomas S., *Comp Sci Technol,* (2002) **62**: 1357.

[128] George J., Bhagawan S.S., Thomas S., *Comp Sci Technol,* (1998) **58**:1471.

[129] Pothen L.A.,Neelakandan N.R.,Thomas S., *J Reinf Plast (*1997)**16**: 8.

[130] Coulter J.P. and. Guceri S.I, *The manufacturing Science of Composites*, Proc. Manufacturing International (1988) 88, 79-86.

[131] Potter K., *Resin Transfer Moulding*, Chapman and Hall (1997).

[132] Cox H.L., *Bit. J. Appl. Phys.,* (1952) 3, 72.

[133] Kelly A. and Tyson W.R., *J. Mech. Phys. Solids.,* (1965) 13, 329

[134] Hartikainen J., Hine P., Friedrich K., *Comp Sci Technol,* (2005) **65**: 257.

[135] Idicula M., Neelakandan N.R., Thomas S., Oommen S., Joseph K., *J Appl Polym Sci,*(2005) **96** : 1699.

[136] Idicula M., Malhotra S.K., Thomas S., *Comp Sci Technol,* (2005) **65**:106.

[137] Kalaprasad G., Joseph K., Thomas S., *J Comp Mater,* (1997) **31**: 509.

[138] Mishra S., *Comp Sci Technol,* (2003) **63**: 1377.

[139] Rozman H.D., Ismail H., *Euro Polym J,* (2001) **37**:1283

[140] Junior C.Z.P., Fonseca V.M., Monteiro S.N., *Polymer Testing,* (2004) **23**:131.

[141] Rout J., Misra M., Tripathy S.S., Mohanty A.K., *Comp Sci Technol,* (2001) **61**: 1303.

[142] Sreekala M.S., Neelakandan N.R., Thomas S., *J Polym Eng,* (1997) **16**:265.

[143] Maya Jacob, Varghese K.T., *Comp Sci Technol*, (2004) **64**: 955.

[144] Haseena A.P., Unnikrishnan G., Thomas S., *Comp Interf*, (2004) **11(7)**: 489.

[145] Burgueno R., Quagliata M.J., Mohanty A.K.,Mehta G., Drzal L.T., Misra M., *Comp. Part A*, (2005) **36**: 581-593.

[146] Clark R.A., Ansell M. P., *J Appl Polym Sci*,(1986) **21**: 269-276.

[147] Pavithran C., Mukherjee P.S., Brahmakumar M.and Damodaran A.D., *J Mater Sci*, (1991) **26**: 455-459.

[148] Punnose G., *Ind Text Journal*, (1952) **63**: 388.

Chapter 2

MATERIALS AND EXPERIMENTAL TECHNIQUES

A brief description of the materials and methods used for the preparation of composites is given in this Chapter. The chemicals used for various fibre treatments are also discussed. A brief description about the different analytical techniques used for the characterization of fibres and composites is 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 30 days. The average length of the fibre is approximately 75-100 cm. The physical and chemical characteristics of isora fibre are given in Chapter 1. (1.7).

2.1.2. Unsaturated polyester resin

General Purpose grade Unsaturated polyester resin (HSR 8113M), was obtained from M/s Bakelite Hylam, Hyderabad. methyl ethyl ketone peroxide (MEKP) and cobalt napthenate were commercial grade supplied by M/s Sharon Engineering Enterprises, Cochin.

2.1.3. Epoxy resin

Commercial grade Epoxy Resin 103, and the room temperature amine hardener 301(polyamine) were supplied by M/s Sharon Engineering Enterprises, Cochin.

2.1.4. Chemicals for fibre modification

Sodium hydroxide, acetic anhydride, glacial acetic acid, benzoyl chloride, Triton (Iso octyl phenoxy poly ethoxy ethanol) were used for fibre surface modification was of reagent grade. Coupling agent 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 30 days and dried. Then it was chopped to different lengths 10, 20, 30, 40 and 50mm for preparing short fibre composites. For the preparation of oriented long fibre composites, fibre in the tape form of length 150mm was used.

2.3.1. Mercerization

a. For preparing randomly oriented fibre composites, fibres of average length 30 mm were treated with NaOH solutions of various concentrations for different time intervals, viz. 2, 4, 6, 8 and 12 hours at room temperature. Finally the fibres were repeatedly washed with water containing a little acetic acid and then dried in an air oven at about 70°C.

b. For preparing long fibre composites, fibres of length 150 mm in tape form were treated with 1% alkali solution for 4 hours. Finally the fibres were repeatedly washed with water containing a little acetic acid and then dried in an air oven at about 70°C.

Mercerization is one of the oldest methods proposed by John Mercer in 1842, which has been used for treating natural fibres [1]. The process involves the conversion of native cellulose (cellulose I) 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 [2]. This led to the formation of more flexible micro fibirils than that present in the native cellulose due to the less crystallinity in 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.

2.3.2. 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.

2.3.3. Acetylation

Alkali treated fibres were soaked in glacial acetic acid for one hour, decanted and then soaked in acetic anhydride containing two drops of concentrated sulphuric acid for five minutes. They were then filtered, washed and dried in an air oven at 70°C.

2.3.4. Benzoylation

Alkali treated fibres were suspended in 10% sodium hydroxide and agitated with 50ml benzoyl chloride for one hour, filtered, washed with water and dried. They were then soaked in ethanol for one hour to remove the unreacted benzoyl chloride, washed with water and finally dried in an air oven at 70°C.

2.3.5. Detergent treatment

Isora fibres of length 150mm in tape form was treated with 5% solution of commercially available detergent solution for 4 hours with occasional stirring. The treated fibres were washed thoroughly with water and dried in an air oven at 70°C.

2.3.6. Ultrasonication

Isora fibres of length 150mm in tape form were supended in an ultrasonicating bath and subjected to ultrasonication for 40 minutes. The fibres were dried in an air oven at 70°C.

2.3.7. Triton treatment

Isora fibres of length 150mm in tape form was treated with 1% alkali solution for 4 hours, washed in water containing a little acetic acid and dried. These fibres were then treated with 5% triton (iso octyl phenoxy poly ethoxy ethanol) solution for 2 hours. Finally the fibres were washed in water and dried in an air oven at 70°C.

2.4. Preparation of composites and test specimens

2.4.1. Short fibre reinforced composites

Randomly oriented isora fibre-polyester composites containing fibres of varying length and fibre volume fractions were prepared by hand lay up method using a three-piece stainless steel mould having dimensions 200×150×30mm^3 [Figure 2.1]. Prior to the composite preparation, the mould surface was polished well and a mould-releasing agent (waxpol) was applied on the surface of the mould. Unsaturated polyester resin (GP) was mixed well with 1% by wt. Cobalt naphthenate accelerator and 1% by wt. MEKP catalyst. The fibre mat was placed in the mould and the resin mixture was poured evenly on it. Using a metallic roller, the air bubbles were carefully removed and the mat was allowed to wet completely. The mould was closed and the excess resin was allowed to flow out as 'flash' by pressing in a hydraulic press. The pressure was held constant during the curing process at room temperature for 24 hours. The composite sheet was post cured at 80°C for 4 hours. Test specimens, according to ASTM standards, were cut from the sheet.

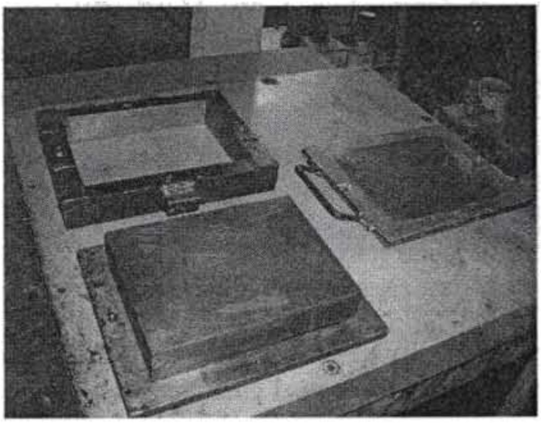


Figure 2.1. Three-piece steel mould used for preparing randomly oriented fibre composites

2.4.2. Oriented long fibre reinforced composites

Oriented long isora fibre reinforced composites were prepared by hand lay up technique using a three-piece stainless steel mould having dimensions 150 × 70 × 2mm^3 [Figure 2.2]. Prior to the composite preparation, the mould surface was polished well and a mould-releasing agent (waxpol) was applied on the surface. A weighed amount of the polyester resin was thoroughly mixed with

0.5% by wt. Cobalt naphthenate accelerator and 0.5% by wt. MEKP catalyst. Using a brush, the resin was applied evenly on the fibre lamina and were stacked one above the other in the mould and the mould was closed. The mould was pressed in a hydraulic press at a pressure of 20 kg m^{-2} at room temperature and the excess resin was allowed to flow out as 'flash'. The pressure was held constant during curing. Mylar film was placed on both sides of the stack for easy release and to obtain superior surface finish of the pressed laminates. The composite sheet was post cured at 80°C for 4 hours. Test specimens, according to ASTM standards, were cut from the sheet.

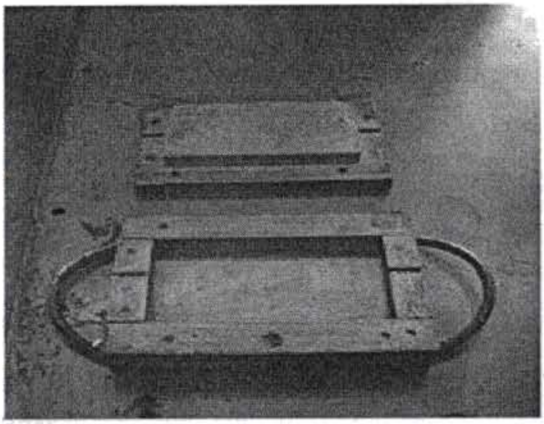


Figure 2.2. Three-piece steel mould used for preparing oriented long isora fibre composites

2.5. Characterisation of fibre and composites

2.5.1. Scanning electron microscopy

The SEM photograph of the fibre surface and cross section of the untreated and treated fibres and fracture surface of the composites were taken using JEOL 35C Model scanning electron microscope. The principle of which was detailed by Johar *et al.*[3]. 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 hours in a Polaron SEM coating unit SC 515. The fractured specimens and gold-coated samples were stored in a desiccator till SEM observations were made. The SEM photographs of the fractured surfaces give information regarding fracture mechanism and interface adhesion of the composites.

2.5.2. Infrared spectroscopy

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

2.5.3. Optical microscopy

An optical stereomicroscope of Leitz metallux 3, Germany was used for observing the impact fracture surface of the composites.

2.5.4. Thermal Analysis

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 60 × 10 × 3 mm^3, as function of temperature at a frequency of 1Hz on a Dynamic Mechanical Thermal Analyzer, DMA Q 800 TA instruments. The properties were determined over a temperature range of 30 to 130°C at a heating rate of 3°C min^{-1}.

2.6. Mechanical property measurements

The standard mechanical properties are determined by the procedures found in ASTM standards for plastics. The mechanical properties studied are tensile strength, Young's modulus, elongation at break (EB) %, flexural strength, flexural modulus and impact strength.

2.6.1. Tensile properties

The tensile properties were tested on a Shimadzu Autograph (AG-150 kN) Universal Testing Machine at a constant rate of traverse of the moving grip of

5mm min.$^{-1}$ for randomly oriented fibre composites (ASTM D 638-99) and 20 mm min^{-1} for oriented fibre composites (ASTM D5083). The test specimens were rectangular in shape with dimensions 150 × 15 × 3 mm^3 for randomly oriented fibre composites and 150 × 10 × 2 mm^3 for oriented fibre composites. The sides of test specimens were polished using emery paper prior to testing. One grip is attached to a fixed and the other to a movable (power-driven) member so that they will move freely into alignment as soon as any load is applied. The test specimen was held tight by the two grips, the lower grip being fixed. The output data in the form of stress-strain graph and elongation, modulus and energy absorbed at various stages of the test directly appears on the console of the microprocessor and as a print out.

2.6.2. Flexural properties

The flexural properties were tested on a Shimadzu Autograph (AG-150 kN) Universal Testing Machine (ASTM D 790-99) at a constant rate of traverse of the moving grip of 5 mm min.$^{-1}$ [Figure 2.3] for randomly oriented fibre composites and 2 mm min.$^{-1}$ for oriented fibre composites. The test specimens were rectangular in shape with dimensions 100 × 15 × 3 mm^3 for randomly oriented fibre composites and 75 × 20 × 2 mm^3 for oriented fibre composites. The specimens were polished using emery paper prior to testing. The depth and width of the specimen was measured nearest to 0.01 mm. The support span was 16 times the depth of the specimen. The specimen was centred on the supports with the long axis of the specimen perpendicular to the loading nose and supports. The load was applied to the specimen and flexural strength and modulus were recorded. The load-deflection curve was also obtained. It is calculated at any point on the stress strain curve by the following equation

$$S = \frac{3PL}{2bd^2} \quad \text{..2.1}$$

where S = stress in the outer fibres at midpoint (MPa), P = Load at any point on the load–elongation curve (N), L = support span (mm), b = width of specimen tested (mm), d = depth of specimen (mm).

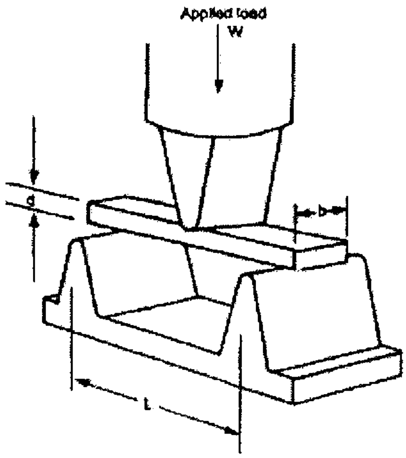


Figure 2.3. Three-point bending

Flexural modulus is the ratio of stress to corresponding strain and is expressed in MPa. It is calculated by drawing a tangent to the steepest initial straight-line portion of the load-deflection curve and using the equation

$$E_B = \frac{L^3 m}{4db^3} \qquad \text{...2.2}$$

Where E_B = modulus of elasticity in bending (MPa), L = support span (mm), b = width of specimen tested (mm), d= depth of specimen (mm), m = slope of the tangent to the initial straight line portion of the load – deflection curve (N mm^{-1} of deflection)

2.6.3. Impact strength

Izod impact strength of unnotched samples of the composite was measured on a Tinius Olsen Model 503 Impact Tester, according to ASTM D256-97 specifications [Figure 2.4]. Impact strength is a measure of the energy required to break a specimen by means of a sharp impact and is also a measure of the shock resistance of a material. The impact tests involve striking a standard shaped specimen with a swinging pendulum. The distance of upswing of the break pendulum after breaking the specimen is compared to the distance travelled when no specimen is present. This gives a measure of the energy required to break the specimen.

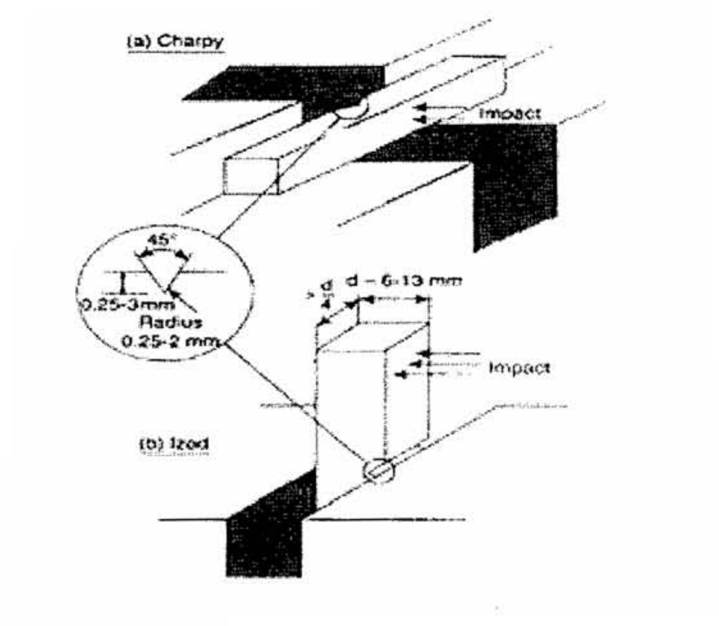


Figure 2.4. Pendulum impact tests

2.7. Water absorption

Samples of approximate dimensions 76 × 25 × 3 mm^3 and 76 × 25 × 2 mm^3 for randomly oriented and oriented fibre composites respectively were used for the measurement of water absorption (ASTM D 570-98). The corners of the samples were curved to avoid non-uniform water diffusion. The water absorption test samples were directly placed in a temperature-controlled oven. The temperature was kept constant at 50°C for 24 hours. The samples were taken out and cooled in a desiccator and the thickness and weight of the samples were measured. The randomly oriented fibre composite samples were immersed in water for 24 hours at room temperature and at 50°C (in a thermostatically controlled air oven). The specimens were removed, wiped dry with absorbent paper and immediately weighed. The increase in weight was found out. The oriented long fibre composite samples were immersed in water at room temperature. The specimens were periodically taken out of water, surface of the samples dried with absorbent paper and reweighed. This process was continued till equilibrium was reached. The mole percent uptake, Q_t of water by 100g. of polymer was plotted against time. The Q_t values were calculated using the equation,

$$Q_t = \frac{M_{(w)} / M_{r(w)}}{M_{i(s)}} \times 100 \qquad \ldots\ldots 2.3$$

Where $M_{(w)}$ is the mass of water at time t, $M_{r(w)}$ the relative molecular mass of water, ie. 18, $M_{i(s)}$ is the initial mass of the sample. When equilibrium was reached, Q_t was taken as the mole percent uptake at infinite time (Q_{∞})

2.8. Aging studies

Prolonged exposure to extreme conditions like heat affects the properties of the composites. The samples were heated in an air-circulating oven at 100°C for 24, 48 and 72 hours. After cooling down and conditioning at room temperature the tensile and flexural properties of these samples were measured.

References

[1] Allen G., (Ed.), *Comprehensive polymer Science-Polymer reactions*, Pergamon Press, (1989) 6.

[2] Anon J., *Tex Res J* (1898) **59**: 772.

[3] Johar O., Samudra A.V., *Characterisation of solid surface*, Kane P.F., Larrabe G.B., Eds, Plenum Press, Newyork,(1974) Ch. 5.

Chapter 3

UNTREATED RANDOMLY ORIENTED ISORA FIBRE REINFORCED POLYESTER COMPOSITES

Abstract

Randomly oriented isora fibre reinforced polyester composites were prepared by compression moulding technique. The influence of fibre length and fibre content on the mechanical properties such as tensile strength, Young's modulus, elongation at break, flexural properties and impact properties of the composites were evaluated. Composites showed an initial decrease in tensile and flexural properties at 10% fibre loading, followed by an increase up to 34% fibre loading. At still higher fibre loading there is a decrease in these properties. SEM studies were carried out to evaluate fibre/matrix interactions. The experimental tensile strength values were compared with the theoretical values.

Results presented in this chapter have been published in
Composite interfaces (2006) **13 (4-6):** 377-390.

3.1. Introduction

Over the last few years, there has been an increasing interest in using the abundant and renewable resources of plant fibres in composite materials with a view to replace, at least partially, the use of expensive synthetic fibres and particulate fillers for a variety of consumer articles [1-5]. The main reasons are that these biodegradable lignocellulosic fibres possess long aspect ratio for efficient stress transfer, their lower cost, non-toxicity and no abrasion during processing and certain aspects of their mechanical properties are comparable to existing inorganic glass fibres [6]. The most widely used thermosetting matrix reinforced by natural fibres is polyester [7-9] as it is available in liquid form, easily processed and cured, low in cost, easily available and has good mechanical properties when reinforced. Isora fibre has already been reported to be a good reinforcement in natural rubber [10]. The performance of short fibre reinforced composites depends on factors like aspect ratio, orientation of fibres and fibre-matrix adhesion [11]. In the case of fibre reinforced composites there exist a critical aspect ratio at which the mechanical properties are maximum. Fibre orientation has a significant influence on the mechanical properties of the composite in that the stress value is maximum along the axis of orientation of the fibre. The ultimate properties of the composites depend on the extent of stress transfer from matrix to fibres. The efficiency of this stress transfer depends on a number of factors such as fibre concentration, fibre dispersion, orientation of fibre, geometry of the fibre and fibre-matrix interfacial adhesion. The fibre/matrix interface has to be sufficiently strong for the composite to obtain better reinforcement. Laly Pothen *et al.* [12] studied the mechanical properties of short banana fibre reinforced polyester composites with special reference to the effect of fibre length and fibre content. Maximum tensile strength was observed for 30mm fibre length while impact strength gave the maximum value for 40 mm fibre length. Uma Devi *et al.* [13] investigated the tensile, flexural and impact behaviour of Pineapple leaf fibre-polyester composites as a function of fibre length and fibre loading. They have reported the optimum mechanical properties for a fibre of length 30 mm. Cao *et al.* [14] reported on the mechanical properties of biodegradable composites reinforced with bagasse fibre and the optimum fibre content was 65%. Mwaikambo *et al.* [15] studied on the performance of cotton-kapok fabric-polyester composites and found that the tensile strength of the composites with untreated fibres was higher than that of composites prepared using treated fibres and the impact strength decreased with increase in fibre volume fraction for the composite. M. Bairdo *et al.* [16] investigated the fibre length distribution and the dependence of mechanical properties of the composite on fibre content of flax fibre-aliphatic polyester composites. K. Joseph *et al.* [17] reported on the mechanical properties of randomly oriented sisal fibre composites of several thermoset resin matrices (polyester, epoxy, phenol-formaldehyde) and a thermoplastic matrix (low density polyethylene). Properties were evaluated with respect to fibre length and fibre loading and they found that all composites showed a general trend of increase in properties with fibre loading. However the optimum length of the fibre required to obtain an increase in properties varied with the matrix. T. M. Gowda *et al.*[18] investigated the mechanical properties of untreated jute fabric-reinforced polyester composites and concluded that although the mechanical properties of jute-polyester composites do not possess strength and modulii as high as those of conventional composites, they do have better strength than wood composites. M. N. C. Martinez *et al.*[19] studied the physical and mechanical properties of Henequen fibres and concluded that it is possible to utilize them as a reinforcing agent in polymeric materials for the preparation of composite materials like other natural hard fibres. K. Okubo *et al.* [20] studied the effectiveness of bamboo fibre bundles as reinforcement for polymer matrix and proved that the tensile strength of the bamboo fibre bundle is as high as that of jute fibre. Geethamma *et al.* [21] investigated the effects of loading and orientation of coir fibres in natural rubber.

In composites, loads are not directly applied on the fibres but are applied to the matrix material and transferred to the fibres through the fibre ends and also through the cylindrical surface of the fibre near the ends. When the length of a fibre is much greater than the length over which the transfer of stress takes place, the end effects can be neglected and the fibre may be considered to be continuous. In the case of short fibre composites, the end effects cannot be neglected and the composite properties are a function of fibre length. In order to achieve the maximum level of stress in the fibre, the fibre length l_f must be at least equal to critical fibre length l_c., the minimum length of fibre required for the stress to reach the fracture stress of fibre. It is reported that the composites with fibre lengths $l_f < 5\ l_c$ has strength significantly lower than that of a continuous fibre composite with same volume fraction (V_f) of fibre. However the strength of short fibre composite increases with length of fibre for a given V_f and for length above 10 l_c, the difference between the strength of the two composites becomes equal [22]. Thus it is very important to optimize the fibre length for a particular matrix/fibre system so that maximum properties can be achieved.

In this chapter a detailed study on the tensile, impact and flexural properties of randomly oriented isora fibre reinforced polyester composites with special reference to the effect of fibre length and fibre loading is proposed. Fibre surface morphology and fibre-matrix adhesion is proposed to be analyzed by Scanning Electron Microscopy (SEM).

3.2. Results and Discussion

3.2.1. Tensile properties

3.2.1.1. Effect of fibre length

The tensile stress-strain curves of untreated short isora-polyester composites containing varying fibre length at constant fibre loading of 30 vol. % are given in Figure 3.1. Fibre lengths used for this study were 10, 20, 30, 40 and 50mm. The stress increases linearly with strain at low elongation. However at higher elongation, non-linear behaviour is observed for all lengths of fibre used.

It is obvious from the figure that for a given strain level, stress increased with fibre length up to 30mm. and then decreased.

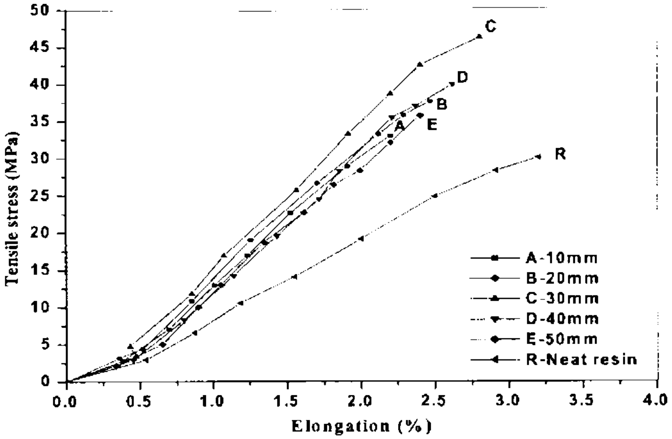


Figure 3.1. Variation of tensile stress with % strain of randomly oriented isora-polyester composites as a function of fibre length (fibre loading 30 % v/v)

The dependence of tensile properties of the composites on fibre length at a fibre loading of 30 vol. %, with standard deviation is given in Table 3.1. The variation of Tensile strength and Young's modulus of the composites is shown Figure 3.2. The tensile strength and Young's modulus of the composite increased linearly with fibre length and reached maximum at 30mm, then decreased for higher fibre lengths.

Table 3.1. Tensile properties of the composite as a function of fibre length (fibre loading 30% v/v)

Fibre length (mm)	Tensile strength (MPa)	Young's Modulus (MPa)	Elongation at break (%)
0 (Neat resin)	30.0 ± 2.0	1068 ± 40	3.2 ± 0.5
10	33.9 ± 2.2	1143 ± 46	2.2 ± 0.2
20	37.6 ± 2.8	1444 ± 59	2.3 ± 0.2
30	45.3 ± 3.6	1650 ± 68	2.6 ± 0.3
40	40.0 ± 2.5	1469 ± 64	2.5 ± 0.2
50	37.0 ± 2.1	1370 ± 59	2.4 ± 0.2

Curtis and Bader [23] found that the ends of fibre acted as notches and generated considerable stress concentrations, which could initiate micro cracks. Tensile strength is therefore low for smaller fibre length. Compared to 10mm, there is 34 % increase in the tensile strength and 44% increase in Young's modulus for 30mm. fibre-composite. Elongation at break value also is found to be maximum for this composite.

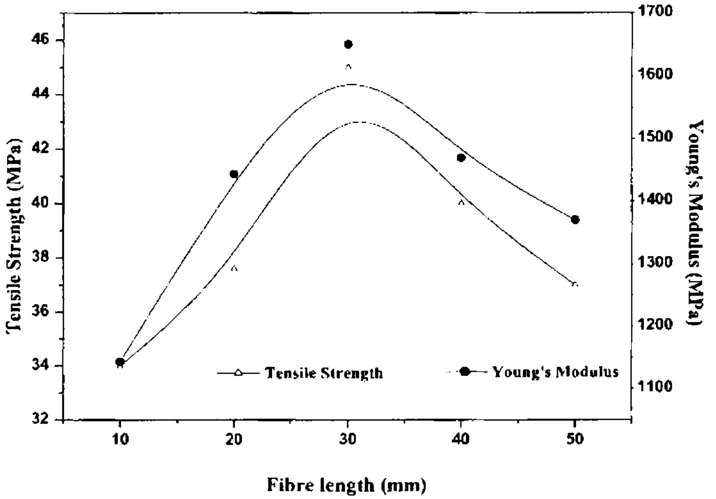


Figure 3.2. Variation of tensile strength and Young's modulus with fibre length of randomly oriented isora-polyester composites (fibre loading 30% v/v)

Hence 30mm can be taken as the optimum length for isora fibre at which effective stress transfer between the fibre and the matrix occurs. At higher fibre lengths, chances of fibre-fibre contact increase causing dispersion problems and fibre curling leading to shortening of effective fibre length below the critical value [12].

3.2.1.2. Effect of fibre loading

The stress-strain behaviour of randomly oriented isora-polyester composites at varying fibre loading is given in Figure 3.3. The tensile stress is found to increase with fibre loading and maximum was found to be at a loading of 34% by volume.

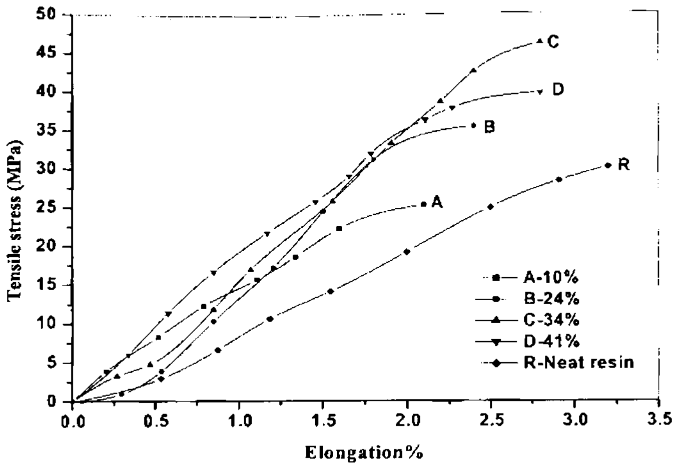


Figure 3.3. Variation of tensile stress with % strain of randomly oriented isora-polyester composite as a function of fibre loading (fibre length 30mm)

The dependence of tensile properties of randomly oriented isora-polyester composite on fibre loading with standard deviation is given in Table 3.2. The variation of tensile strength and Young's modulus of the composite with fibre loading is shown in Figure 3.4.

Table 3.2. Tensile properties of the composite as a function of fibre loading (fibre length 30mm)

Fibre loading (% v/v)	Tensile strength (MPa)	Young's Modulus (MPa)	Elongation at break (%)
0 (Neat resin)	30.0 ± 2.0	1068 ± 40	3.2 ± 0.5
10	26.2 ± 1.8	1342 ± 55	2.1 ± 0.2
24	36.4 ± 2.4	1617 ± 70	2.4 ± 0.2
34	49.2 ± 3.6	1755 ± 73	2.6 ± 0.3
41	39.6 ± 2.8	1700 ± 44	2.5 ± 0.3

It is reported that at low fibre loading, fibres act as flaws and the volume percent of the fibre is not enough to exceed the strength of the matrix [24].

The tensile properties show a linear increase after the initial decrease at 10% fibre loading and reached a maximum value at 34% loading.

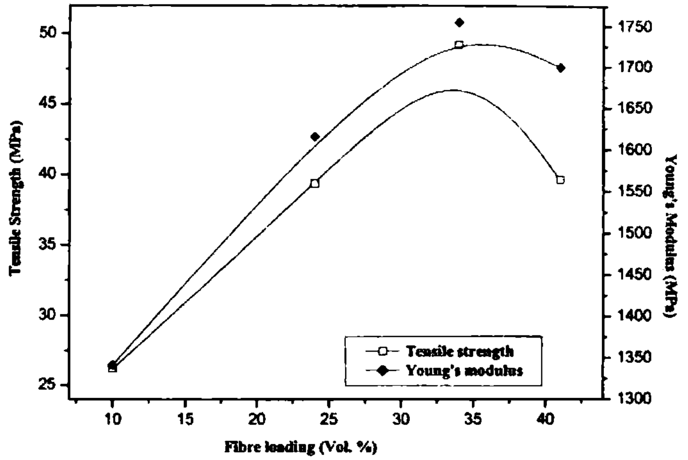


Figure 3.4. Variation of tensile strength and Young's modulus with fibre loading of randomly oriented isora-polyester composites (fibre length 30mm)

The increase in tensile strength and Young's modulus of the composite is 64 %, compared to neat resin. At 41% fibre loading, the properties decreased. So the optimum fibre loading is 34%, which is adequate for proper wetting of fibres with matrix resin. The decrease in tensile strength of the composites with further increase in fibre loading may be due to improper wetting and adhesion between fibre and resin resulting in inefficient stress transfer. Introduction of fibre into the polyester matrix lowers the elongation at break values, indicating improved stiffness of the composite compared to neat resin. On further fibre loading elongation at break values increased, reached a maximum value at 34% loading after which a decrease is observed.

Scanning electron microscopy (SEM) provides an excellent technique for examination of surface morphology of fibres and fracture surfaces of fibre composites. Figure 3.5 shows SEM photograph of untreated isora fibre surface. The multicellular nature of the untreated fibres is evident in the figure. The porosity of the fibres and their fibrillar structure is revealed from the fibre topography. The porous surface morphology is useful to provide better mechanical inter locking of the matrix in composite fabrication.

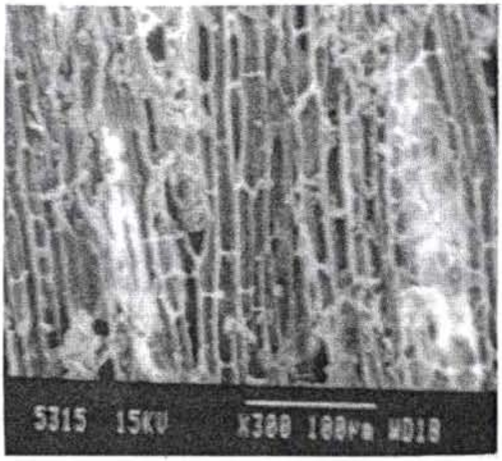
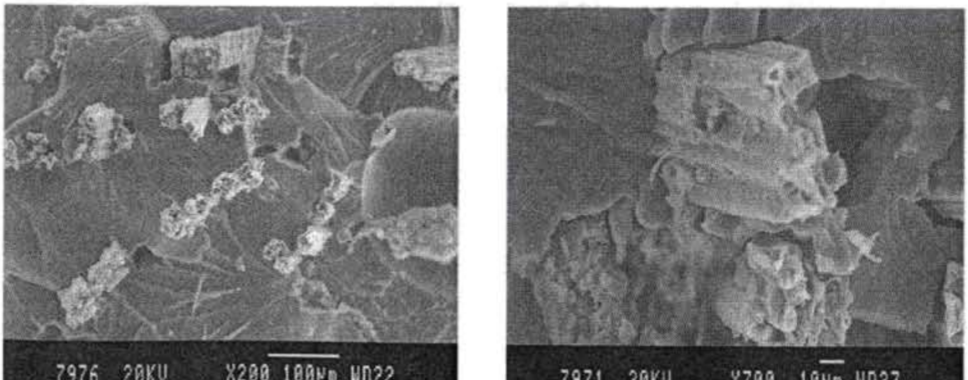


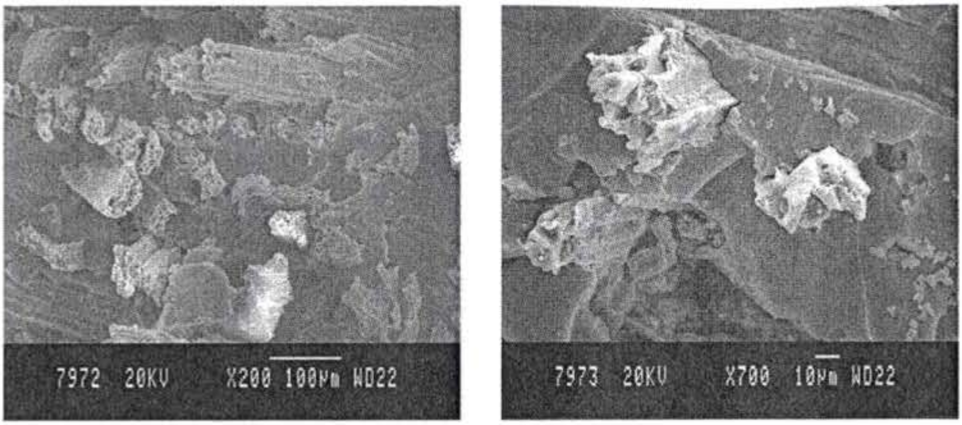
Figure 3.5. SEM photograph of untreated isora fibre surface (magnification × 300)

SEM photographs of the tensile fractured surface of short isora/polyester composites containing 24 and 34 vol.% fibre, are shown in Figures 3.6 and 3.7 respectively in two magnifications (a) and (b)



(a) (b)

Figure 3.6. Tensile fracture surface of randomly oriented isora-polyester composite **(a)** × 200 and **(b)** × 700 showing fibre pull out (fibre loading 24% v/v)



(a) (b)

Figure 3.7. Tensile fracture surface of randomly oriented isora-polyester composite (a) × 200 and (b) × 700 showing fibre pull out (fibre loading 34% v/v)

Figure 3.6 shows fibre pull out, debonding and fibrillation. At higher fibre loading, fibre-matrix adhesion is greater which is evident from the SEM photograph. (Figure 3.7)

3.2.2. Flexural Properties

Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis. The stresses induced due to the flexural load are combination of compressive and tensile stresses. For polymeric materials that break easily under flexural load, the specimen is deflected until rupture occurs in outer fibre layers.

3.2.2.1. Effect of fibre length

The stress-strain curves of untreated isora-polyester composites under flexure as function of fibre length at constant fibre loading of 30% by volume are given in Figure 3.8. In the case of neat polyester, the flexural stress showed linear relationship with strain. But the flexural behaviour of the composites is non linear. It is clear from the figure that for a given strain level flexural stress of the composites increased with fibre length up to 40mm and then decreased at 50mm.

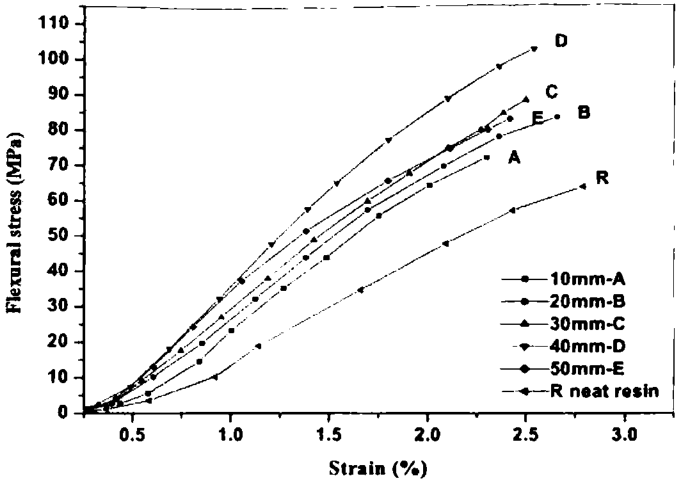


Figure 3.8. Variation of flexural stress with % strain of randomly oriented isora-polyester composites as a function of fibre length (fibre loading 30 % v/v)

The effect of fibre length on the flexural properties of untreated randomly oriented isora-polyester composites, at a fibre loading of 30 vol.%, with standard deviation is given in Table 3.3. Figure 3.9 shows the variation of flexural strength and flexural modulus of the composite with fibre length.

Table 3.3. Flexural properties of the composite as a function of fibre length (fibre loading - 30% v/v)

Fibre length (mm)	Flexural strength (MPa)	Flexural modulus (MPa)	Maximum strain (%)
0 (Neat resin)	60.0 ± 3.7	2628 ± 101	2.80 ± 0.15
10	71.0 ± 3.1	4658 ± 124	2.46 ± 0.12
20	82.0 ± 5.2	4756 ± 143	2.51 ± 0.13
30	92.0 ± 6.4	4828 ± 158	2.53 ± 0.13
40	107.0 ± 5.9	5650 ± 186	2.58 ± 0.14
50	83.0 ± 4.3	4998 ± 178	2.43 ± 0.12

The flexural strength and flexural modulus of the composites increased regularly with fibre length and is found to be maximum for the composite containing fibre of length 40mm as shown in Figure 3.9. Compared to the neat resin the increase in flexural strength and flexural modulus of the composite prepared using 40mm fibre is 78% and 115% respectively. Flexural strain of the composite also varied with fibre length in a similar manner.

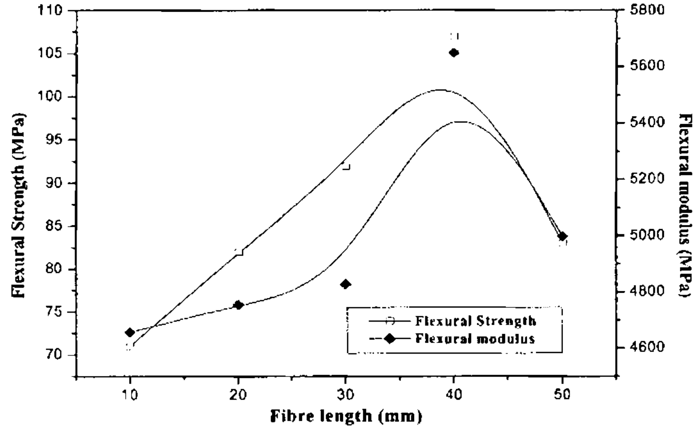


Figure 3.9. Variation of flexural strength and flexural modulus with fibre length of randomly oriented isora- polyester composite (fibre loading 30% v/v)

3.2.2.2. Effect of fibre loading

The effect of fibre loading on the stress-strain behaviour of untreated randomly oriented isora-polyester composite in flexure, using fibre of length 30 mm is given in the Figure 3.10. For a given strain level, the flexural stress increased with fibre loading and is maximum for 34% fibre loading.

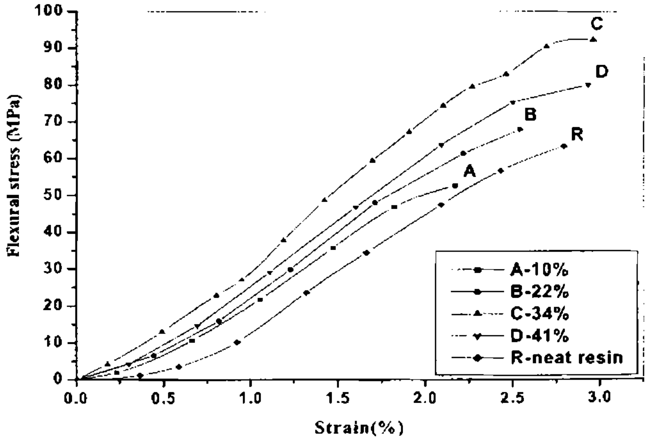


Figure 3.10. Variation of flexural stress with % strain of randomly oriented isora-polyester composites as a function of fibre loading (fibre length 30 mm)

The effect of fibre loading on the flexural properties of randomly oriented isora-polyester composite, with standard deviation is given in the Table 3.4. The variation of flexural strength and flexural modulus with fibre loading of the composite is shown in Figure 3.11. The flexural strength and flexural modulus of the composite containing 10% by volume fibre are lower than that of neat resin, which is due to inefficient stress transfer [24].

Table 3.4 - Flexural properties of the composite as a function of fibre loading (fibre length 30mm)

Fibre loading (% v/v)	Flexural strength (MPa)	Flexural modulus (MPa)	Maximum strain (%)
0	60 ± 3.7	2628 ± 101	2.80 ± 0.15
10	53 ± 2.5	2434 ± 110	2.17 ± 0.11
22	66 ± 3.0	3462 ± 140	2.92 ± 0.14
34	95 ± 4.5	4898 ± 200	3.19 ± 0.16
41	82 ± 4.1	4779 ± 180	2.93 ± 0.15

Flexural strength and flexural modulus of the composite increased linearly with fibre loading from 10% to 34%, the increase being 58% and 86% respectively compared to the neat resin. However when the fibre loading was increased further to 41%, the flexural strength decreased by 13.7% and flexural modulus by 2.5%. The initial increase in flexural strength with increasing fibre loading is due to increased interaction between fibre and matrix whereas the decrease of flexural strength at higher fibre content is due to increased fibre to fibre interaction and poor dispersion of fibres in the matrix.

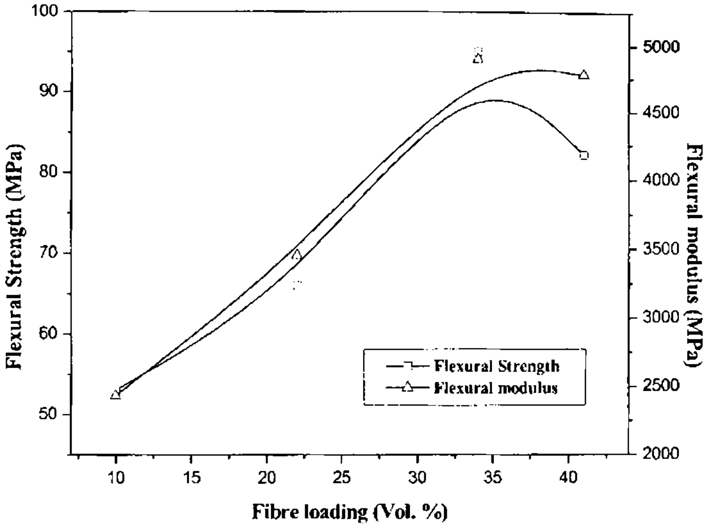


Figure 3.11. Variation of flexural strength and flexural modulus with fibre loading of randomly oriented isora- polyester composites (fibre length 30 mm)

3.2.3. Impact properties

The fracture toughness of the composites is one of the important engineering properties. Generally the impact strength may increase by the presence of fibres. The presence of filler can impede crack growth due to the possibility of imposing a greater tendency for plastic deformation in the matrix [25].

The dependence of Impact strength of untreated randomly oriented isora-polyester composites on fibre loading is given in Figure 3.12. The impact strength of the composites is increasing linearly with fibre loading up to 48% and shows a downward trend afterwards. Compared to neat resin, there is 231% increase in impact strength for the composite containing 48% fibre by volume.

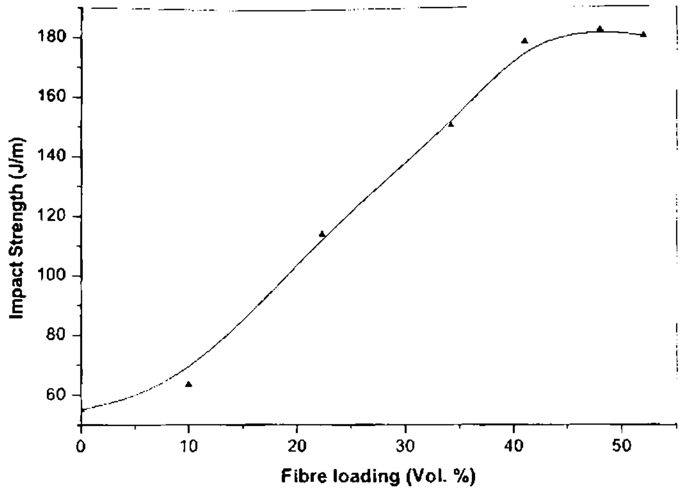


Figure 3.12. Variation of Impact strength with fibre loading of randomly oriented isora-polyester composites

The increase in impact strength is associated with an ability to produce an increase in the cohesive strength of the matrix or to the change in the distribution of stresses over a large area. During impact testing, the craze formed at a point of maximum strain grows until it meets another particle or till the stress concentration at the craze tip falls to zero. Thus instead of producing large crazes leading to cracks, when filler is present, a large number of micro cracks are formed. Another possibility that leads to enhance impact resistance is that of shear yielding in toughened plastics or a combination of crazing and yielding.

In the case of fibre reinforced resins the improvement in impact strength may also be attributed to the extra energy needed for the fibre pull out, debonding or redistribution of stress, involving creation of new surfaces. Factors affecting the mode of fracture in fibre reinforced composites are: (i) fibre and matrix strength (ii) load transfer efficiency (iii) resistance to crack propagation (iv) bond strength between fibre and matrix and (v) volume concentration of the fibre and its geometrical organization [26].

3.3. Theoretical modeling of tensile properties

The modulus of a material depends primarily on geometry, particle size distribution and concentration of the filler. In addition to the above factors, tensile strength depends strongly on the geometry of the filler particle and polymer/filler interaction. Several theories have been proposed to model the tensile properties of composite material. For determining the properties of randomly oriented fibres in a rigid matrix, Series and Hirsch's model are useful.

a) Series model

According to this model, tensile strength and modulus of the composite are given by the following equations

$$\sigma_c = \frac{\sigma_m \sigma_f}{\sigma_m V_f + \sigma_f V_m}$$

$$E_c = \frac{E_m E_f}{E_m V_f + E_f V_m}$$

Where E_c, E_m and E_f are the Young's moduli of the composite, matrix and fibre respectively. σ_c, σ_m and σ_f are the ultimate strength the composite, matrix and the fibre respectively [27].

b) Hirsch model

According to this model the tensile strength and modulus are calculated using the following equations

$$\sigma_c = x(\sigma_m V_m + \sigma_f V_f) + (1-x)\frac{\sigma_m \sigma_f}{\sigma_m V_f + \sigma_f V_m}$$

$$E_c = x(E_m V_m + E_f V_f) + (1-x)\frac{E_m E_f}{E_m V_f + E_f V_m}$$

where 'x' is a parameter between 0 and 1 and it is reported that 'x' determines the stress transfer between the fibre and matrix [28]. For calculations, the value of x was varied to obtain best-fit values with experimental results.

Theoretical values of tensile strengths were calculated using above models and is compared with the experimental values as in Figure 3.13. It is observed that the theoretical tensile strength values of the composite are comparable to the experimental values except at 10% and 41% fibre loading.

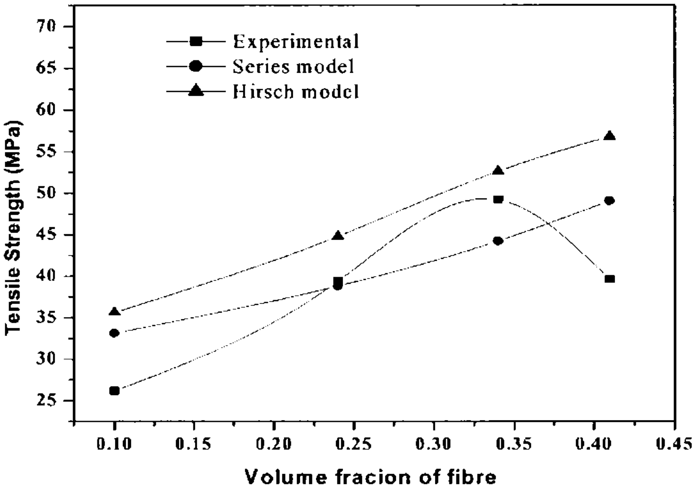


Figure 3.13. Comparison of experimental and theoretical tensile strength values of randomly oriented isora-polyester composites

Theoretical Young's modulus values calculated using Series and Hirsch models are compared with the experimental values in Figure 3.14. It is observed that Hirsch model values are in good agreement with experimental values up to 34%loading. Series model values are lower than the experimental values up to 34% loading. The deviations arise because the interaction between the components is not taken into consideration in series model. According to this model, the fibre and matrix exist as two components without any adhesion. But in actual composite system there is a chance of interaction between the components depending on the chemical nature of the constituents.

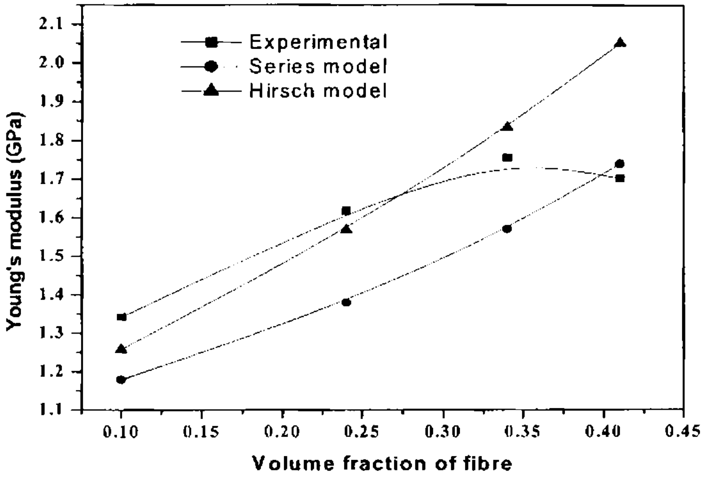


Figure 3.14. Comparison of experimental and theoretical Young's modulus values of randomly oriented isora-polyester composites

3.4. Conclusion

The tensile strength, Young's modulus and elongation at break of randomly oriented isora-polyester composites increased with fibre length and reached a maximum for 30mm length. There is an initial reduction in tensile strength of polyester at 10% fibre loading. After that the tensile strength increased with fibre loading and attained maximum value at 34% fibre loading. A decrease in tensile strength is observed for higher loadings.

Flexural strength, flexural modulus and flexural strain of the composite were maximum for a fibre length of 40mm and for a fibre loading of 34% by volume. The impact strength of the composite increased linearly with fibre loading and is maximum at 48% fibre loading, after which the change is negligible.

References:

[1] Zafeiropoulos N. E., Baillie C. A., Marrhews F. L., *Composites: Part A* (2001) **32:** 25.

[2] Tripathy S. S., Di Landro L., Fontanelli D., Marcetti A, Levita G. *J. Appl. Polym. Sci.* (2000) **75:**1585.

[3] Paramasivan T. Abdul Kalam A. P. J., *Fibre Sci. Tech.* (1974) **7:** 85.

[4] Mc Laughlin E. C., *J. Mater. Sci.* (1980) **15:** 886.

[5] Satyanarayana K. G., Sukumaran K., Kulkarni A. G., Pillai S. G. K., Rohatgi P. K., *Composites,* (1986) **17:** 329.

[6] Bledzki A. K., Gassan J., *Prog. Polym. Sci.,* (1999) **24:** 221.

[7] Sanadi A. R, Prasad S.V, Rohatgi P. K. *J. Mater. Sci.* (1986) **21:** 4299-304.

[8] Pavithran C., Mukherjee P.S., Brahmakumar M., Damodaran A. D., *J. Mater. Sci. Lett.* (1987) **6:** 882-884.

[9] White N. M., Ansell M. P., *J. Mater. Sci.* (1983)**18:**1549-56.

[10] Lovely M., Joseph K. U. and Rani J. *Prog In Rubb Plast and Recycling Technol,* (2004) **20(4):** 337.

[11] Callister W. D., Jr., *Materials Science and Engineering,* John Wiley and Sons, Inc., New York, (1985).

[12] Pothan L. A., Thomas S., Neelakandan N. R., *J. of Reinforced Plastics and Composites (*1997) **16(8):** 744-765.

[13] Uma Devi L., Bhagavan S. S., Thomas S., *J. Appl. Polym. Sci.* (1997) **64:**1739.

[14] Cao Y., Shibata S., Fukumoto I., *Composites: Part A* (2006) **37:** 423-429.

[15] Mwaikambo L.Y., Bisanda E.T. N., *Polymer Testing* (1999)**18:**181-198.

[16] Baiardo M., Zini E., Scandola M., *Composites: Part A* (2004) **35:** 703-710.

[17] Joseph K., Varghese S., Kalaprasad G., Thomas S., Prasannakumari L., Koshy P. and Pavithran C., *Eur. Polym. J.* (1996) **10:** 1243-1250.

[18] Gowda T. M., Naidu A. C. B., Chhaya R., Composites: *Part A* (1999) **30:** 277-284.

[19] Martinez M. N. C., Franco P. J. H., Gonzalez-chi P. I., Vega M. A., *J. Appl. Polym. Sci.* (1991) **43:** 749-756.

[20] Okubo K., Fujii T., Yamamoto Y., *Composites: Part A* (2004) **35:** 377-383.

[21] Geethamma V. G., Mathew K. T., Lakshminarayanan R., Thomas S., *Polymer*, (1998) **39(6-7):**1483-1491.

[22] Mathews F. L., Rawlings R. D., *Copmposite materials, Engineering and Science,* Chapman & Hall, (1994) Ch. 10.

[23] Curtis P. T. and Bader M. G., *J. Mater. Sci.* (1978) **3:** 377.

[24] Milewski J. V. and Katz H. S., *Handbook of Reinforcements for Plastics,* Van Nostrand Reinhold, N. Y., (1987).

[25] Nair K. C. M., Diwan S. M., Thomas S., *J. Appl. Polym. Sci.*(1996) **60:**1483-1497.

[26] Sheldon R. P., *Composite Polymeric Materials,* Applied Science Publishers, 1982

[27] Broutman L. J. and Krock R. H., *Modern composite materials,* AddisonWesley, Reading, MA, 1967.

[28] Kalaprasad G., Joseph K., Thomas S., *J. Mater. Sci.* (1997) **32:** 4261.

Chapter 4

ALKALI TREATED RANDOMLY ORIENTED ISORA FIBRE REINFORCED POLYESTER COMPOSITES

Abstract

Short isora fibre has been modified with alkali treatment to improve the interfacial bonding with unsaturated polyester resin. The effect of alkali treatment on the surface morphology has been characterized by IR Spectroscopy and SEM studies. The effect of concentration of alkali and duration of alkali treatment on the properties of the composite was evaluated and optimised. Tensile, flexural and impact performance of the composites showed enhancement, compared with that of untreated fibre composite.

4.1. Introduction

Lignocellulosic fibres are highly hydrophilic in nature and show poor wetting behaviour with hydrophobic organic polymer matrices, which leads to a weak bond at the interface [1-3]. The quality of the fibre–matrix interface is significant for the application of natural fibres as reinforcement fibres. Physical and chemical methods can be used to optimize this interface. These modification methods are of different efficiency for the adhesion between matrix and fibre [4]. An old method of cellulose fibre modification is mercerization, which has been widely used on natural fibres. Mercerization is an alkali treatment of cellulose-fibres; which depends on the type and concentration of the alkaline solution, its temperature, time of treatment, tension of the material as well as on the additives [5, 6]. Optimal conditions of mercerization ensure the improvement of the tensile properties [2,7,8] and absorption characteristics [2,4,5], which are important in the composing process. As discussed in Chapter 1, cellulose forms the main structural component of vegetable natural fibres, the non-cellulosic components, e.g. lignin and hemicellulose, also play an important part in the characteristic properties of the fibres. Hemicellulose, which is thought to consist principally of xylan, polyuronide and hexosan, has shown to be very sensitive to the action of caustic soda, which exerts only a slight effect on lignin or α-cellulose. Studies about the alkali treatment of jute-fibres, for instance, report about the removal of lignin and hemi cellulose, which improves the tensile characteristics of the fibres [9]. When natural fibres are stretched, such rearrangements amongst the fibrils would result in better load sharing by them and hence result in higher stress development in the fibre. In contrast, softening of the inter-fibrillar matrix adversely affects the stress transfer between the fibril and thereby the overall stress development in the fibre under tensile deformation. As lignin is removed gradually, the middle lamella joining the ultimate cells is expected to be more plastic as well as homogeneous due to the gradual elimination of microvoids, while the ultimate cells themselves are affected only slightly. Additionally, treatment with NaOH leads to a decrease in the spiral angle, i.e. closer to fibre axis, and increase in molecular orientation. A fair amount of randomness is introduced in the orientation of the crystallites due to the removal of non-cellulosic matter [10]. The elastic moduli of fibres, for instance, are expected to increase with increasing degree of molecular orientation. Well-oriented cellulosic fibres such as flax have much higher Young's modulus than fibres with medium orientation, such as cotton. In addition to the modification of orientation and the consolidation of weak points, other important factors with regard to the mechanical properties could be the crystallite length and degree of crystallinity as well as the removal of fractions of cellulose at a very low degree of polymerization. Tests made by Prasad *et al.* [11] on leather fibres, and by Chand *et al.* [12] on sisal fibres showed distinct index changes achieved by an alkalization process in 8% NaOH solution. An increase of 25% in tensile strength was reached in leather fibres and of 100% in sisal fibres-also depending on the respective soaking time. In addition to the increase of the mechanical properties through alkalization [11-13], an increase of composite quality is to be expected of laminates due to the improved fibre–matrix adhesion. In the fibre extraction (pull-out test), the cohesion of polyester resin alkalized coconut and sisal fibres were characterized by Prasad *et al.* [11] and by Chand *et al.*[12]. The pull-out load of alkalized sisal fibres increased considerably up to an alkalizing time of 90 hours. After that, the pull out load as well as the adhesion decreased distinctly. A principally similar debonding stress was registered with coconut-fibre–polyester composites [11]. Ray *et al.* [14] investigated the mechanical properties of vinyl ester matrix composites reinforced with alkali treated jute fibres and found that the modulus and tenacity of the fibre were increased by the treatment with alkali. They also found that the fibre pull out was predominant for 2 hour alkali treated fibres, while for 8 hour alkali treated fibres, it was fibre fracture and the combined mode of fracture occurred in between. The mechanical properties of mercerized banana fibre reinforced polyester composites were studied by Pothen *et al.* [15].

In this chapter a detailed study on the tensile, impact and flexural properties of alkali treated randomly oriented isora fibre reinforced polyester composites with special reference to the effect of treatment time and concentration of alkali is proposed. The effect of chemical modification of the fibre surface is proposed to be analysed by IR spectroscopy. Fibre surface morphology and fibre-matrix adhesion on alkalization will be analysed by Scanning Electron Microscopy (SEM).

4.2. Results and discussion

4.2.1. IR Spectroscopy

4.2.1.1. Untreated fibre:

The IR spectra of untreated (U) and alkali treated (A) isora fibre is given in Figure 4.1. 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 3300-3320 cm^{-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 and 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.

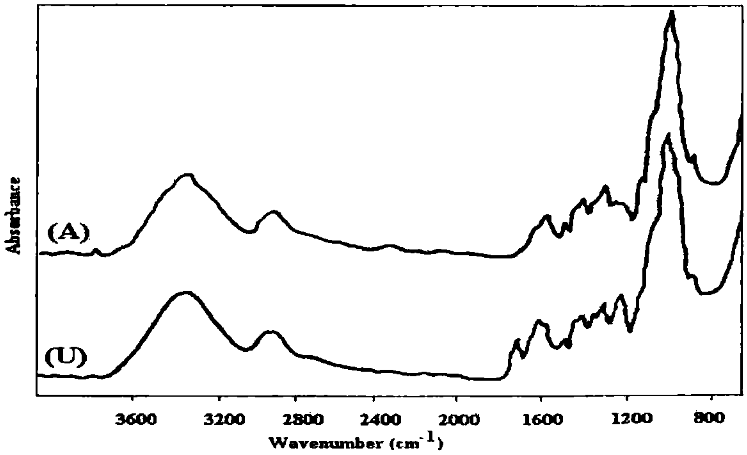


Figure 4.1. IR spectra of untreated (U) and alkali treated (A) isora fibre

4.2.1.2. 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}. Also, on mercerization, the peak at 1730 cm^{-1} in the spectrum of the raw fibre 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.

4.2.2. Morphology of alkali treated fibre:

Figure 4.2 shows SEM photograph of alkali treated isora fibre surface. On alkali treatment, the pores became clearer and the fibres became thinner. This may be due to the dissolution and leaching out of hemi cellulose and lignin components of the fibre. This roughened the fibres, enhancing the mechanical interlocking at the surface.

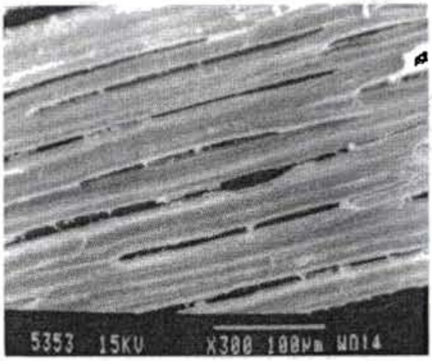
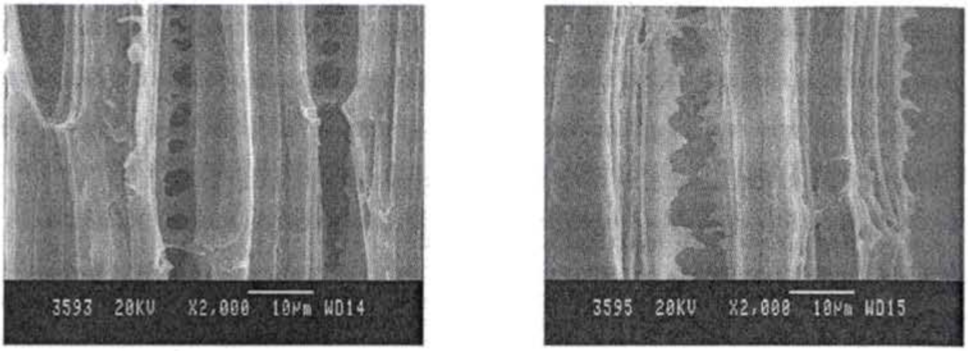


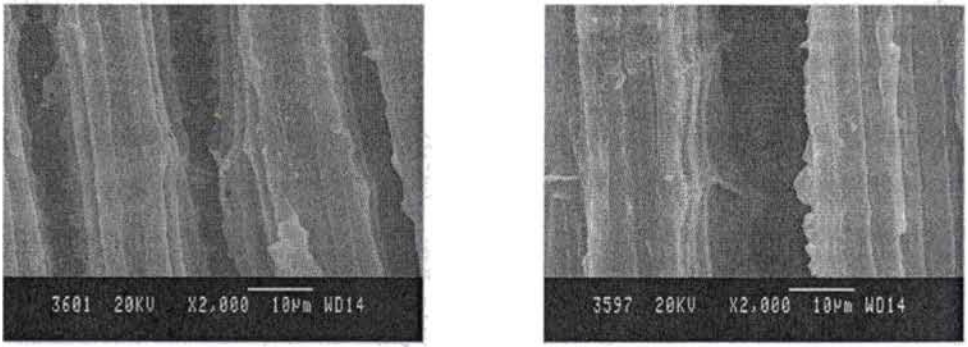
Figure 4.2. SEM photograph of alkali treated isora fibre surface (magnification × 300)

4.2.2.1. Effect of duration of alkali treatment on the morphology of the fibre

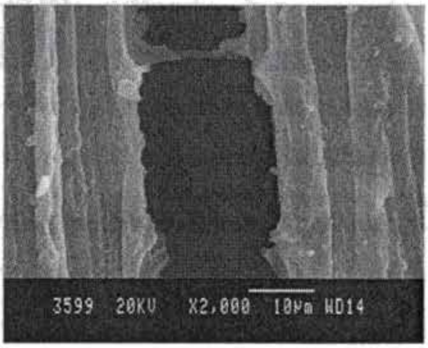
Isora fibre is a composite material with fibrous reinforcement and a mixture of hemi cellulose and lignin as matrix. SEM photographs of the alkali treated fibre at various time intervals of treatment in alkali (5% NaOH) are given in Figure 4.3. When the treatment time of the fibre in alkali was increased, it can be seen that the materials in the interfibrillar region were obviously etched away and the fibrous region became more pronounced as interfibrillar region is removed. SEM picture of the untreated isora fibre (Fig. 3.5) shows 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.



(a) 4 hours **(b) 12 hours**



(c) 24 hours **(d) 48 hours**



(e) 72 hours

Figure 4.3. SEM photographs of alkali treated fibres (at different time intervals of soaking in alkali) at magnification × 2000

When the fibres are treated 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 4.3. When the treatment time was increased to 24-48 hours, a much greater proportion of the tyloses is found to be removed. At still higher treatment time, the SEM pictures show complete exposure of the fibrils indicating the leaching of the intercellular binding material and the cuticle layer.

4.2.3. Tensile properties

4.2.3.1. Effect of duration of alkali treatment

Isora fibres of length 30mm. were treated with 5% alkali solution [16] for 2, 4, 6, 8, 10 and 12 hours. Randomly oriented fibre composites were prepared using these fibres. The effect of treatment time of alkali on the tensile properties of the composites, with standard deviation is given in Table 4.1. Variation of tensile strength and Young's modulus with duration of alkali treatment of composites containing 22 vol. % fibre is shown in Figure 4.4. Maximum tensile strength and modulus was obtained for 4 hour treatment after which the values decreased steadily.

Table 4.1. Effect of duration of alkali treatment on tensile properties of the composite (Concentration of NaOH 5%, fibre loading 22 % v/v)

Duration (hours)	Tensile strength (MPa)	Young's Modulus (MPa)	Elongation at break (%)
2	30 ± 2.0	2269 ± 80	1.46 ± 0. 08
4	33 ± 1.7	2464 ± 102	1.41 ± 0.07
6	31.5 ± 2.1	2392 ± 95	1.37 ± 0.05
8	30.5 ± 2.2	2340 ± 90	1.28 ± 0.06
12	30 ± 2.0	2300 ± 86	1.22 ± 0.06

The increase in tensile strength is 9% and modulus 8.5%, compared to 2 hour treated fibre composite. Elongation at break values of the composite decreased with increase in duration of treatment indicating improved stiffness. Compared to untreated fibre composite (Table 3.2), the elongation at break values of the composite are smaller indicating enhanced brittleness of the composite on alkalization of the fibre. So the optimum time of alkali treatment is 4 hours for which the properties are maximum. Varada Rajulu *et al.* [17] reported that for the lignocellulosic fabric *Hildegardia* the properties were maximum on treatment of the fabric with 5% NaOH for 4 hours.

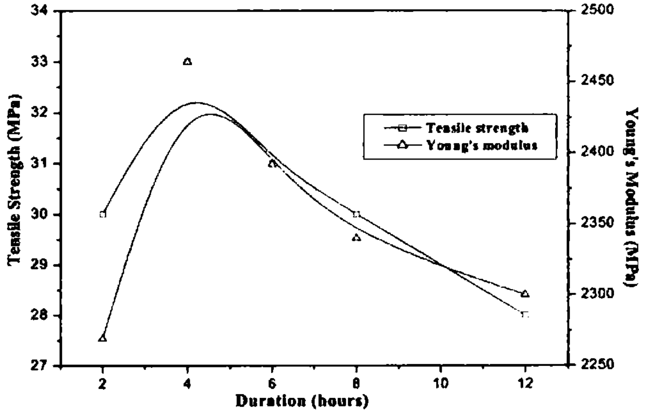


Figure 4.4. Variation of tensile strength and Young's modulus with duration of alkali treatment of randomly oriented isora-polyester composite (fibre loading 22% v/v)

4.2.3.2. Effect of concentration of alkali treatment

Isora fibres of length 30mm were treated with alkali solutions of varying concentrations of 0.5, 1, 2, 4 and 5% for 4 hours and randomly oriented isora-polyester composites were prepared using these fibres. The tensile properties of the composites, with standard deviation are given in Table 4.2. Variation of tensile strength and Young's modulus of the composite with concentration of alkali is shown in Figure 4.5. Maximum tensile strength was obtained for 1% alkali treated fibre composite, the increase being 27% compared to the untreated fibre composite (Table 3.1). At higher concentrations of alkali, tensile strength decreased steadily. Similar results were reported for bagasse fibre in an aliphatic polyester matrix [18]. Young's modulus values of the composite showed a sharp increase of 12.4% when alkali concentration is increased from 0.5% to 1%, but for higher concentrations of alkali, only marginal increase is observed. The improvement in tensile properties can be attributed to the improved wetting of alkali treated fibre with polyester [11].

Table 4.2. Effect of concentration of alkali on tensile properties of the composite (fibre loading 22 % v/v, duration: 4 hours)

Alkali concentration (% w/v)	Tensile strength (MPa)	Young's Modulus (MPa)	Elongation at break (%)
0.5	37 ± 2.5	2025 ± 81	2.40 ± 0.11
1	47 ± 2.8	2276 ± 85	2.26 ± 0.10
2	42 ± 2.1	2310 ± 96	2.96 ± 0.14
4	36 ± 1.8	2336 ± 102	1.55 ± 0.09
5	33 ± 1.7	2336 ± 102	1.41 ± 0.07

On alkali treatment, lignin and hemi cellulose, the cementing materials present in the fibre, get dissolved. This makes the interfibrillar region less dense and less rigid as a result of which the fibrils become more capable of orienting themselves along the tensile deformation [19].

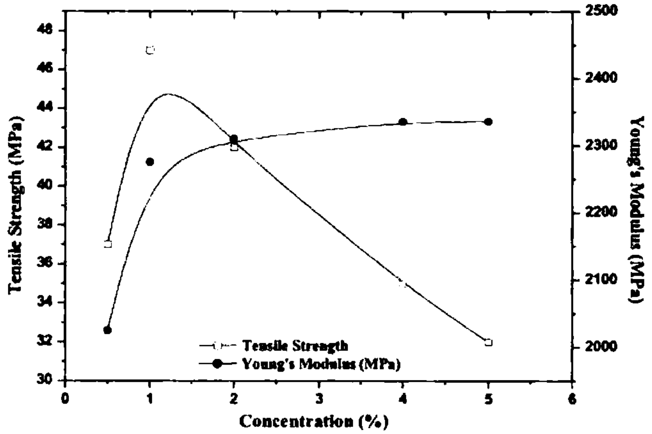
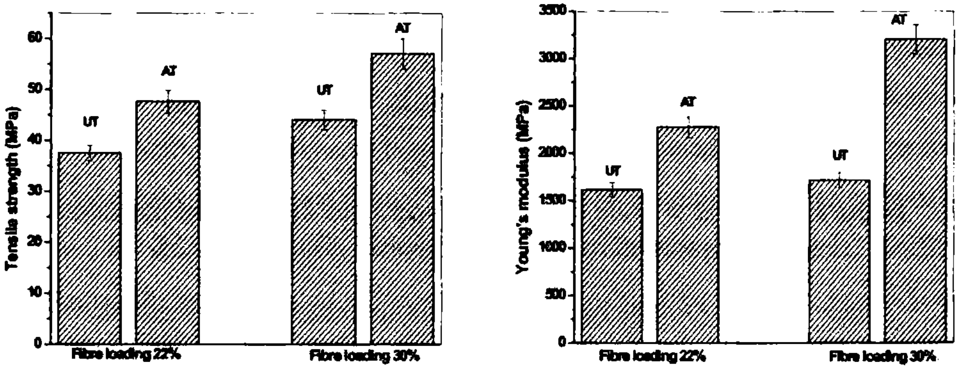


Figure 4.5. Variation of tensile strength and Young's modulus with alkali concentration, of randomly oriented isora-polyester composite (fibre loading 22 % v/v)

Many authors [20-23] have reported on the change in crystallinity through alkali treatment for coir [11, 20], flax [21], cotton [22] and jute [23] fibres. The increase in the percentage crystallinity index of alkali treated fibres occurs because of the removal of the cementing materials, which leads to a better packing of cellulose chains and enhanced mechanical properties. More than that increase in surface area of the fibre occurs due to the dissolution of lignin, hemi cellulose and alien substances associated with the fibre. Alkali treatment cleans the surface debris and develops micro porosity with many pits and holes on the fibre surface by the removal of globular protrusions of fibre surface present in the untreated fibre. This leads to a larger area of contact and greater mechanical interlocking between fibre and matrix, making the interfacial adhesion stronger and the mechanical properties higher. Moreover, alkali treatment leads to fibre fibrillation, i.e. breaking down of the composite fibre bundle into smaller fibres. In other words, alkali treatment reduces fibre diameter and thereby increases the aspect ratio [24]. The decrease in tensile properties in the case of higher alkali concentration may be due to cell wall thickening, which leads to poor adhesion with polyester resin. So optimum concentration of alkali is 1% for which the properties are maximum.

4.2.3.3. Effect of fibre loading

The variation of tensile strength and Young's modulus of the composite with alkali treatment of the fibre, at two different fibre loadings are given in Figures 4.6 (a) and (b) respectively. On alkali treatment (AT) there is 27% increase in tensile strength at 22% fibre loading whereas 30% increase is observed at 30% fibre loading compared to untreated fibre composite (UT).



(a) (b)

Figure 4.6. Variation of (a) tensile strength and (b) Young's modulus with fibre loading of alkali treated randomly oriented isora-polyester composite

The corresponding increase in Young's modulus values are 41% and 86% respectively.

4.2.4. Flexural properties

4.2.4.1. Effect of duration of alkali treatment

The effect of fibre treatment time of alkali on the flexural properties of randomly oriented isora-polyester composite, with standard deviation is given in Table 4.3 and the variation of flexural strength and flexural modulus of the composite are shown in the Figure 4.7.

Table 4.3. Effect of duration of alkali treatment on Flexural properties (Concentration of NaOH-5%, fibre loading -22 % v/v)

Duration (hours)	**Flexural strength (MPa)**	**Flexural Modulus (MPa)**	**Maximum strain (%)**
0	60 ± 3	2628 ± 115	2.85 ± 0.14
2	65 ± 3.1	3957 ± 140	2.59 ± 0.13
4	74 ± 3.5	4250 ± 160	2.75 ± 0.14
6	70 ± 3.3	4210 ± 155	2.49 ± 0.12
8	68 ± 3.2	4155 ± 148	2.71 ± 0.15
12	63 ± 3.1	3970 ± 140	2.52 ± 0.12

Compared to neat resin, the increase in flexural strength and flexural modulus for the 2 hour treated composite are 8.3% and 50% respectively. The flexural strength, flexural modulus and flexural strain values are maximum for 4 hour treated fibre composite. The increase in flexural strength and flexural modulus when compared to 2 hour treated composite are 14% and 7.5% respectively.

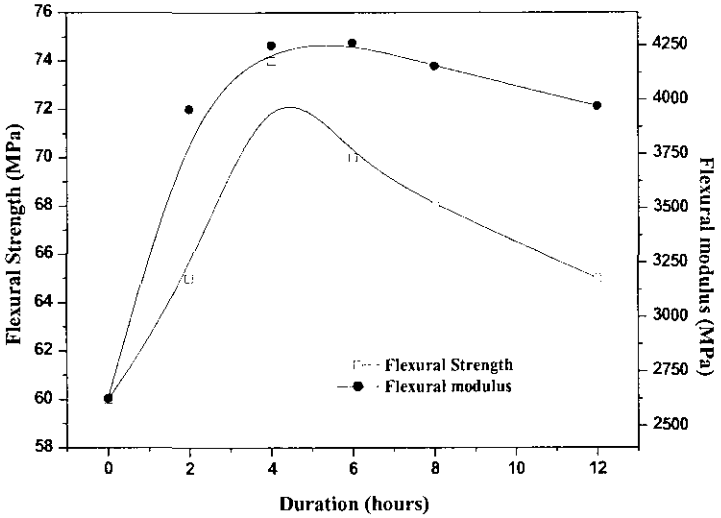


Figure 4.7. Variation of flexural strength and flexural modulus with duration of alkali treatment of randomly oriented isora-polyester composite (fibre loading 22 vol.%)

The increase in flexural strength and flexural modulus on alkali treatment of the fibre can be attributed to the improved wetting of the treated fibre with polyester. The optimum treatment time is 4 hours. A marginal increase in flexural properties was observed by Boynard *et al.*[25] for alkali treated sponge gourd fibre reinforced polyester matrix composites, which is attributed to improved mechanical interlocking by the removal of outer surface of the fibres with the exposition of the inner fibrillar structure and consequent increase of the fibre surface area.

4.2.4.2. Effect of concentration of alkali treatment

The effect of concentration of alkali on the flexural properties of randomly oriented isora fibre-polyester composites, with standard deviation is given in Table 4.4. The variation of flexural strength and flexural modulus of the composites are shown in the Figure 4.8.

Table 4.4. Effect of concentration of alkali on flexural properties of the composite (duration-4 hours, fibre loading-22 % v/v)

Alkali concentration (% w/v)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Maximum Strain (%)
0	66 ± 3	3462 ± 115	2.92 ± 0.14
0.5	79 ± 3.8	3820 ± 140	2.52 ± 0.13
1	83 ± 4.0	3900 ± 145	2.56 ± 0.12
2	78 ± 3.8	3940 ± 160	2.91 ± 0.15
4	75 ± 3.6	3933 ± 152	2.80 ± 0.14
5	74 ± 3.6	3933 ± 152	2.75 ± 0.13

Flexural strength of the composites increased with concentration of alkali and is maximum for 1% concentration. For higher concentration of alkali, flexural strength decreases. Flexural modulus of the composites also increased with concentration of alkali and reached a maximum value for an alkali concentration of 2%, after which a leveling effect is observed. Flexural strain of the composite increased with alkali concentration, attained maximum value for 2% concentration and then decreased for higher concentrations. The improvement of flexural strength and flexural modulus of the composite is attributed to the formation of rough fibre surface on alkali treatment leading to the improved wetting of fibres with the matrix.

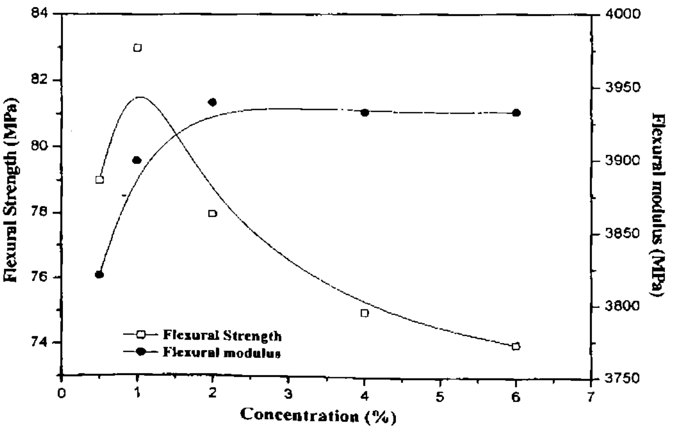
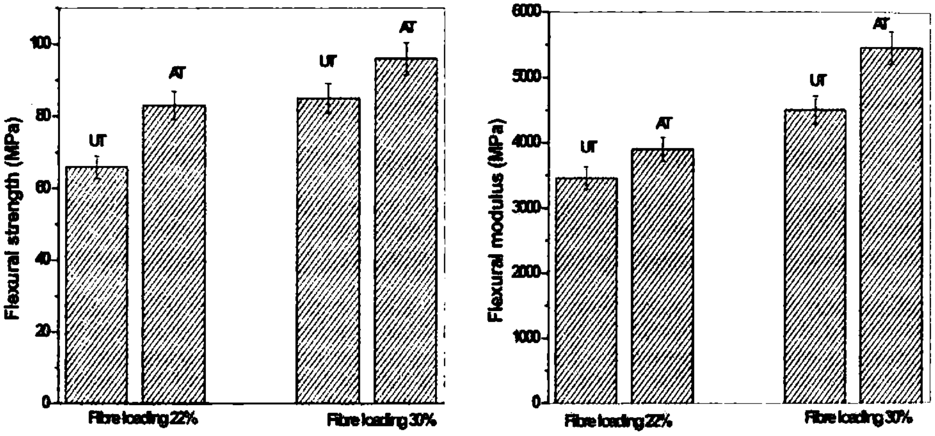


Figure 4.8. Variation of flexural strength and flexural modulus with concentration of alkali treated randomly oriented isora-polyester composite (fibre loading 22 vol. %)

4.2.4.3. Effect of fibre loading

The variation of flexural strength and flexural modulus of the composite with alkali treatment of the fibre, at two different fibre loadings are given in Figures 4.9 (a) and (b) respectively. On alkali treatment there is 26% increase in flexural strength of the composite at 22% fibre loading, whereas 13 % increase is observed at 30% fibre loading, compared to untreated fibre composite. The corresponding increase in flexural modulus values of the composite are13% and 21% respectively.



(a) (b)

Figure 4.9. Variation of (a) flexural strength and (b) flexural modulus with fibre loading, of alkali treated randomly oriented isora-polyester composite

4.2.5. Impact strength

4.2.5.1. Effect of alkali treatment

The impact performance of fibre-reinforced composites depends on many factors including the nature of the constituent, fibre/matrix interface, the constitution and geometry of the composite and test conditions. The impact failure of a composite occurs by factors like matrix fracture, fibre/matrix debonding and fibre pull out. Fibre pull out is found to be an important energy dissipation mechanism in fibre reinforced composites [26]. The applied load transferred by shear to fibres may exceed the fibre/matrix interfacial bond strength and then debonding occurs. When the stress level exceeds the fibre strength, fibre fracture occurs. The fractured fibres may be pulled out of the matrix, which involves energy dissipation [27].

On alkali treatment, the impact strength of the composite containing 30% fibre by volume increased by 27%. Based on the above discussion, the increase in impact strength can be accounted. Evidence for debonding in the untreated fibre composite and fibre/matrix adhesion in the alkali treated fibre composite are obtained from the SEM photographs (Figure 4.11).

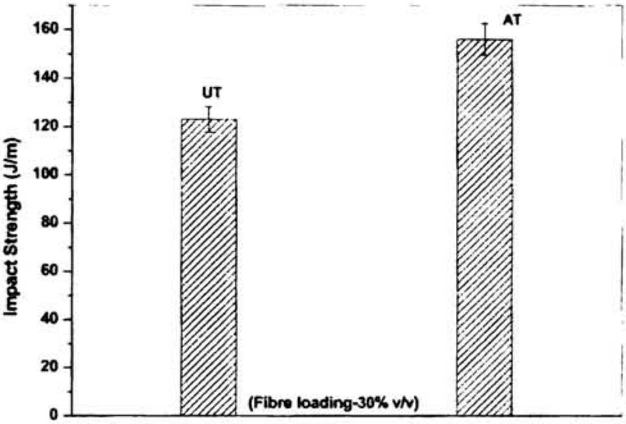
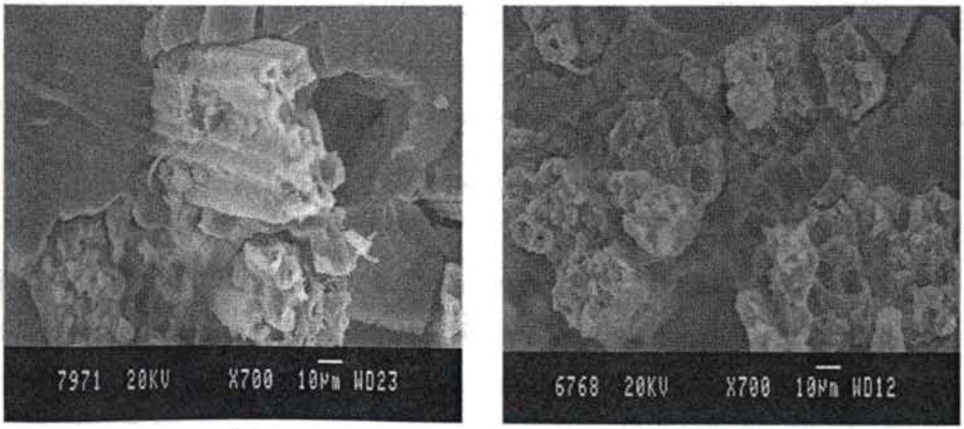


Figure 4.10. Effect of alkali treatment on the impact strength of randomly oriented isora-polyester composite



(a) (b)

Figure 4.11. SEM photographs of the tensile fractured surface of (a) untreated and (b) alkali treated isora-polyester composite (× 700)

4.2.5.2. Effect of duration of alkali treatment

The dependence of impact strength of randomly oriented isora-polyester composite on treatment time of the fibre in alkali is given in the Figure 4.11. Compared to 2-hour treated fibre composite, the impact strength of the 4-hour treated fibre composite is lower. After that the impact strength increased for longer treatment time. Ray *et al.* [14] observed that in composites having weak interfacial bonding the crack propagated along the fibre/matrix interface causing debonding which leads to significant increase in the energy absorbing capacity of the composites as a result of the large new surfaces produced and frictional work resulting from differential displacement between matrix and fibre thereby increasing the impact fatigue resistance of the composites.

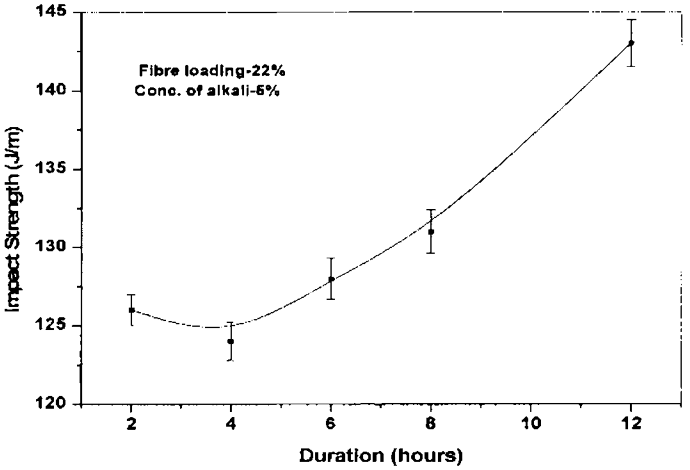


Figure 4.11. Variation of impact strength with duration of alkali treatment of randomly oriented isora-polyester composite

Cook and Gordon [28] have reported that weak fibre/matrix interface will result in tough composites that itself is formed from two brittle phases. The opening up of a new surface at the interface will result in absorption of energy, crack diversion and so forth.

The fibre/matrix adhesion to a great extent determines the strength of the composites. A weak interface will not facilitate efficient stress transfer and the resultant composite will also be weak. But the toughness of the composite will be high. So the composites having strong interface will have low toughness value compared to that of one having weaker interface. The low impact strength of the 4-hour alkali treated fibre composite is assumed to be due to the strong interface as evidenced from the mechanical properties of the composite. This results in the fracture of the fibre at the crack-plane with little fibre pull out causing decrease in toughness and hence the impact strength of the composite. The higher values of impact strength for other composites can be attributed to the increase of toughness of the composite with fibres treated with alkali for longer time.

4.3. Conclusion

The tensile strength and Young's modulus values of alkali treated randomly oriented isora-polyester composite were found to be maximum for a fibre treatment time of 4 hours. The elongation at break of the composite decreased with treatment time. An alkali concentration of 1% yielded maximum tensile strength while a concentration of 4% yielded maximum modulus for the composite. Flexural properties of the composite also showed a similar dependence on alkali treatment time and alkali concentration. The impact strength of the composite decreased with alkali treatment time of fibre and attained a minimum value for 4 hour treatment. However, with prolonged treatment, impact strength increases.

References

[1] Roe P. J., Ansell M. P., *J. Mater. Sci.* (1985) **20:** 4015.

[2] Sridhar M. K., Basavarappa G., Kasturi S. G., Balasubramaniam N., *Ind. J.Technol.* (1984) **22:** 213.

[3] Mukherjee R. N., Pal S. K., Sanyal S. K., Phani K. K., *J. Polym. Mater.* (1984) **1:** 69.

[4] Bledzki A. K., Reihmane S., Gassan J., *J. Appl. Polym. Sci.* (1988) **36:** 523-534.

[5] Nevell T. P, Zeronian S. H., *Cellulose chemistry and its applications*. New York: Wiley, (1985).

[6] Safonov V. V. *Treatment of textile materials*. Moscow: Legprombitizdat, (1991).

[7] Ugbolue S. C. O. *Text Inst* (1990) **20(4):** 41–43.

[8] Kroschwitz J. I. *Polymers: fibres and textiles*. New York: Wiley, (1990).

[9] Bledzki A.K., Gassan J., *Prog. Polym. Sci. (1999)* **24:** 221–274.

[10] Sreenivasan S., Bahama Iyer P, Krishna Iyer K. R., *J. Mater. Sci*(1996) **31:** 721.

[11] Prasad S. V., Pavithran C., Rohatgi P. K., *J. Mater. Sci.* (1983) **18:**1443-54.

[12] Chand N., Rohatgi P. K., *Polym Commun* (1986) **27:**157–160.

[13] Gassan J, Bledzki A. K., *Ninth Int Conf on Mechanics of Composite Materials.*, Riga, Latvia, 17–20 October 1995.

[14] Ray D., Sarkar B. K., Rana A. K., Bose N. R., *Composites: Part A* (2001) **32:** 119-127.

[15] Pothen L. A., George J., Thomas S., *Comp Interfaces* (2002) **9:**335.

[16] Lovely M., Joseph K.U., Rani J., *Journal of natural fibres,* (2006) **3(4):** 110.

[17] Varada Rajulu A., Meng Y. Z., Li X. H., Rao B., Ganga Devi L., Raju K. M., Reddy R. R., *J. Appl. Polym. Sci.* (2003) **90:** 1604-1608.

[18] Cao Y., Shibata S., Fukumoto I. *Composites: Part A* (2006) **37:** 423-429.

[19] Bledzki A.K., Gassan J., *Prog. Polym. Sci. (1999)* **24:** 221–274.

[20] Varma D. S., Varma M., Varma I. K., *Text Res Inst* (1984) **54:** 349.

[21] Sreenivasan S., Bahama Iyer P., Krishna Iyer K.R., *J Mater Sci,* (1996) **31**: 721.

[22] Sharma H.S.S., Fraser T.W., Mc Call D., Lyons G., *J Text Inst* (1995) **86:** 539.

[23] Shelat B. R., Radhakrishnan T., Iyer B. V., *Text Res J* (1960) **33:** 836.

[24] C. de Albuquerque, K. Joseph, L. H. de Carvalho, J. R. M. d' Almeida *Comp. Sci. Technol.*, (2000) **60:** 833-844.

[25] Boynard C. A., Monterio S. N., d'Almeida J. R. M., *J.Appl.Polym. Sci.* (2003) **87:** 1927.

[26] Wells J. K., Beaumont P. W., *J Mat Sci.* (1985) **20:** 1275.

[27] Thomason J. L., Vlung M. A., *Comp Part A,* (1997) **28A:** 277.

[28] Cook J., Gordon J. E., Proc. R. Soc. London, (1964) **A282:** 508.

Chapter 5

CHEMICALLY MODIFIED RANDOMLY ORIENTED ISORA FIBRE REINFORCED POLYESTER COMPOSITES

Abstract

Short isora fibre surface was modified chemically to bring about improved interfacial interaction between the fibre and the polyester matrix. The fibre surface was chemically modified by acetylation, benzoylation, silane and triton treatments. Modified surfaces were characterized by IR Spectroscopy and SEM. Chemical modification was found to have a positive effect on the fibre/matrix interactions. The improved fibre/matrix interaction is evident from the enhanced tensile and flexural properties. The lower impact properties of the composites, except triton treated fibre composite, further point to the improved fibre/matrix adhesion, compared to the untreated fibre composites.

5.1. Introduction

Cellulose based natural fibres are a potential resource for making low cost composite materials, where high strength and stiffness are not of first priority[1]. Although plant fibres are generally considered to be viable for use in composites, the problem of compatibility of the fibre with the matrix is to be solved. Plant fibres, due to the abundance of hydroxyl groups, are incompatible with hydrophobic polyester resin. This incompatibility leads to a poor interfacial adhesion between the fibre and matrix, poor wetting of the fibres by the resin and a reduction in mechanical performance when the composite is exposed to moisture. Thus, in order to develop composites with good properties, it is necessary to improve the interface between the matrix and the lignocellulosic materials used as fillers. In order to improve interfacial bonding, modification of the fibre surface is essential [2-5].

When two materials are incompatible, it is often possible to bring about compatibility by introducing a third material that has properties intermediate between those of the other two by forming weak boundary layers, deformable layers or restrained layers. Coupling agents can improve the wettability between polymer and substrate or can form covalent bonds with both materials [1]. Chemical or irradiation induced removal of some hydroxyl groups has been used to improve hydrophobicity and chemical bonding at the interface [6-8]. Silane interfacial coupling agents widely used on glass fibre to form stable covalent bonds to both the mineral fibre surface and the resin are potentially suitable for use on cellulosic fibres. Acetylation is an effective method of modifying the surface of natural fibres and making it more hydrophobic. In addition, acetylation is one of the most studied reactions of lignocellulosic materials [9]. Hill and Khalil [10] studied the effects of chemical modification of coir and oil palm fibres by acetylation, silane treatment and titanate coupling agent, on the mechanical properties of the polyester composites. They found that interfacial strength between the fibre and matrix was increased by acetylation.

Rout *et al.* [11] observed that fibre surface modification by chemical treatment significantly increased the mechanical performance of coir-polyester composites. To improve the moisture resistance, Chand *et al.* acetylated sisal fibre and studied its tensile strength [12]. It was shown that acetylation could reduce the moisture content, but the tensile strength of the acetylated fibre was reduced due to the loss of hemi cellulose in the fibre during acetylation. Zafeiropoulos *et al.* [9] studied the effect of acetylation on flax fibres and found that the presence of moisture is beneficial for the reaction and also acetylation increased the weight percent gain (WPG) of fibres at high levels. This implied that the treatment is affecting the bulk and not just the surface of the fibres. Uma Devi *et al.* [13] investigated the effect of silane A-172 treatment on the mechanical properties of pine apple leaf fibre (PALF) reinforced polyester composites and observed significant improvement in the tensile strength for the treated fibre-composite.

In this Chapter, the effect of various fibre surface modifications on the mechanical properties of short isora fibre reinforced polyester composites is proposed to be evaluated. The surface modification is proposed to be effected by treatment with acetic anhydride, benzoyl chloride, vinyl triethoxy silane and triton X-100 (iso octyl phenoxy poly ethoxy ethanol). The physical changes induced by these treatments will be analyzed by Scanning electron microscopy (SEM). The effects of these modifications on the tensile, flexural and impact properties of the composites are also proposed to be evaluated.

5.2. Results and Discussion

5.2.1. Physical changes: SEM studies

The SEM photographs of the chemically treated isora fibre surface are given in the Figure 5.1. SEM gives strong evidence for the physical and micro structural changes occurred on the fibre surface during chemical treatment, compared to the SEM of untreated fibre given in Figure 3.5. On modification, the pores became clearer and the fibres became thinner. This may be due to the dissolution and leaching out of fatty acids and lignin components of the fibre.

This roughened the fibres, enhancing the mechanical interlocking at the interface. As a result of the introduction of functional groups by chemical treatment, the fibre surface became irregular and rough as shown in the Figure 5.1 Similar changes have been reported in grafted natural fibres such as cotton and jute [14].

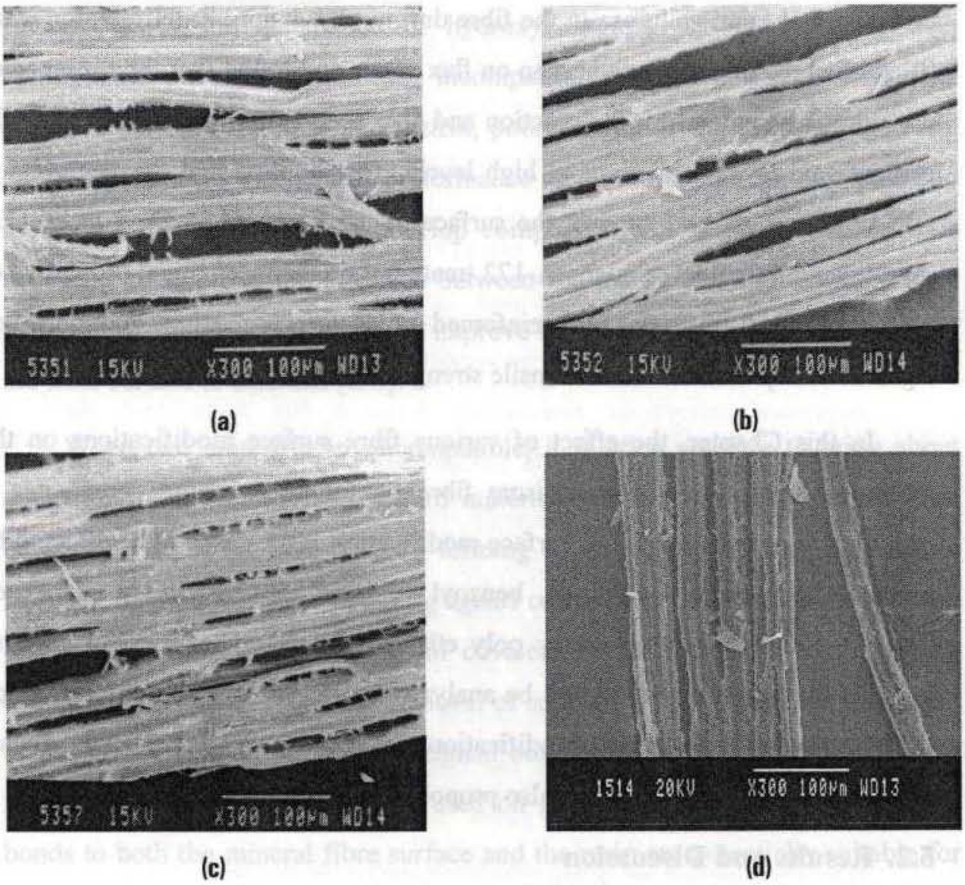


Figure 5.1 (a-d): SEM photographs of **(a)** acetylated **(b)** benzoylated **(c)** silane treated and (d) triton X-100 treated- isora fibre

The fibrils are well exposed on chemical treatment. On triton treatment, the fibre fibrillation occurred to a great extent, thus reducing the fibre diameter and resulting in considerable increase in fibre aspect ratio (Figure 5d). Indeed, with the use of solvents, these chemical treatments lead to a swelling effect, leaching out of the waxes, gums and partial removal of lignin and hemi-cellulose, which are the cementing materials in vegetable fibres [15-17].

5.3. Chemical modifications: IR spectroscopy

The IR spectra of the raw and treated isora fibres are given in Figure 5.2. The IR peaks of the untreated fibre are already explained (4.2.1). On chemical modification of the fibre by acetylation, benzoylation and silane treatment, the peaks corresponding to the functional groups were observed in the IR spectra. For acetylated fibre a peak at 1700 cm^{-1} indicates the introduction of an acetyl group. As a result of esterification of the hydroxyl groups, the hydroxyl vibrational absorption at 3300 cm^{-1} decreased.

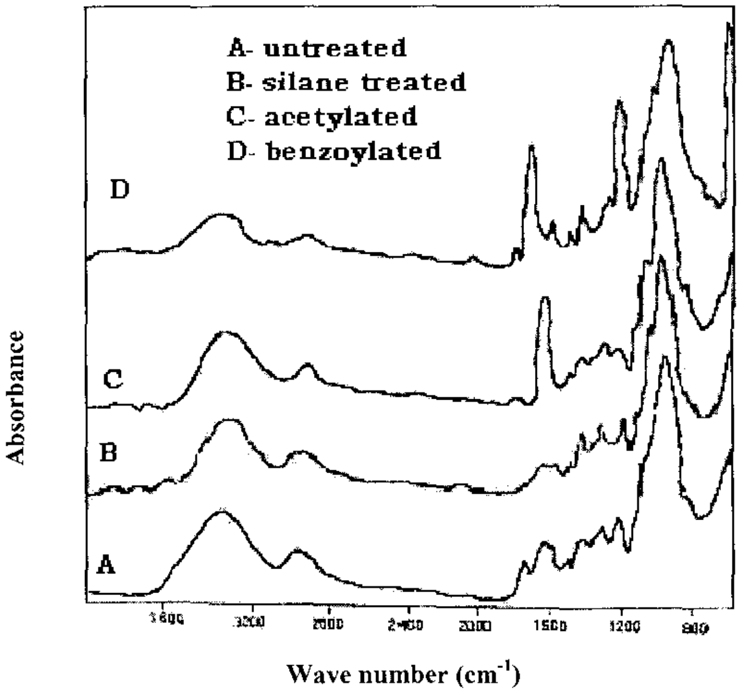


Figure 5.2. IR spectra of untreated and chemically modified isora fibre.

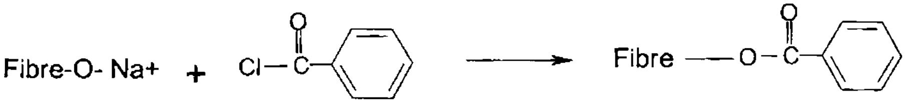
IR spectra of benzoylated fibre indicates an absorption in the range 1400-1600 cm^{-1} due to the C=C stretching of aromatic rings and a carbonyl group absorption in the range 1700 cm^{-1} is also observed. In the case of silane treated fibres, an additional peak at 3500 cm^{-1} indicates intermolecular hydrogen bonding between the silanol -OH and cellulosic –OH of the fibre.

5.4. Reaction scheme of chemical treatments

a) Benzoylation

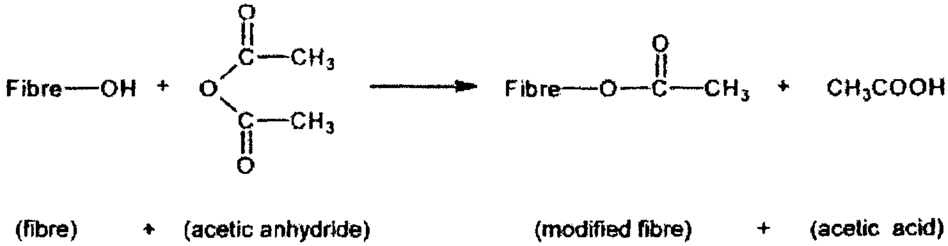
The reaction between the fibre surface and benzoyl chloride can be represented as

$$\text{Fibre-OH} + \text{NaOH} \longrightarrow \text{Fibre-O}^{-}\text{Na}^{+}$$



b) Acetylation

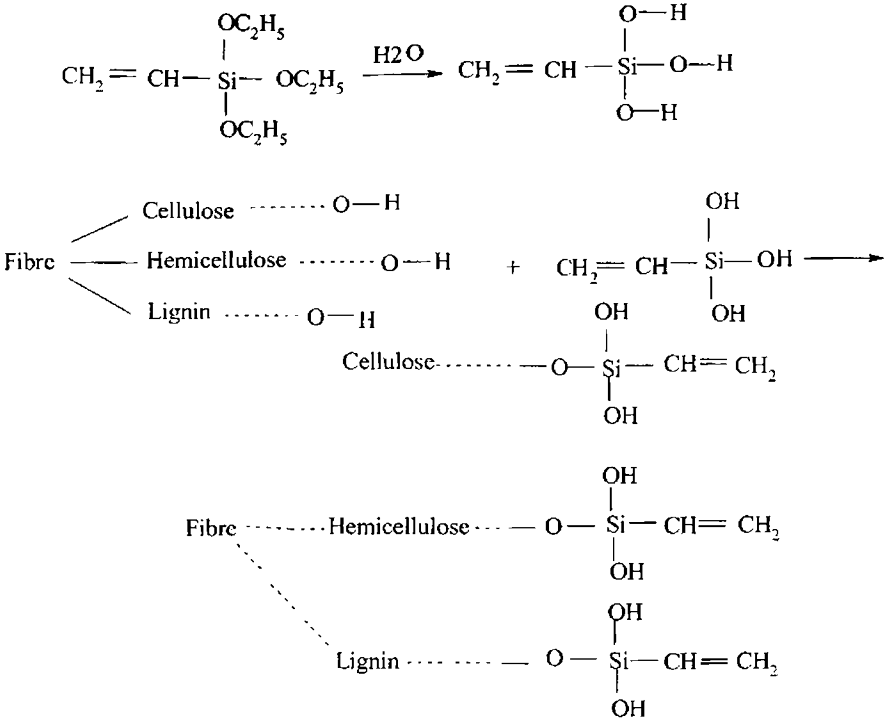
During acetylation, the typical reaction taking place on the fibre surface can be represented as



c) Silane (vinyl triethoxy) treatment

The organo functional group in the silane coupling agent (here CH_2=CH-) causes the reaction with the polymer. This could be a co-polymerization, and/or the formation of an interpenetrating network. The curing reaction of a silane treated substrate enhances the wetting by the resin.

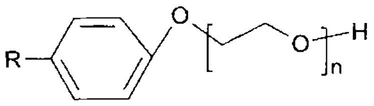
The general mechanism of formation of bonds of alkoxysilanes with the fibre surface [16], which contains hydroxyl groups, is as follows:



Alkoxysilanes undergo hydrolysis, condensation and the bond formation stage, under base as well as acid catalyzed mechanisms. In addition to these reactions of silanols with hydroxyls of the fibre surface, the formation of polysiloxane structures can take place.

d) Triton X 100 tratment

Chemically triton X 100 is Iso octyl phenoxy poly ethoxy ethanol, with structure shown below.



R= isooctyl, n=10.

It is a non ionic synthetic surfactant and has a hydrophilic head and hydrophobic tail. The main function of a surfactant is cleansing action.

Non ionic surfactants are the most widely used for surface cleaning and have no charge in aqueous solutions. They are resistant to water hardness. The advantages of triton X 100 are:

1. Excellent detergent and oil in water emulsifier for many applications
2. Excellent wetting agent and
3. Effective performance across a broad temperature range.

5.5. Mechanical properties of the composite

5.5.1. Tensile properties

The effects of various chemical treatments on tensile strength, Young's modulus and elongation at break values of the chemically modified, randomly oriented isora-polyester composites are given in the Figures 5.3, 5.4 and 5.5 respectively.

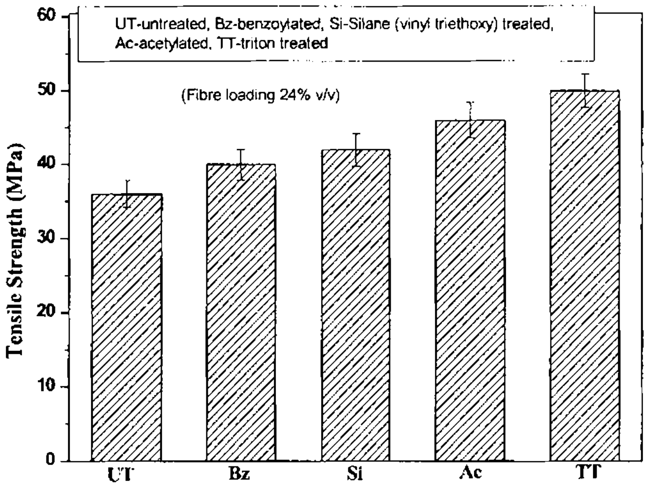


Figure 5.3. The effect of different chemical treatments on the tensile strength of randomly oriented isora-polyester composites

The effect of chemical treatments, on the tensile strength of the composites is given in Figure 5.3. It is observed that fibre modification improved the tensile strength of all composites and the improvement followed the order: triton treated (TT) > acetylated (Ac) > Silane treated (Si) > Benzoylated (Bz) > Untreated

(UT). The maximum improvement in tensile strength was observed for triton treated fibre composite. Compared to the untreated fibre composite, the percentage increase in tensile strength of treated fibre composites are TT-39%, Ac-27.8%, Si-16.7% and Bz-11%. The improvement in tensile strength can be attributed to the improved adhesion between the fibre and the matrix on chemical modification of the fibre.

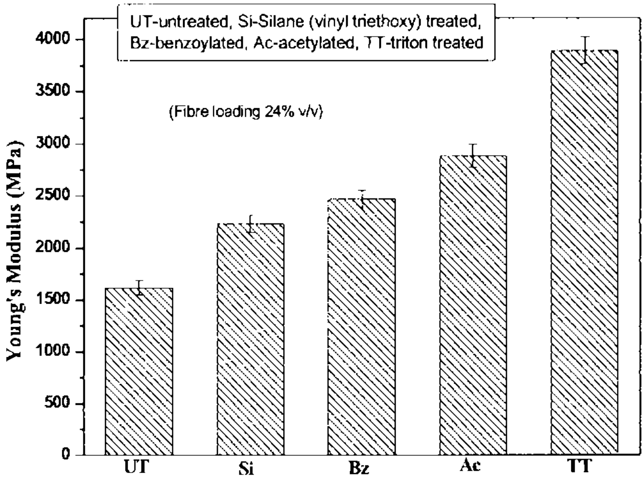


Figure 5.4. The effect of different chemical treatments on the Young's modulus of randomly oriented isora-polyester composites

The Young's modulus of the composites (Figure 5.4) also improved on chemical modification of fibre and followed the order: TT > Ac > Bz > Si > UT. Compared to the untreated fibre composite, the percentage increase in Young's modulus of treated fibre composites are TT-113, Ac-78, Bz-52.6, Si-37.8. The improvement in Young's modulus also is due to the improvement in adhesion between the fibre and the matrix, on chemical modification of the fibre.

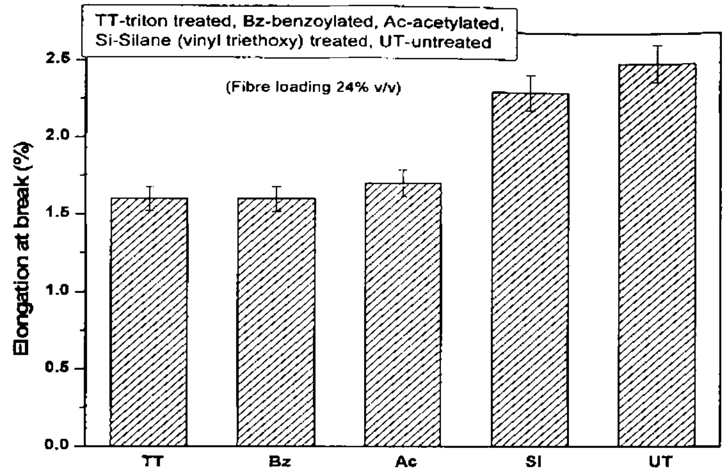


Figure 5.5. The effect of different chemical treatments on the Elongation at break of randomly oriented isora-polyester composites

The percentage elongation at break values of short isora-polyester composite varied with fibre treatment as shown in the Figure 5.5. It is observed that on chemical modification of the fibre, elongation at break values of the composites decreased and followed the order: UT > Si > Ac > Bz > TT. As expected from the modulus values, TT fibe composite has the lowest and silane treated fibre composite has the highest elongation at break values. When the fibre-matrix adhesion is higher, the composite will fail at a lower elongation. The reduced elongation at break values of the composites confirms the improved adhesion between the fibre and resin.

Now, we can examine the mechanism involved in the improvement of adhesion in each case. The improvement in tensile properties of benzoylated fibre composite is attributed to the presence of phenyl groups in the treated fibre which interacts with the benzene rings and methyl groups present on polyester, which improves the thermodynamic compatibility between the fibre and polyester. Also the reduction in hydrophilicity of the fibre on benzoylation makes the fibre more compatible with the hydrophobic polyester.

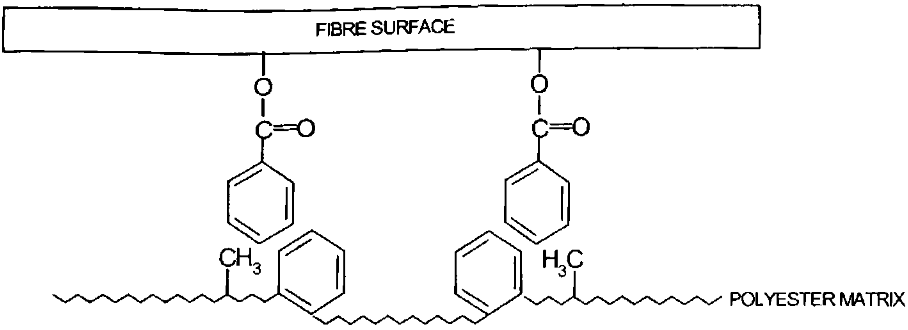


Figure 5.6. A hypothetical model of interface of benzoylated isora-polyester composite

In addition to this, benzoylation makes the surface of the fibre very rough and provides better mechanical interlocking with the polyester matrix. A hypothetical model of interface of benzoylated isora fibre-polyester composite is shown in Figure 5.6.

Acetylated fibre composites show improvement in properties, next to triton treated fibre composites. Rong et al. [17] have reported such results for acetylated jute fibre reinforced epoxy composites. They concluded that the improvement in interfacial bonding is due to the H-bonds between acetyl groups of the acetylated fibre and hydroxyl or amine groups in epoxy resin and mechanical interlocking between epoxy and the caved fibre surface due to alkali pretreatment. Since there is no possibility of H-bond formation between acetyl groups of the acetylated fibre and the unsaturated polyester resin, the improvement in tensile properties can be attributed to the second factor, which is the mechanical interlocking between the polyester resin and the fibre surface. This is supported by the rough surface morphology of the acetylated fibre evident from the SEM micrograph (Figure 5.1.a). Also the hydrophobic methyl groups attached to the fibre interacts with the methyl and benzene rings present in the polyester, thereby increasing the compatibility with the hydrophobic polyester matrix. A hypothetical model of the interface of acetylated isora fibre-polyester composite is shown in Figure 5.7. Another important contributing factor is the reduction in the hydrophilicity of the fibre as a result of acetylation, which makes the fibre more compatible with hydrophobic polyester.

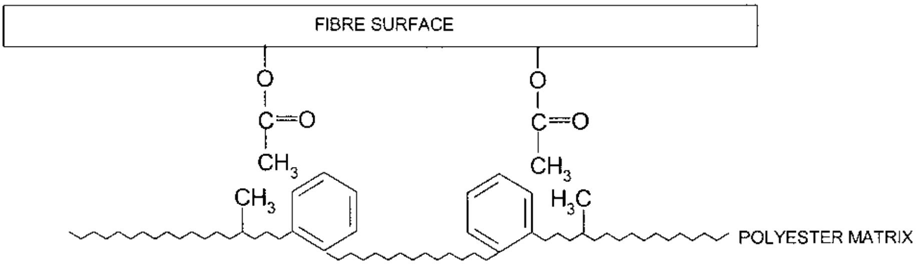


Figure 5.7. A hypothetical model of interface of acetylated isora-polyester composite

Vinyl triethoxy silane has two functional groups, a hydrolysable group which can condense with the hydroxyls of the fibre and an organo functional group (CH_2=CH-) capable of interacting with the matrix. The hydrolysed silanol forms strong covalent bonds or hydrogen bonds with-OH group of cellulose.

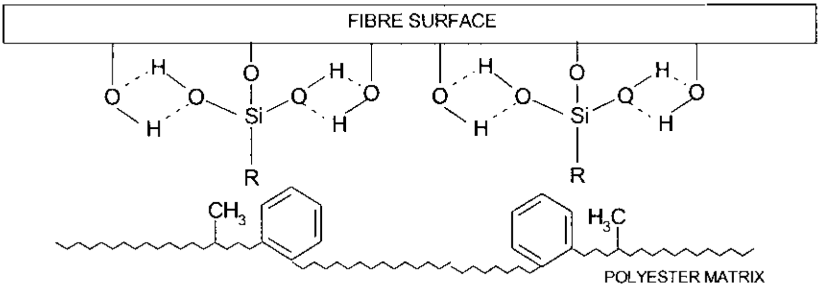


Figure 5.8. A hypothetical model of interface of silane treated isora-polyester composite

The individual coupling agent molecules attached to cellulose forms a continuous link. The long hydrophobic polymer chain can adhere to the matrix mainly because of Van der waals type attractive force. As a result, silane-coupling agents form a bridge at the interface. The hydrophobic alkyl groups (R = CH_2=CH-) attached to the fibre as a result of silane treatment increases the compatibility with the hydrophobic polyester matrix and improves the mechanical properties of the composite. A hypothetical model of the interface of silane treated fibre-polyester composite is shown in Figure 5.8.

On triton treatment of the alkali pre-treated fibre, which has less dense interfibrillar region and more oriented fibrils, become more dispersable and well exposed as evident from the SEM photograph in Figure 5.1. (d). The aspect ratio of the fibre is also enhanced. The increased dispersability results in a larger area of contact and improved wetting of the fibre. This leads to greater mechanical interlocking between fibre and matrix, making the interfacial adhesion stronger and the mechanical properties higher. This explains the maximum values of tensile strength and Young's modulus for triton treated fibre composite. Similar result was reported by D. Ray et al. [18] for alkali treated jute fibre-vinylester resin composite. They found that alkali-treated fibres were dispersed more readily and uniformly in the resin than the untreated ones. Treated fibres were seen to be finely separated from one another whereas the untreated fibres remained mostly in clusters (Figure 5.9).

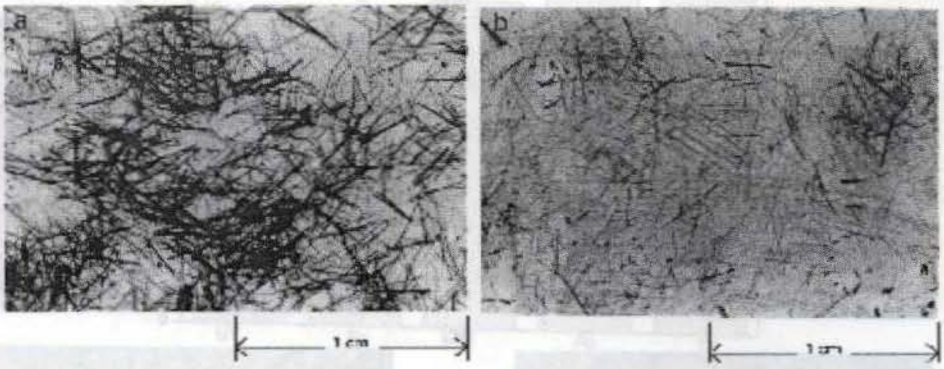
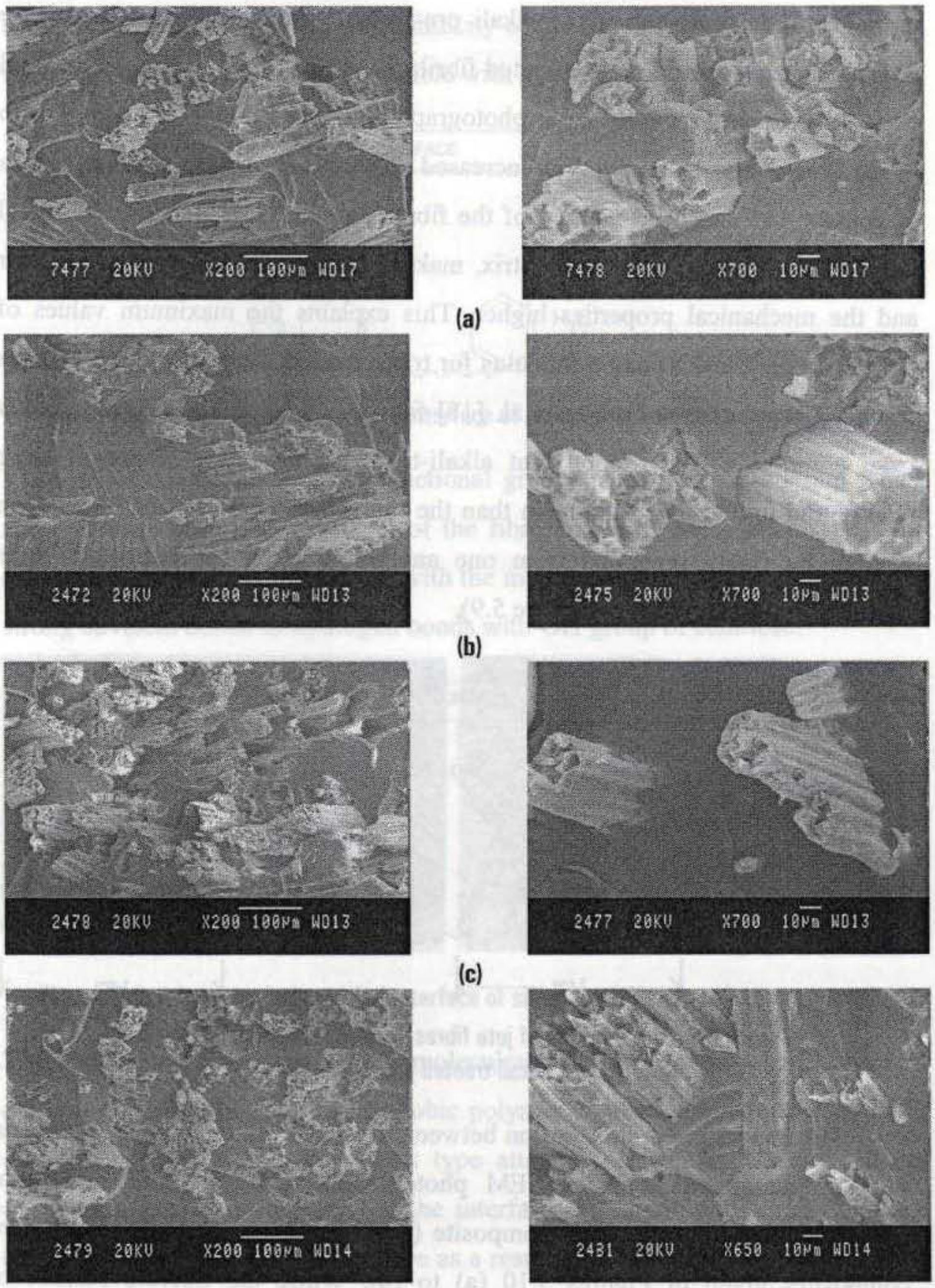


Figure 5.9. Dispersability of jute fibres in vinylester resin: **(a)** raw jute; **(b)** 2 h. alkali-treated jute. [Ref: 18]

The improvement in adhesion between the treated fibre and polyester resin can be understood from the SEM photographs of the fracture surface of untreated isora fibre-polyester composite (Figure 3.6) and that of treated fibre composites given in Figures 5.10 (a) to (d). While the fracture surface of untreated fibre composite shows holes and fibre ends indicating poor adhesion between the fibre and matrix, fracture surface of treated fibre composites shows fibre breakage rather than pull out, indicating better interfacial strength.



(a)

(b)

(c)

(d)

Figure 5.10. SEM photographs of the tensile fracture surface of **(a)** triton treated **(b)** acetylated **(c)** silane treated and **(d)** benzoylated randomly oriented isora-polyester composites (magnification × 200 and × 700)

5.5.2. Flexural properties

The effect of fibre modification on flexural strength, flexural modulus and flexural strain of short isora fibre reinforced polyester composites are shown in the Figures 5.11, 5.12 and 5.13 respectively. All fibre treatments resulted in improvement in flexural strength and flexural modulus of the composites. The improvement in flexural strength of the composites followed the order: TT > Ac > Si > Bz > UT. The percentage increase in flexural strength compared to untreated fibre composite is TT-50, Ac-27.3, Si-10.6, and Bz-4.5.

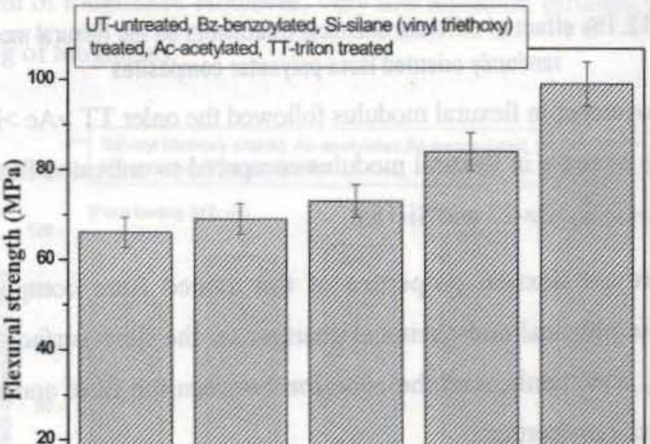


Figure 5.11. The effect of different chemical treatments on the flexural strength of randomly oriented isora-polyester composites

In the case of composites, the flexural properties are controlled by the resistance to interlaminar failure. Therefore, high flexural strength and modulus of treated fibre composite is due to better interfacial adhesion in the composite.

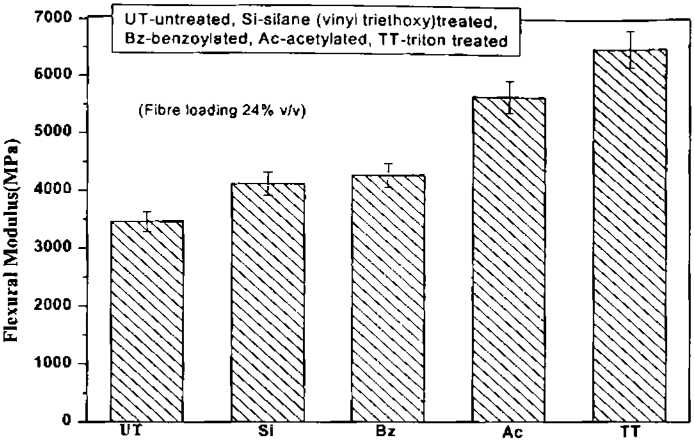


Figure 5.12. The effect of different chemical treatments on the flexural modulus of randomly oriented isora-polyester composites

The improvement in flexural modulus followed the order TT >Ac >Bz >Si >UT. The percentage increase in flexural modulus compared to untreated fibre composite is- TT-88.4, Ac-63.2, Bz-23 and Si-18.8.

The improved flexural properties of the treated fibre composite can be attributed to the physical and chemical changes on the fibre surface effected by the treatments, which enhanced the adhesion between the fibre and matrix as in the case of tensile properties.

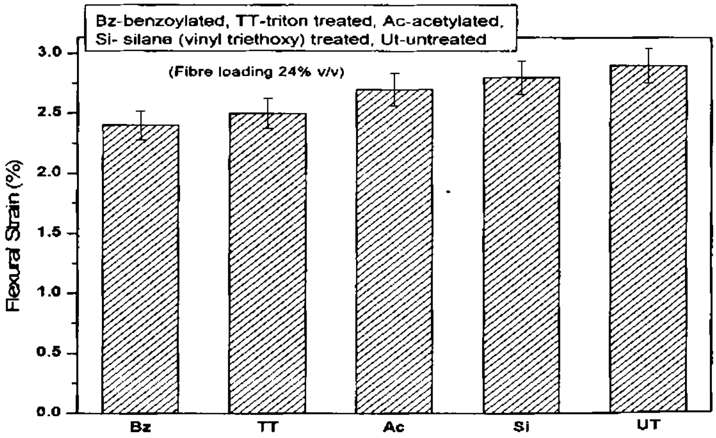


Figure 5.13. The effect of different chemical treatments on the flexural strain of randomly oriented isora-polyester composites

Flexural strain values of all treated fibre composites are lower than that of untreated fibre composite, and followed the order: UT > Si > Ac > TT >Bz. This is due to improved bonding between the treated fibre and resin.

5.5.3. Impact properties

The impact strength of a composite is influenced by many factors such as the toughness properties of the reinforcement, the nature of interfacial region and the frictional work involved in pulling the fibres from the matrix [10]. The nature of interface region is of extreme importance in determining the toughness of the composite. The lowering of adhesion between fibre and matrix leads to improvement of toughness. However, very low adhesion efficiency may result in the lowering of toughness.

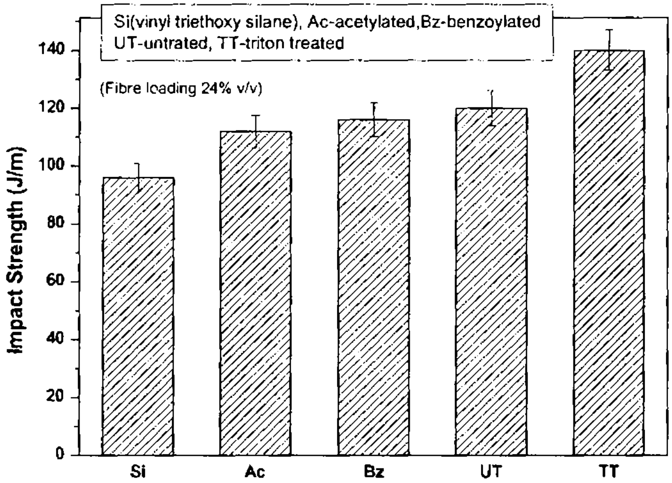


Figure 5.14. The effect of different chemical treatments on the impact strength of randomly oriented isora- polyester composites

The variation of impact strength with different chemical treatments is given in the Figure 5.14. It is observed that the impact strength decreased as the interfacial bond strength increased except in the case of triton treated fibre composite. The impact strength followed the order: TT > UT > Bz > Ac > Si. While silane treatment, acetylation and benzoylation of the fibre resulted in reduction in the impact strength of the composites, triton treatment of the fibre enhanced the impact strength of the composite, compared to untreated fibre composite. It is an established fact that a strong interface between the fibre and the matrix reduces the impact strength of the composites [19-21]. At high levels of adhesion, the failure mode is brittle and relatively little energy is absorbed. In the case of a weak interface the triaxial stresses at the tip of an advancing crack cause debonding to occur and a crack bunting mechanism takes place and improves the toughness of the material [22].

In the case of triton treated fibre, the treatment has improved the dispersion of the fibre in the resin. In addition, in this case the adhesion between the matrix and the fibre may be intermediate and leads to progressive delamination which require additional energy and hence an improved impact strength. Hill and Abdul Khalil [10] also got an improvement in impact strength for acetylated oil palm fibre reinforced polyester. In acetylated fibre the improved impact strength is assumed to be due to the improved toughness of the fibre. Similar results have been reported earlier [23]. When the fibre-matrix adhesion is strong, the mechanism of failure changes from fibre debonding and pull out to brittle failure and reduce the impact strength.

5.6. Conclusion

Isora fibre was modified chemically by acetylation, benzoylation, silane treatment and triton treatment. All fibre modifications improved the tensile and flexural properties of the composite. The decrease in hydrophilicity and increase in thermodynamic compatibility of the treated fibre with the polymer matrix are responsible for the improvement in the mechanical properties. The maximum improvement in tensile properties was observed for triton treatment. SEM studies also suggest strong fibre-matrix adhesion in treated randomly oriented isora-polyester composites. In all cases except triton treatment, fibre modification decreases the impact strength of the composites.

References

[1] Bledzki A.K., Reihmane S., Gassan J., *J. Appl. Polym. Sci.* (1996) **59:** 1329-1336.

[2] Lu J. Z., Wu Q., Negulescu I I., *J. Appl. Polym. Sci.*(2005) **96:** 93.

[3] Hristov Y. N., Lach R., Grellmann W., *Polym. testing* (2004) **23:** 581.

[4] Tserki V., Zafeiropoulos N. E., Simon F., Panayiotou. *Comp. Part A:* (2005) **36:** 1110.

[5] Bisanda E.T.N., Ansell M.P., *Comp. Sci. Technol.,* (1991) **41:**165- 178.

[6] Owolabi O., Czvikovszky T. and Kovacks I., *J. Appl. Polym. Sci.* (1985) **30:** 1827-36.

[7] Heikal S. O. and Kalyoubi S. F., *J. Appl. Polym. Sci.* (1982) **27:** 3027-41.

[8] Kubota H. and Ogiwara., *J. Appl. Polym. Sci.* (1970) **14:** 2879-85.

[9] Zafeiropoulos N. E.,Williams D. R., Baillie C. A., Matthews F. L. *Comp. Part A:* (2002) **33:** 1083-1093.

[10] Hill C. A. S., Abdul Khalil H. P. S., *J. Appl. Polym. Sci.* (2000)**78:** 1685-97.

[11] Rout J. Misra M., Tripathy S. S., Nayak S. K. and Mohanty A. K., *Comp. Sci. Technol.* (2001) **61**:1303-1310.

[12] Chand N, Verma S, Khazanchi A.C. *Journal of Materials Science Letters* (1989) **8:**1307-9.

[13] Uma Devi L., Bhagavan S. S., Thomas S., *J. Appl. Polym. Sci.* (1997) **64:** 1739-48.

[14] Thejappa W., Pandey S. N., *J.Appl.Polym. Sci.* (1982) **27:** 2307.

[15] Bessadok A., Marais S., Gouanve F., Colasse, L., Zimmerlin I., Roudesli S., Metayer M. *Comp Sci Technol.,* (2007) **67: (3-4)** 685-697.

[16] Bledzki A.K., Gassan J., *Prog. Polym. Sci. (1999)* **24:** 221–274.

[17] Rong M. Z., Zhang M. Q., Liu Y., Yang G. C., Zeng H. M. *Comp Sci Technol., (2001)* **61(10):** 1437-47.

[18] Ray D., Sarkar B.K., Rana A.K., Bose N.R., *Composites: Part A* (2001) **32:** 119–127.

[19] Hacox N. L., *Composites* (1971) **3:** 41.

[20] Bader M. G., Bailey J. E. and Bell I., *J. Phys. D. Appl. Phys.* (1973) **6:** 572.

[21] Yeung P. and Broutman L. J. *Polymer Eng. Sci,* (1978) **18:** 62.

[22] Cook J., Gordon J. E., Proc. R. Soc. London, (1964) **A282:** 508.

[23] Rowell R. M., Banks W. B., *Brit. Polym. J.* (1947) **91:** 987.

Chapter 6

ORIENTED LONG ISORA FIBRE REINFORCED POLYESTER COMPOSITES

Abstract

The tensile, impact and flexural properties of oriented untreated and alkali treated long isora fibre reinforced polyester composites with reference to the effect of fibre loading are described in this chapter. The effect of fibre surface modifications like ultrasonication, alkali, triton and detergent treatments, on the mechanical properties of the composite is also discussed. Fibre surface morphology and fibre-matrix adhesion have been analysed by Scanning Electron Microscopy (SEM). Chemical modification was found to have a positive effect on the fibre/matrix interactions. The improved fibre/matrix interaction is evident from the enhanced tensile, flexural and impact properties of the composites. The experimental tensile strength values were compared with the theoretical values.

Part of the results presented in this chapter has been published in
Composite interfaces (2007) **14 (7-9)**: 631 – 646.

6.1. Introduction

A unidirectional composite consists of parallel fibres embedded in a matrix. Several unidirectional layers can be stacked in a specified sequence of orientation to fabricate a laminate that will meet design strength and stiffness requirements [1]. Each layer of a unidirectional composite is referred to as simply a layer, ply or lamina. The essential point about a unidirectional fibre composite is that its stiffness and strength are different in different directions. This behaviour is in contrast to short fibre composite which has the same elastic properties in all directions. The longitudinal strength of unidirectional composite is far greater than that in any other direction. A unidirectional composite may be modeled by assuming fibres to be uniform in properties and diameter, continuous and parallel throughout the composite. It may be further assumed that a perfect bonding exists between the fibres and the matrix so that no slippage can occur at the interface and the strains experienced by the fibre, matrix and composite are equal.

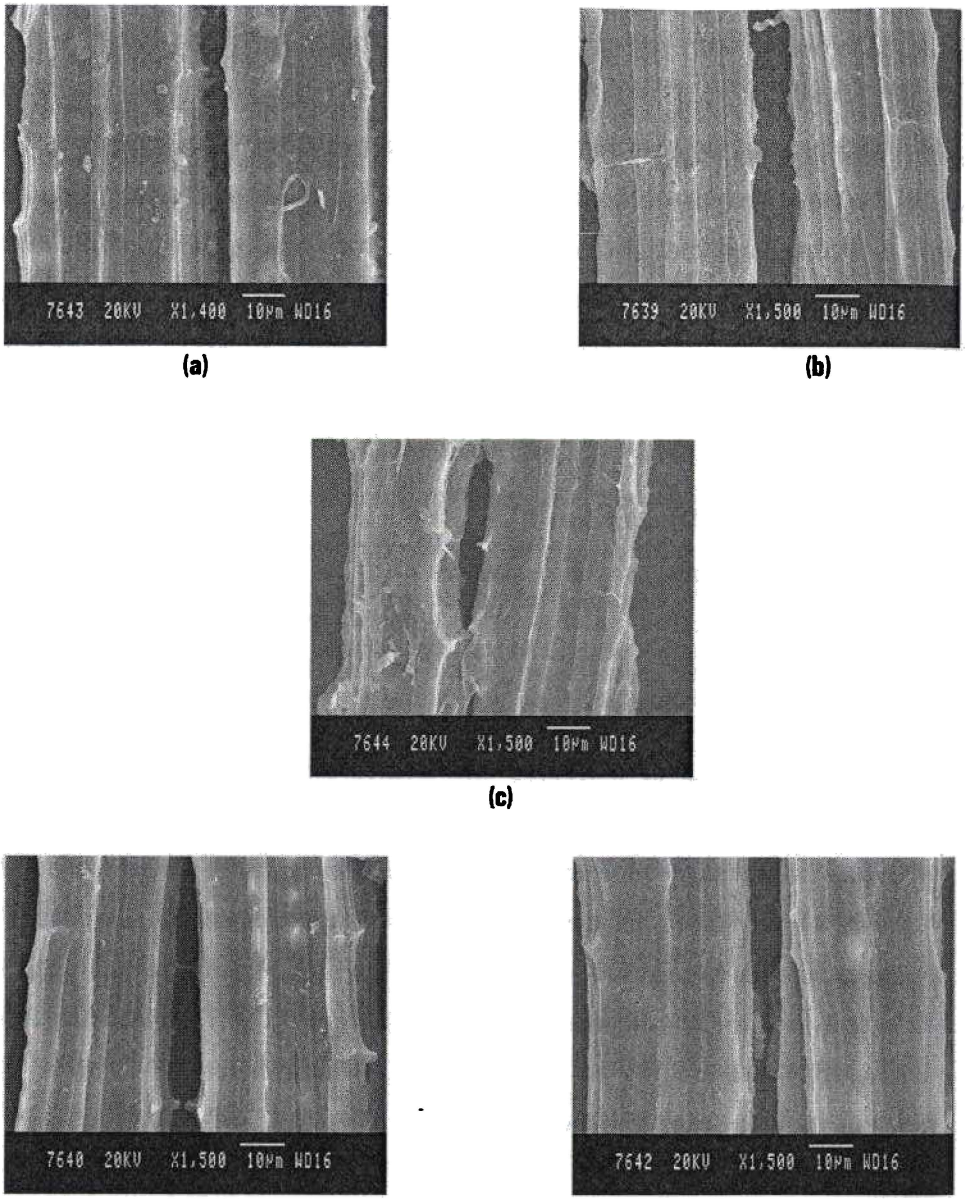
Sanadi *et al.* [2] observed that the tensile strength of the unidirectional continuous sun hemp polyester composites increased linearly with fibre loading according to the rule of mixtures. Izod impact strength also increased linearly with fibre loading. Aziz *et al.* [3] studied the effect of alkalization and fibre alignment on the mechanical and thermal properties of long and random kenaf and hemp fibre composites and concluded that alkalized long kenaf-polyester composites possessed superior mechanical properties to alkalized long hemp-polyester composites. For the hemp-polyester composites a high flexural modulus and a high flexural strength are associated with a low work of fracture. Herrera-Franco *et al.* [4] studied the mechanical behaviour of high-density polyethylene reinforced with continuous henequen fibres. They observed that a chemical interaction was promoted by using an optimum concentration of silane coupling agent and from the SEM photographs of the failure surface, concluded that with increasing fibre-matrix interaction, the failure mode changed from interfacial failure to matrix failure.

The tensile, impact and flexural properties of oriented untreated and alkali treated long isora fibre reinforced polyester composites are proposed to be investigated in this chapter. The effect of fibre surface modifications like alkali treatment, triton treatment, ultrasonication and detergent treatment, on the mechanical properties of the composite will also be evaluated. Fibre surface morphology and fibre-matrix adhesion are proposed to be analysed by Scanning Electron Microscopy (SEM).

6.2. Results and Discussion

6.2.1. Physical changes: SEM studies

Scanning electron microscopic studies were carried out on the untreated and treated isora fibres to understand the morphological changes that occurred on treatment of the fibres. The SEM photographs of the longitudinal surface of untreated and treated fibres are given in Figures 6.1(a) to (e). Untreated fibre surface (a) shows the presence of impurities whereas the surfaces of treated fibres are very clear. This is due to the removal of surface impurities. The surface of the treated fibres appears to be quite smooth but earlier works on the fibre modification reveals that the chemical treatment roughens the fibre surface [3]. This enhances the mechanical interlocking at the interface, which helps to improve the mechanical properties of the composite.



(a)

(b)

(c)

(d)

(e)

Fig. 6.1. SEM photographs of the longitudinal surface of isora fibre (a) untreated (b) alkali treated (c) triton treated (d) detergent treated and (e) ultrasonicated. (magnification × 1500)

6.2.2. Tensile properties

6.2.2.1. Effect of fibre loading on untreated fibre composite

The effect of fibre loading on the tensile properties of the untreated, oriented long isora-polyester composite with standard deviation is given in Table 6.1 and the variation of tensile strength and Young's modulus with fibre loading of the composite is shown in the Figure 6.2.

Table 6.1. Tensile properties of untreated oriented long isora-polyester composites as a function of fibre loading

Fibre loading (% v/v)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)
0	30.0 ± 2	1.068 ± 0.04	3.2 ± 0.5
25	119 ± 5	4.216 ± 0.17	3.0 ± 0.4
33	150 ± 6	6.502 ± 0.26	2.9 ± 0.4
43	200 ± 8	7.777 ± 0.30	2.8 ± 0.3
52	183 ± 7	7.286 ± 0.29	2.4 ± 0.3

The tensile strength and Young's modulus of the composite increased regularly with fibre loading and attained maximum value at 43% loading. Tensile strength and Young's modulus values showed a downward tendency on further fibre loading. The percentage elongation at break values of the composites decreased with fibre loading, indicating enhanced stiffness. So the optimum fibre loading for the tensile properties of the composite is 43% at which there is maximum wetting of the fibre and effective stress transfer at the fibre/matrix interface. The decrease in tensile properties at higher loading may be due to improper wetting and adhesion

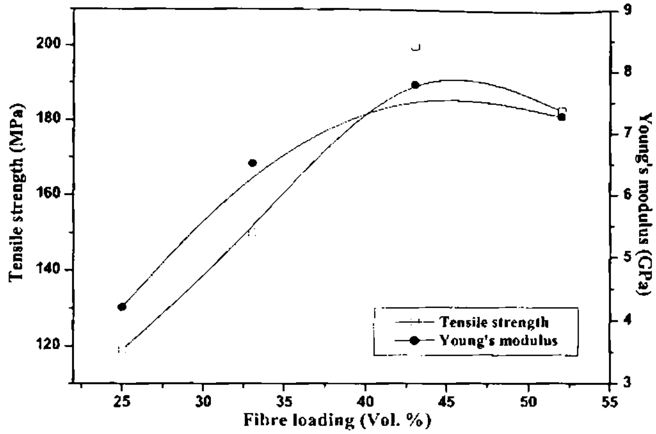


Figure 6.2. Variation of tensile strength and Young's modulus with fibre loading, of untreated oriented long isora-polyester composites

The tensile strength and modulus values are in good agreement with the rule of mixtures for unidirectional continuous fibre reinforced composites as discussed in Section 6.3 [5].

6.2.2.2. Effect of fibre loading on alkali treated fibre composite

The effect of fibre loading on the tensile properties of the alkali treated, oriented long isora fibre composites with standard deviation is given in the Table 6.2. The variation of tensile strength and Young's modulus with fibre loading of the alkali treated fibre composites are shown in the Figure 6.3.

Table 6.2. Tensile properties of the alkali treated, oriented long isora-polyester composites as a function of fibre loading

Fibre loading (% v/v)	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)
0	30.0 ± 2	1.068 ± 0.04	3.2 ± 0.5
32	183.7 ± 7	6.985 ± 0.28	3.6 ± 0.6
43	222 ± 9	7.6 ± 0.31	4.0 ± 0.7
55	250 ± 10	8.35 ± 0.34	4.1 ± 0.7
66	271 ± 11	9.156 ± 0.37	4.3 ± 0.8
70	265 ± 10	8.945 ± 0.36	4.1 ± 0.7

The tensile strength and Young's modulus of the alkali treated fibre composite increased linearly with fibre loading and reached maximum at 66% loading by volume. Above this fibre loading tensile strength and modulus values showed a downward tendency. The percentage elongation at break (E.B.) values also varied with fibre loading in a similar manner. The E. B. values of the alkali treated fibre composites are higher than that of the untreated fibre composites which indicates improved toughness of the composite on alkali treatment of the fibre which is also supported by the high impact strength of the alkali treated composite compared to untreated fibre composite (Figure 6.11). So the optimum fibre loading for the tensile properties is 66% at which there is maximum wetting of the fibre and effective stress transfer at the fibre/matrix interface.

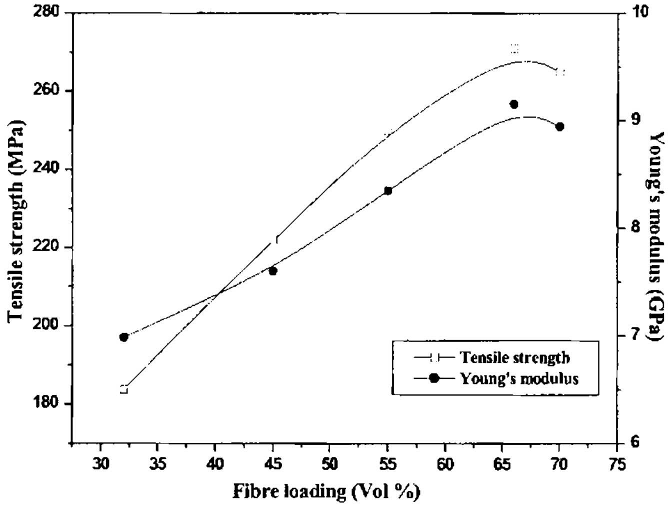


Figure 6.3. Variation of tensile strength and Young's modulus with fibre loading of alkali treated oriented long isora-polyester composites

It is observed that on alkali treatment, the optimum fibre loading for the tensile properties of the composite is increased from 43% to 66%, which is an indication of enhancement in fibre/matrix adhesion.

6.2.2.3. Effect of fibre treatments

The effect of various surface modifications on the tensile properties of the oriented long isora fibre-polyester composites is given in the Figures 6.4, 6.5 and 6.6. Fibre treatment improved the tensile properties of the composites in all cases. Figure 6.4 shows the effect of various fibre treatments on the tensile strength of the composite. The tensile strength of the composite increased in the order Untreated (UT) < Detergent treated (DT) < Ultrasonicated (US) < Triton treated (TT) < Alkali treated (AT). The percentage increase in tensile strength of the treated fibre composites compared to UT fibre composite is as follows: DT-4.4, US-13.1, TT-31.7 and AT-42.

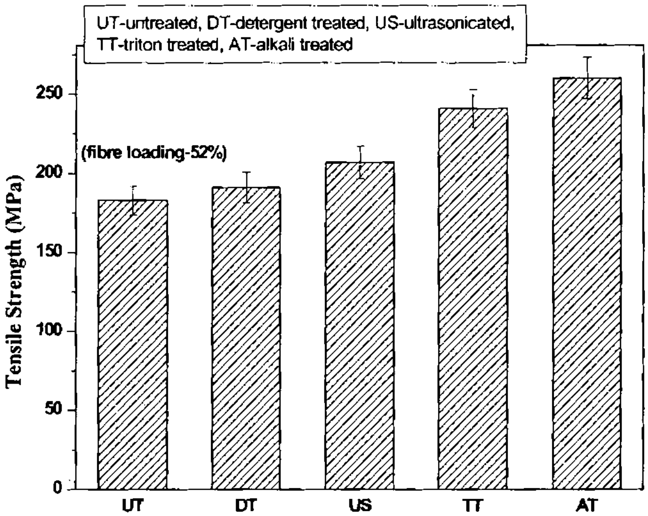


Figure 6.4. Effect of various fibre treatments on the tensile strength of oriented long isora-polyester composites

The increase in Young's modulus values of the composites on surface modification of the fibre followed the same trend. The percentage increase in the property compared to UT fibre composite is: DT-1.5, US-6.7, TT-14.3 and AT-16.7

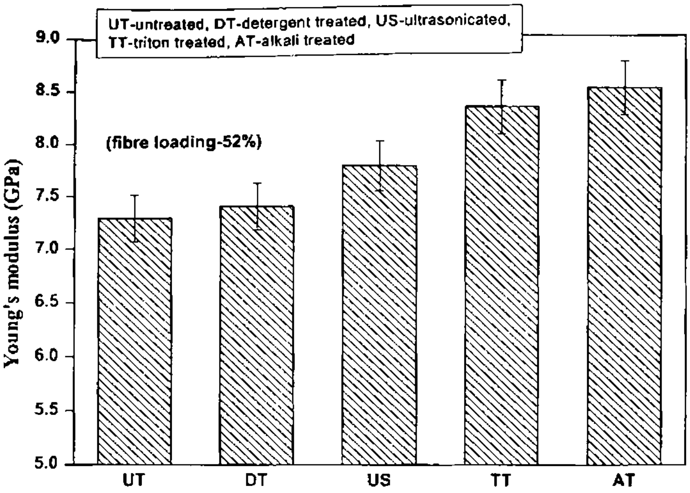


Figure 6.5. Effect of various fibre treatments on Young's modulus of oriented long isora-polyester composites

On fibre surface modification, elongation at break values of the composites also increased indicating enhanced toughness of the composites. This is supported by the increase in the impact strength of the treated fibre composites. (Figure 6.11)

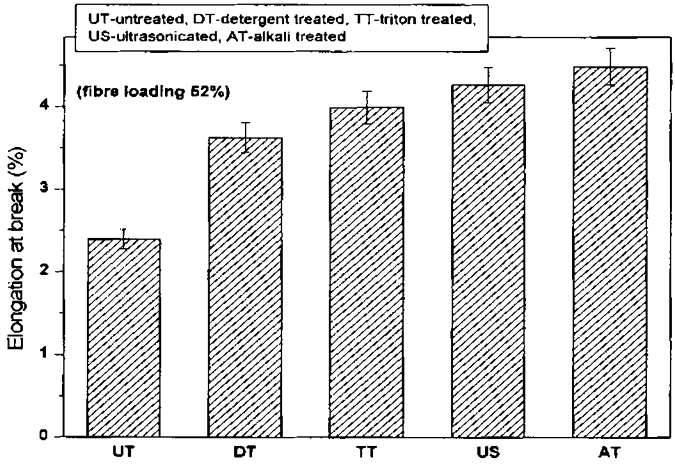
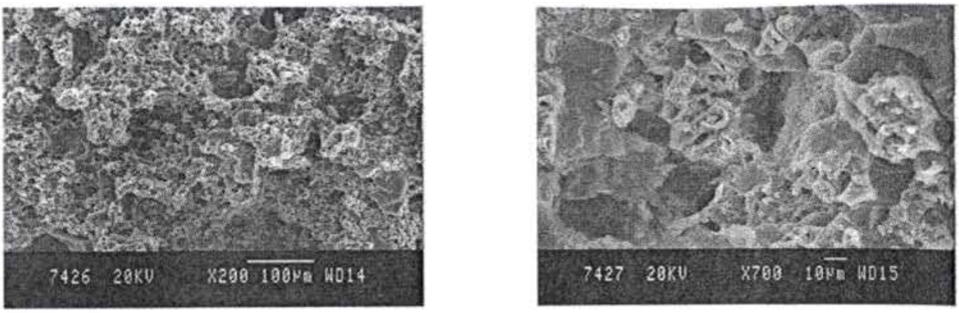
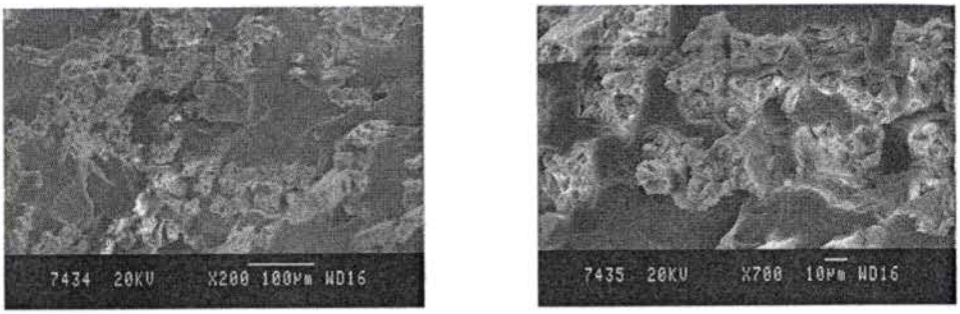


Figure 6.6. Effect of various fibre treatments on % elongation at break of oriented long isora-polyester composites

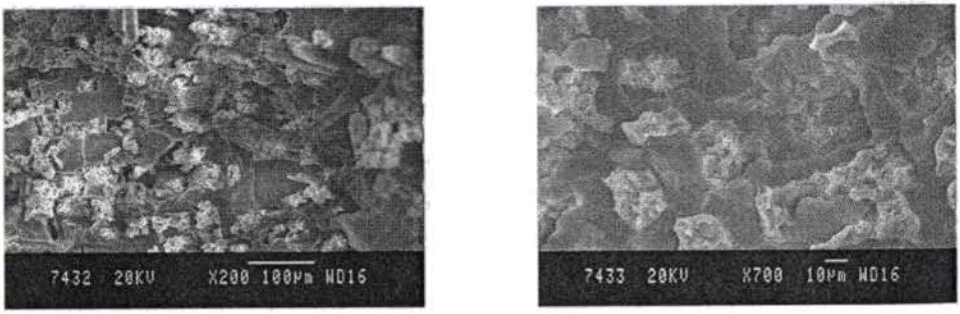
The varying degrees of adhesion between various treated fibres and the matrix is evident from the SEM photographs of the tensile fracture surface of the composites given in the Figures 6.7 (a) – (e).



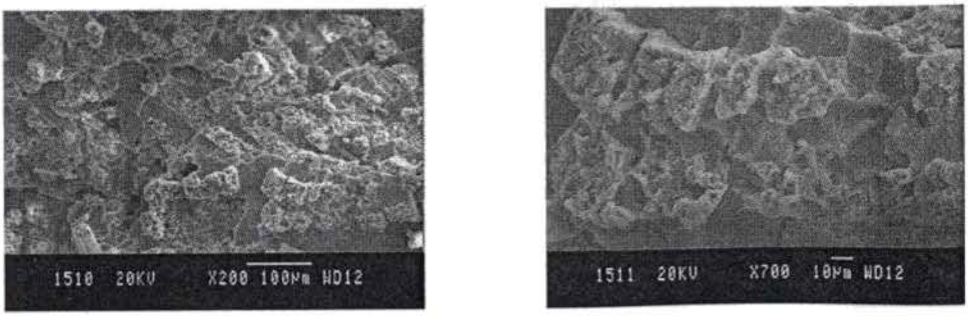
(a) untreated



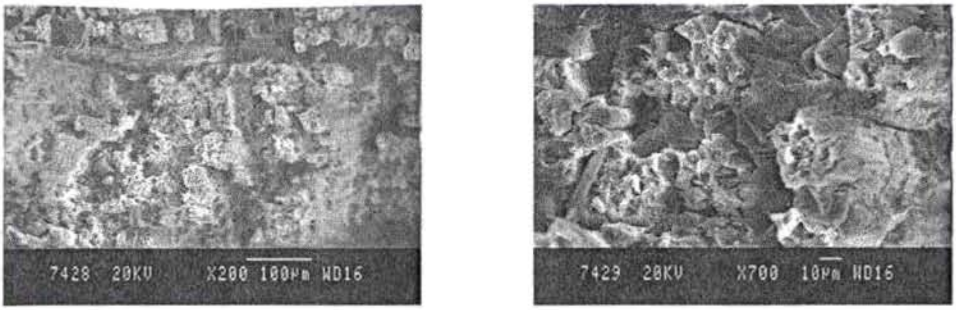
(b) detergent treated



(c) ultrasonicated



(d) triton treated



(e) alkali treated

Figure 6.7. (a)-(e) Tensile fracture surface of treated oriented long isora-polyester composites at magnifications × 200 and × 700

6.2.3. Flexural properties

6.2.3.1. Effect of fibre loading on untreated fibre composite

The effect of fibre loading on the flexural properties of untreated long isora-polyester composites with standard deviation is given in Table 6.3. The variation of flexural strength and flexural modulus of the composite is shown in the Figure 6.8.

Table 6.3. Flexural properties of untreated oriented long isora-polyester composites as a function of fibre loading

Fibre Loading (% v/v)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Maximum Strain (%)
0	60.0 ± 3.7	2.63 ± 0.10	2.9 ± 0.15
23	170 ± 6.8	5.01 ± 0.20	3.2 ± 0.19
28	179 ± 6.9	7.0 ±0.28	3.3 ± 0.20
40	205 ± 8.2	10.57 ± 0.42	3.4 ± 0.22
46	217 ± 9	12.21 ±0.49	3.5 ± 0.25
56	246 ± 10	14.40 ± 0.58	3.55 ± 0.27
60	236 ± 9.5	13.9 ± 0.56	3.48 ± 0.25

The flexural strength and modulus of the composite increased regularly with fibre loading, reached maximum at 56% loading, then decreased for higher loadings. The increase in flexural strength is 310% and flexural modulus 447%, compared to the values of neat resin. So the optimum fibre loading for flexural properties of the untreated oriented long isora fibre-polyester composite is 56%.

Increase in flexural strength with increasing fibre loading is due to increased interaction between fibre and matrix whereas the decrease of flexural strength at higher fibre loading is due to increased fibre-to-fibre interaction and dispersion problems resulting in poor stress transfer.

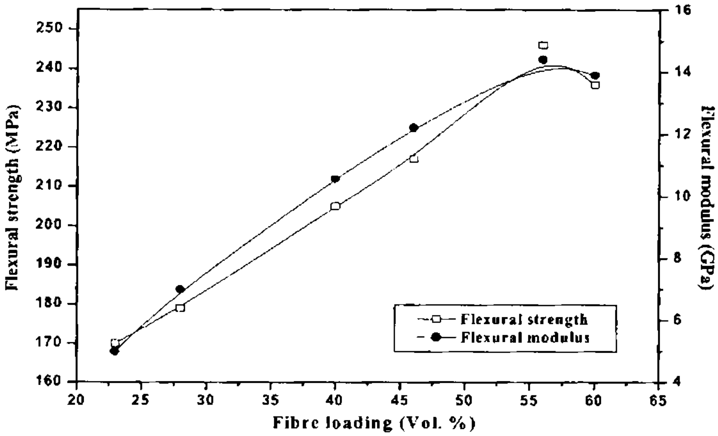


Figure 6.8. Variation of flexural strength and flexural modulus with fibre loading, of untreated oriented long isora-polyester composites.

6.2.3.2. Effect of fibre loading on alkali treated fibre composite

The effect of fibre loading on the flexural properties of the alkali treated oriented long isora-polyester composites with standard deviation is given in Table 6.4. The variation of flexural strength and flexural modulus with fibre loading of the alkali treated fibre composites are shown in the Figure 6.9.

Table 6.4. Flexural properties of the alkali treated, oriented long isora-polyester composites as a function of fibre loading

Fibre loading (%v/v)	Flexural strength (MPa)	Flexural modulus (GPa)	Maximum strain (%)
0	60.0 ± 3.7	2.63 ± 0.10	2.9 ± 0.15
23	190 ± 8	8.0 ± 0.32	3.12 ± 0.18
38.5	225 ± 9	12.5 ± 0.5	3.05 ± 0.16
50	270 ± 11	15.0 ± 0.6	2.80 ± 0.14
59	288 ± 12	16.4 ± 0.66	2.66 ± 0.13
66	301 ± 12	18.7 ± 0.75	2.60 ± 0.13
70	290 ± 10	18.2 ± 0.73	2.52 ± 0.12

The flexural strength and flexural modulus of the alkali treated fibre composite increased regularly with fibre loading, and attained maximum value at 66% loading, after which the values decreased marginally for higher fibre loading. So the optimum fibre loading for flexural properties of the alkali treated fibre composite is 66%. Alkali treatment of the fibre enhanced the optimum fibre loading for flexural properties from 56% to 66%, which indicates enhanced fibre/matrix adhesion in the treated fibre composite. The increase in flexural strength is 401% and flexural modulus 611%, compared to neat resin.

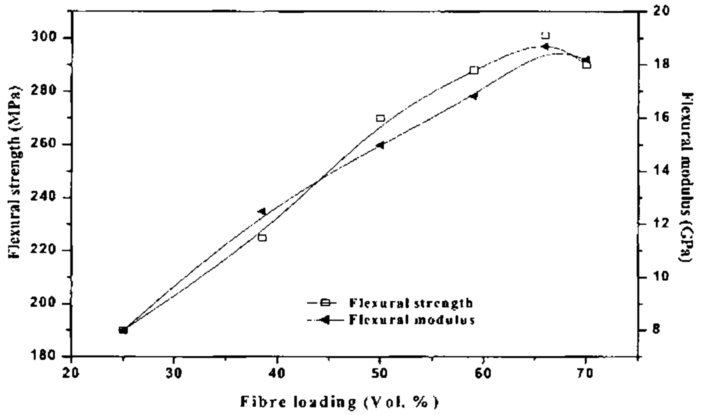


Figure 6.9. Variation of flexural strength and flexural modulus with fibre loading of alkali treated, oriented long isora-polyester composites

6.2.3.3. Effect of fibre treatments

The effect of various surface modifications of the fibre on the flexural properties of the oriented long isora-polyester composites, with standard deviation is given in the Figures 6.10, 6.11 and 6.12. Figure 6.10 shows the effect of fibre treatment on the flexural strength of the composites compared to untreated fibre composite. Flexural properties of the composite are found to be improved by all fibre treatments. The flexural strength increased in the order UT < DT< US < AT < TT. The percentage increase in flexural strength of the treated fibre composites compared to untreated fibre composite is as follows: DT-4.2, US-10.8, AT-15.8 and TT-20.

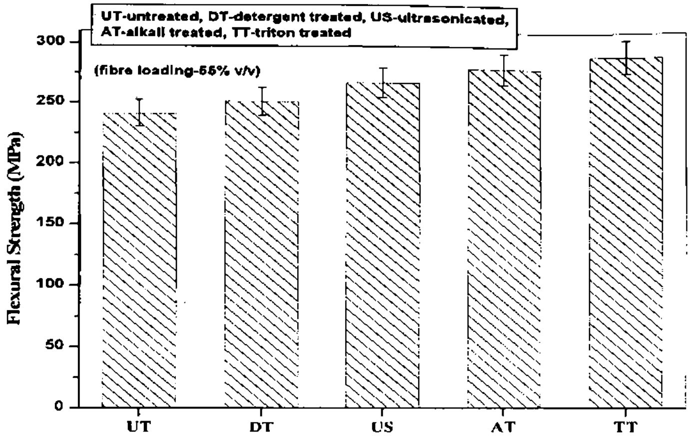


Figure 6.10. Effect of various fibre treatments on flexural strength of oriented long isora-polyester composites

The effect of fibre treatment on the flexural modulus of the oriented long isora-polyester composites, with standard deviation is given in the Figure 6.11. On fibre treatment, flexural modulus of the composite varied in the same manner as that of flexural strength. Compared to untreated fibre composite the percentage increase in flexural modulus of the treated fibre composite is: DT-3.5, US-12.2, AT-16.5 and TT-31.3. The increase in flexural properties of the composite on treatment of fibre is due to improved bonding between the fibre and resin.

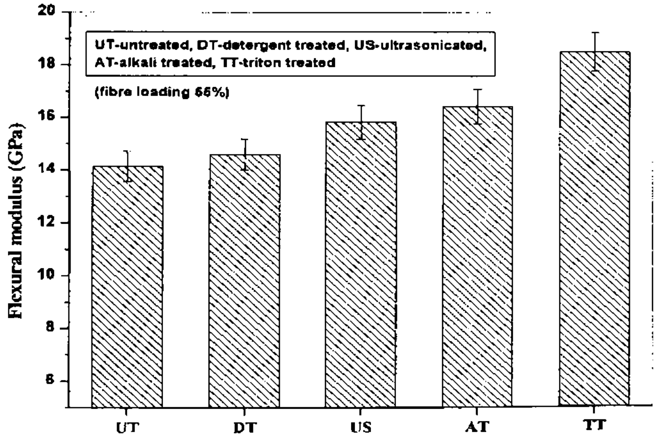


Figure 6.11. Effect of various fibre treatments on flexural modulus of oriented long isora-polyester composites

On fibre treatment, flexural strain of the composite varied in the order: TT < AT < US < DT < UT. (Figure 6.12). The decrease in percentage strain of the treated fibre composites compared to the untreated fibre composite is TT-36.9, AT-33.5, US-30.4 and DT-27.6.

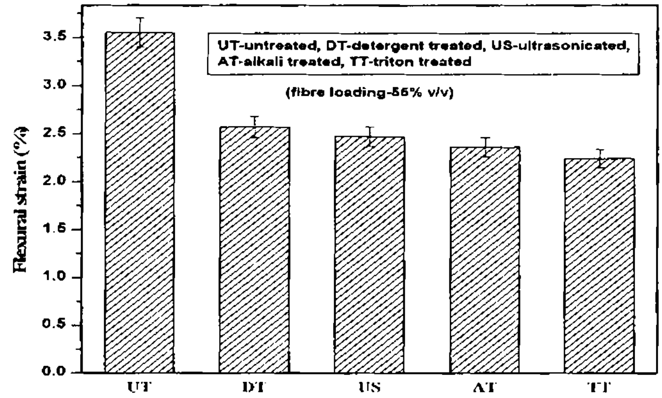


Figure 6.12. Effect of various fibre treatments on the flexural strain of oriented long isora-polyester composites

6.2.4. Impact strength:

6.2.4.1. Untreated fibre composite

Figure 6.13 shows the variation of impact strength of the untreated, oriented long isora fibre-polyester composite as a function of fibre loading.

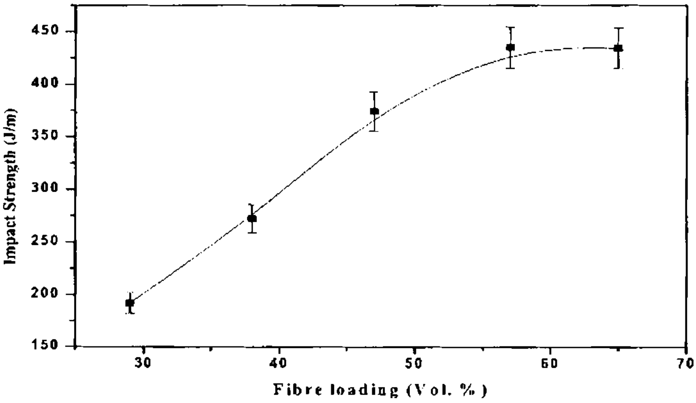


Figure 6.13. Variation of impact strength with fibre loading of untreated, oriented long isora-polyester composites

Impact strength of the composite increased with fibre loading, reached a maximum value at 57% by volume of fibre. With further increase in fibre loading, there is no significant increase in impact strength. The fibres play an important role in the impact resistance of the composites as they interact with the crack formation in the matrix and act as stress transferring medium.

6.2.4.2. Treated fibre composite

The effect of various fibre modifications on the impact strength of oriented long isora fibre-polyester composite is given in the Figure 6.14. On fibre treatment, impact strength of the composites improved, the improvement followed the order: AT > TT > US > DT > UT. Compared to untreated fibre composite the percentage increase in impact strength of the treated fibre composites is: DT-13.8, US-21, TT-39 and AT-47.

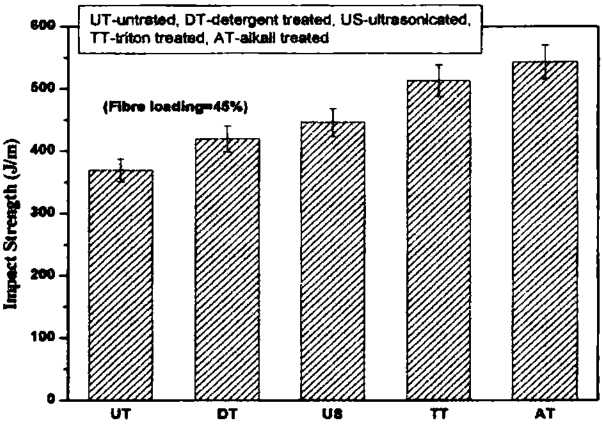


Figure 6.14. Effect of various surface modifications on the impact strength of oriented isora-polyester composites

The impact failure of a composite occurs by factors like matrix fracture, fibre/matrix debonding and fibre pull out. Fibre pull out is found to be an important energy dissipation mechanism in fibre reinforced composites [6]. The applied load transferred by shear to fibres may exceed the fibre/matrix interfacial bond strength and then debonding occurs.

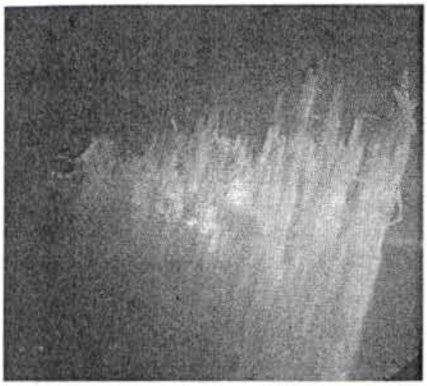


Figure 6.15. Optical photograph of the impact fracture surface of oriented long isora-polyester composite

When the stress level exceeds the fibre strength, fibre fracture occurs. The fractured fibres may be pulled out of the matrix, which involves energy dissipation [7]. The impact fracture of the composites were hinge type and not brittle. Fibre breakage and pull out are the main energy dissipating mechanisms here, which is evident from the Figure 6.15. This mechanism involves more energy. So the increase in impact strength of the treated fibre composites can be accounted.

6.3. Theoretical modeling

For determining the tensile properties of unidirectional continuous fibre reinforced composites the rule of mixtures (ROM) and Hirsch model (Chapter 1-Section 3.3) can be used. ROM is given by the following equations:

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

$$E_c = E_f V_f + E_m V_m$$

Where σ_c, σ_f and σ_m are the stress of the composite, fibre and matrix; E_c, E_f, and E_m are the modulus of composite, fibre and matrix; V_f and V_m are the volume fraction of fibre and matrix.

Theoretical values of tensile strengths and Young's modulus were calculated using the above models and compared with the experimental values.

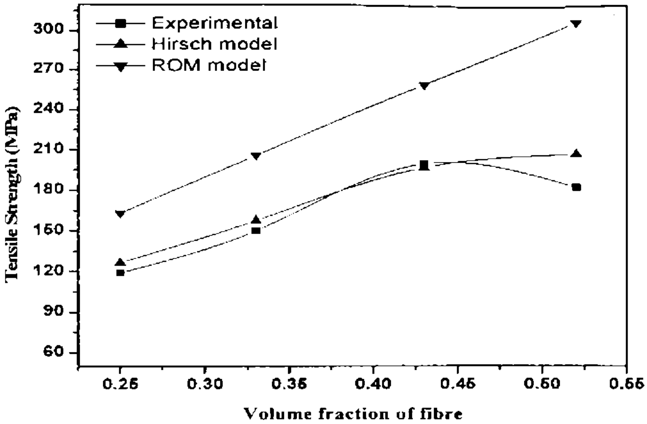


Figure 6.16. Comparison of experimental and theoretical tensile strengths of untreated oriented long isora-polyester composites

In Figure 6.16 theoretical and experimental values of tensile strength of untreated oriented long isora-polyester composites are plotted. It is observed that the Hirsch model values are in good agreement with the experimental values. ROM model values are higher than the experimental values. This may be because the isora fibres are not perfectly unidirectional, due to branching of the fibres

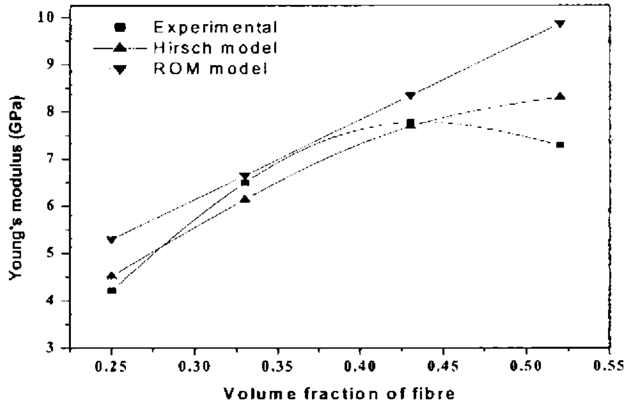


Figure 6.17. Comparison of experimental and theoretical Young's modulus, of untreated oriented long isora-polyester composites

Theoretical and experimental values of Young's modulus of untreated oriented long isora-polyester composites are plotted in Figure 6.17. Here also the experimental values are in very good agreement with the theoretical values.

The Hirsch model and experimental tensile strength values of alkali treated oriented long isora-polyester composites shown in Figure 6.18 are in good agreement whereas the ROM model shows deviation from the experimental values above 60% fibre loading.

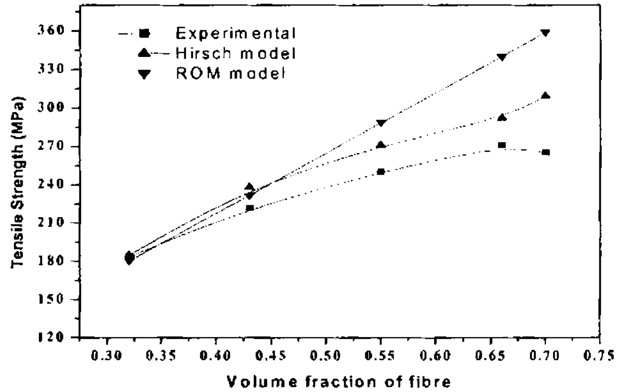


Figure 6.18. Comparison of experimental and theoretical tensile strengths of alkali treated oriented long isora-polyester composites

The experimental and Hirsch model Young's modulus values of alkali treated oriented long isora-polyester composites are in good agreement as shown in Figure 6.19 whereas the ROM values are higher.

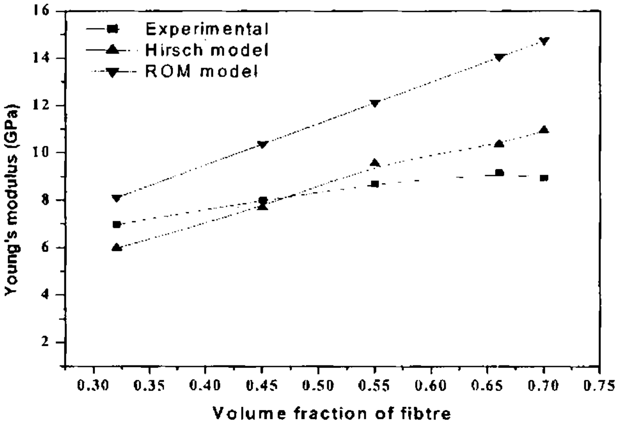


Figure 6.19. Comparison of experimental and theoretical Young's modulus of alkali treated oriented long isora-polyester composites

The value of 'x' in Hirsch model that determines the stress transfer between the fibre and matrix is found to be high (0.8-0.9) for oriented fibre composites compared to randomly oriented fibre composite (0.05). This indicates effective stress transfer between long isora fibre and polyester resin due to the strong interaction between the two.

6.4. Conclusion

The tensile strength and Young's modulus values of untreated oriented long isora-polyester composites increased regularly with fibre loading and attained a maximum value at 43% loading after which a downward trend was observed. The elongation at break values of the composites decreased with fibre loading. The maximum flexural strength and modulus were observed for 56% loading.

On alkali treatment of the fibre, the optimum loading for tensile properties increased from 43% to 66% and for flexural properties, from 56% to 66%, which is an indication of improved interfacial adhesion between the treated fibre and matrix.

Of the various treatments, alkali treatment showed maximum improvement in tensile, flexural and impact properties. Impact strength of the composite increased with fibre loading, reached a maximum value for 57% by volume of fibre after which there was no significant increase in impact strength.

References

[1] Agarwal B. D., Broutman L J. *Analysis and performance of fibre composites,* Ch. 2, John Wiley & Sons, New York. (1980).

[2] Sanadi A. R, Prasad S.V, Rohatgi P. K. *J. Mater. Sci.* (1986) **21:** 4299-4304.

[3] Aziz S. H., Ansell M. P., *Comp. Sci. and Technol.* (2004) **64:** 1219-1230.

[4] Herrera- Franco P. J., Valadez-Gonzalez A., *Comp. Part A:* (2004) **35:** 339-345.

[5] Tsai S. W. and Hahn H. T., *Introduction to Composite materials,* Technomic Publishing, Lancaster, PA, (1980).

[6] Wells J. K., Beaumont P. W., *J Mat Sci.* (1985) **20:** 1275.

[7] Thomason J. L., Vlung M. A., *Comp Part A,* (1997) **28A:** 277.

Chapter 7

ISORA FIBRE REINFORCED EPOXY COMPOSITES

Abstract

The tensile, impact and flexural properties of oriented and randomly oriented isora fibre reinforced epoxy composites with special reference to the effect of fibre loading are described in the chapter. The effect of fibre surface modifications like alkali, triton and detergent treatments and ultrasonication, on the properties of the composite is also discussed. Chemical modification of fibre was found to have enhanced the fibre/matrix interactions. The improved fibre/matrix interaction is evident from the improved tensile, flexural and impact properties of the composites. The tensile fractographs of the composites were studied by SEM to analyse the fibre/matrix interaction. The experimental tensile strength values were compared with the theoretical values.

Part of the results presented in this chapter has been published in ***Plastics, Rubber and Composites*** (2007) **36 (6)**: 259-266.

7.1. Introduction

Epoxy resins find wide applications in the production of composite materials as matrix, in spite of the relatively high cost, due to their easy processability, excellent wetting properties with reinforcements, good weathering resistance, excellent dimensional stability and the wide variety of grades available [1]. Other characteristic features of epoxy resins are their high chemical and corrosion resistance, good thermal and mechanical properties, outstanding adhesion to various substrates, flexibility, low cure shrinkage and good electrical properties [2]. The major advantage of these composite structures over traditional metallic materials like steel and aluminium are their favourable mechanical and physico-chemical properties and high strength to weight ratio. Rong *et al.* [3] studied the effect of fibre treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites and concluded that sisal fibres can be effectively modified by chemical and physical treatments. They also reported that adhesion at the interface between sisal bundles and matrix and that between ultimate cells play a key role in determining the mechanical behaviour of the laminates. Van de Weyenberg *et al.* [4] reported on improving the properties of unidirectional flax fibre reinforced epoxy composites by applying an alkaline fibre treatment and they found that this treatment resulted in a significant increase in both longitudinal and transverse composite properties, due to improvement of the fibre-matrix adhesion. Gassan and Bledzki [5] optimized the mechanical properties of tossa jute fibres using NaOH-treatment process with different alkali concentrations and shrinkages. Shrinkage of the fibres during alkali treatment had the most significant effect on the fibre structure and as a result, on the mechanical properties. Bledzki *et al.* [6] also studied the influence of fibre treatments on unidirectional hemp and flax fibres reinforced epoxy and polypropylene composites. They have reported that the structural conversion of the fibres and the mechanical properties can be affected in a broad range by using appropriate mercerization parameters like shrinkage, fibre stress, NaOH concentration, temperature and duration of alkali treatment. Bisanda and Ansell [7] reported that silane treatment improved moisture resistance and compressive strength of sisal-epoxy composites. Van de Weyenberg *et al.* [8] have studied the influence of processing and chemical treatment of flax fibres on the mechanical properties of the fibre reinforced epoxy composites. They inferred that retting action, which removed pectins, seems to be an important step to obtain better quality composites and a combined treatment of alkali and dilute epoxy gives best mechanical properties of the composite. Hepworth *et al.* [9] described a treatment that enables epoxy resin to penetrate into the cell walls of plant fibres. The treatment involves swelling the plant cell walls with urea solution, washing out the excess urea and then replacing water with alcohol in a graded series. Using this method they were able to make unidirectional flax-epoxy composites that showed large increase in stiffness when compared to composites made from untreated fibre. Gassan and Gutowski [10] reported on the effects of corona discharge and UV treatment on the properties of jute-epoxy composites. They concluded that, to improve the overall mechanical properties of jute/epoxy composites, an appropriate balance need to be achieved between increased polarity of fibre surface and the decrease of fibre strength subsequent to excessive surface oxidation by corona discharge or UV radiation. Jindal [11] studied the impact properties of bamboo fibre reinforced epoxy composites and found that impact strength of these composites is poor. Use of Kenaf fibre as a reinforcing agent in epoxy system was reported by Zimmerman and Losure [12]. J. George *et al.* [13] investigated mechanical properties of flax fibre reinforced epoxy composites and found that the thermal stability of the fibre is increased after chemical treatment. The mechanical properties of the composites were improved significantly after treatment.

Several other works have been reported using epoxy resin as matrix [14-25].

A detailed study on the tensile, impact and flexural properties of oriented and randomly oriented isora fibre reinforced epoxy composites is proposed in this chapter. Fibre surface morphology and fibre-matrix adhesion will be analysed by Scanning Electron Microscopy (SEM).

7.2. Results and discussion

7.2.1. Randomly oriented isora fibre reinforced epoxy composites

7.2.1.1. Tensile properties

a) Untreated fibre composite

The effect of fibre loading on the tensile properties of untreated randomly oriented isora-epoxy composite with standard deviation is given in Table 7.1. The variation of tensile strength and Young's modulus of the composite with fibre loading is shown in Figure 7.1. At low fibre loading, fibres act as flaws and the volume percent of the fibre is not enough to exceed the strength of the matrix [26].

Table 7.1. Effect of fibre loading on the tensile properties of untreated randomly oriented isora-epoxy composites (fibre length = 30mm)

Fibre loading (% v/v)	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
0 (neat resin)	45 ± 2.2	1500 ± 60	4.5 ± 0.18
10	31 ± 1.4	1362 ± 57	2.5 ± 0.13
24	37 ± 1.6	2180 ± 85	2.5 ± 0.14
29	46 ± 2.1	2324 ± 88	2.6 ± 0.14
37	55 ± 2.6	2672 ± 95	2.7 ± 0.15
45	60 ± 2.8	2784 ± 99	2.8 ± 0.16
52	56 ± 2.7	2690 ± 97	2.6 ± 0.14

The tensile strength of the composite decreased up to a fibre loading of 24 vol. % and exceeds that of resin only at a loading of 29 vol. %. After that a linear increase is observed. The tensile strength of the composite reached a maximum value at a fibre loading 45 vol. %. The increase in tensile strength compared to neat resin is 33% at this fibre loading. Thereafter a decrease in tensile strength is observed.

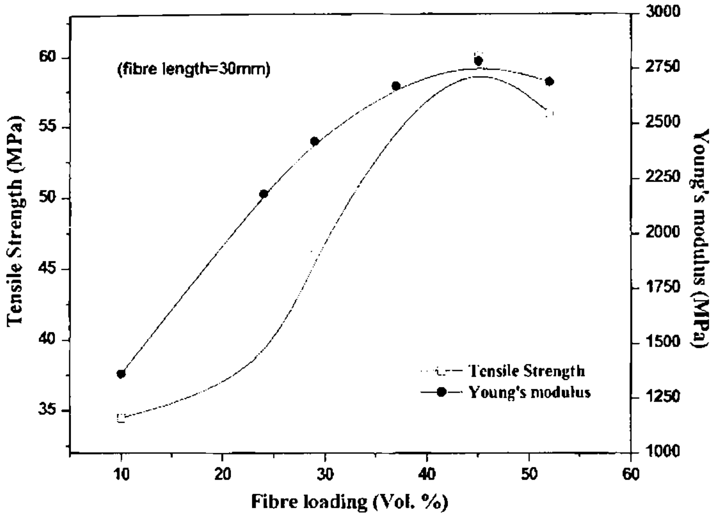
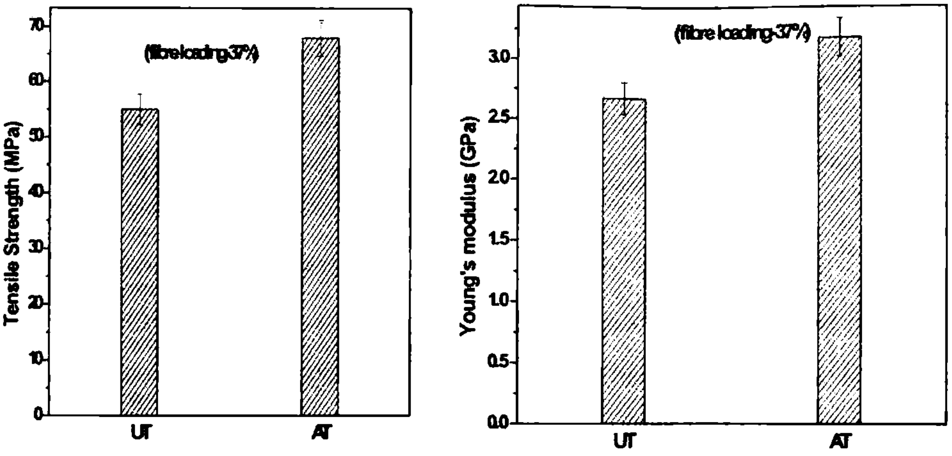


Figure 7.1. Variation of tensile strength and Young's modulus with fibre loading of untreated randomly oriented isora-epoxy composites

But Young's modulus values showed a linear increase after the initial decrease at 10% fibre loading and reached a maximum value at 45 % fibre loading. After that the property decreased for higher fibre loading. Compared to neat resin, this increase in Young's modulus is 85.6%. So the optimum fibre loading is 45%, which is adequate for proper wetting of fibres with epoxy resin. The decrease in tensile properties of the composites with further increase in fibre loading may be due to improper wetting and adhesion between the fibre and resin resulting in inefficient stress transfer. Elongation at break (EB) values of the composites is lower than that of neat resin, indicating improved stiffness. EB value is maximum for the composite containing 45% fibre.

b) Alkali treated fibre composite

The effect of alkali treatment on the tensile strength and Young's modulus of randomly oriented isora-epoxy composite is given in Figures 7.2 (a) and (b) respectively.



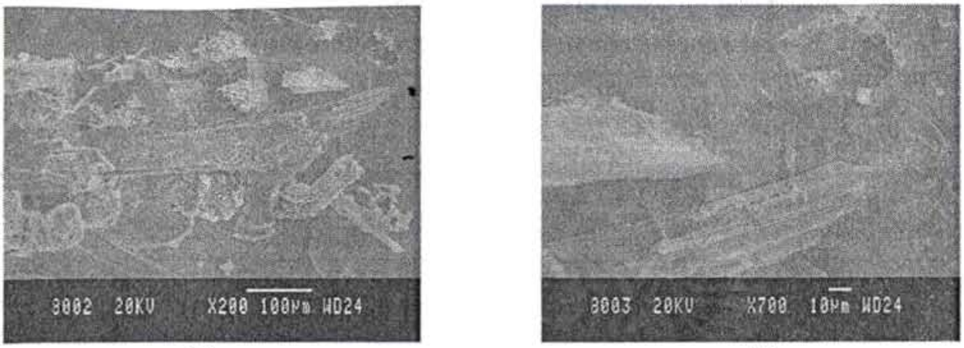
(a) (b)

Figure 7.2. Effect of alkali treatment on (a) tensile strength and (b) Young's modulus of randomly oriented isora-epoxy composite.

Alkali treatment of the fibre improved the tensile properties of the composite. For a fibre loading of 37 vol. %, tensile strength improved by 23.6% and Young's modulus by 19.5%. Elongation at break of the composite decreased on alkali treatment indicating enhanced stiffness of the composite.

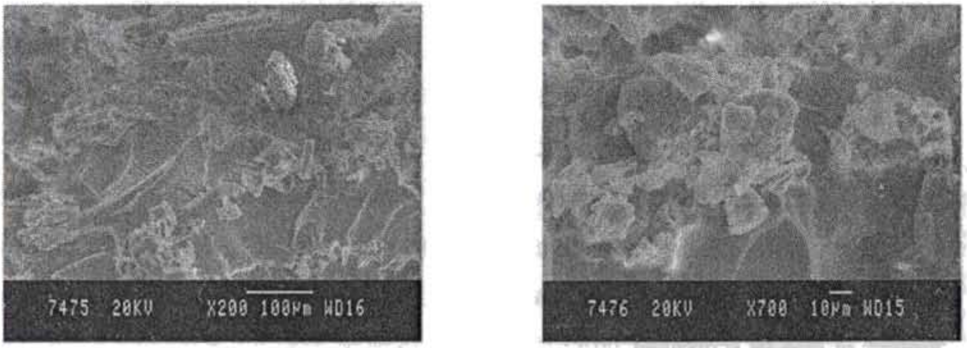
The improvement in tensile properties can be attributed to the improved wetting of alkali treated fibre with epoxy resin [27]. On alkali treatment, lignin and hemi cellulose, the cementing materials present in the fibre get dissolved. This makes the interfibrillar region less dense and less rigid as a result of which the fibrils become more capable of orienting themselves along the tensile deformation [28].

The improved wetting of the fibre with the matrix is evident from the SEM photograph of the tensile fracture surface of the alkali treated fibre composite (Figure 7.4) compared to that of untreated fibre composite (Figure 7.3)



(a) (b)

Figure 7. 3. Tensile fracture surface of untreated randomly oriented, isora-epoxy composite (a) × 200 and (b) × 700, showing fibre pull out



(a) (b)

Figure 7. 4. Tensile fracture surface of alkali treated randomly oriented, isora-epoxy composite (a) × 200 and (b) × 700

7.2.1.2. Flexural properties

a) Untreated fibre composite

The effect of fibre loading on the flexural properties of randomly oriented isora-epoxy composite with standard deviation is given in the Table 7.2. The variation of flexural strength and flexural modulus of the composite with fibre loading is given in Figure 7.5. The flexural strength of the composites containing 10 and 25 vol. % fibres has lower flexural strength compared to neat resin. After that flexural strength of the composite increased with fibre loading and reached maximum at 45% fibre loading, the increase being 19.5%. Flexural strength of the composite decreased at higher fibre loadings.

Table 7.2. Effect of fibre loading on the flexural properties of randomly oriented isora-epoxy composites (fibre length=30mm)

Fibre loading (% v/v)	Flexural strength (MPa)	Flexural modulus (GPa)	Maximum strain (%)
0 (neat resin)	87 ± 3.5	2.322 ± 0.09	4.31 ± 0.18
10	65 ± 2.7	2.666 ± 0.11	2.09 ± 0.08
25	83 ± 3.7	4.619 ± 0.19	2.65 ± 0.12
37	91 ± 4.0	5.903 ± 0.25	2.37 ± 0.10
45	104 ± 4.3	6.121 ± 0.26	2.65 ± 0.13
52	96 ± 4.4	5.954 ± 0.24	2.52 ± 0.12

Flexural modulus of the composite increased linearly right from the beginning and reached maximum at 45% fibre loading, the increase being 163%, after which a lowering of modulus was observed. So the optimum fibre loading for randomly oriented isora-epoxy composite is 45 vol. %, which is adequate for proper wetting of the fibre and thereby maximum stress transfer between the fibre and resin. The lower flexural strength of the composite compared to neat resin at lower fibre loadings is due to inefficient stress transfer. Increase in flexural strength with increasing fibre content is due to increased interaction and adhesion between fibre and resin. The decrease of flexural strength at higher fibre loading is due to increased fibre-to-fibre interaction and dispersion problems.

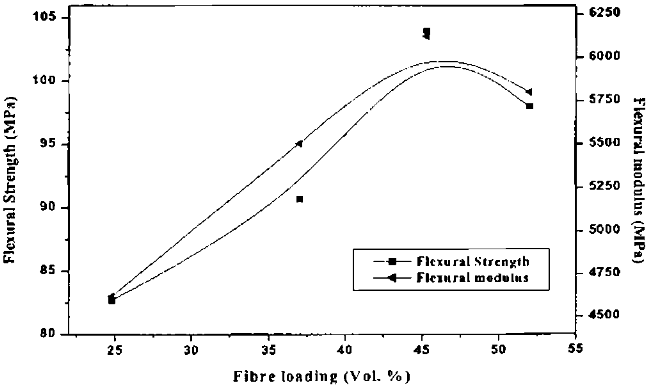


Figure 7.5. Variation of flexural strength and flexural modulus with fibre loading, of randomly oriented isora-epoxy composite

b) *Alkali treated fibre composite*

On alkali treatment, flexural properties of the composite were found to be improved. At a fibre loading of 37 vol. %, the flexural strength of the composite improved by 9% and a marginal increase of 3.5% in flexural modulus was also observed (Figure 7.6). The increase in flexural strength and flexural modulus on alkali treatment of fibre can be attributed to the formation of rough fibre surface leading to the improved wetting of fibres with the matrix.

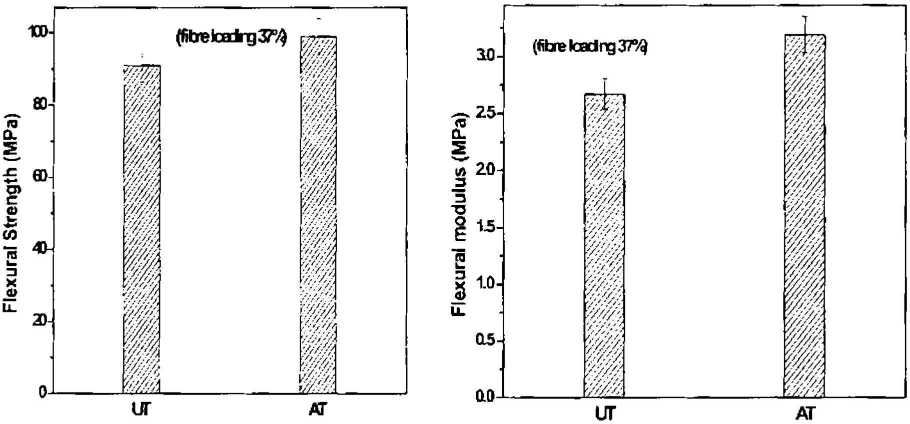


Figure 7.6. Effect of alkali treatment on the flexural strength and flexural modulus of randomly oriented isora-epoxy composite.

7.2.1.3. Impact properties

a) *Effect of fibre loading*

The variation of impact strength of untreated randomly oriented isora-epoxy composites with fibre loading is given in Figure 7.7. The impact strength of the composites is increasing linearly with fibre loading up to 56%. The increase in impact strength is not significant above 56% fibre loading. Compared to neat resin (67 J/m), there is 134% increase in impact strength for the composite containing 56% fibre by volume.

The improvement in impact strength of the composite may be attributed to the extra energy needed for the fibre pull out, debonding or redistribution of stress.

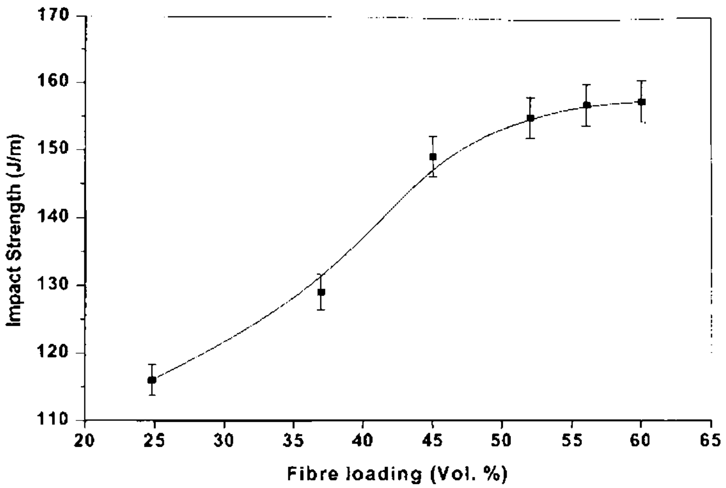


Figure 7.7. Effect of fibre loading on the impact strength of randomly oriented isora-epoxy composite

b) *Effect of alkali treatment*

The effect of alkali treatment on the impact strength of randomly oriented isora-epoxy composite containing 34 vol. % fibre is given in Figure 7.8.

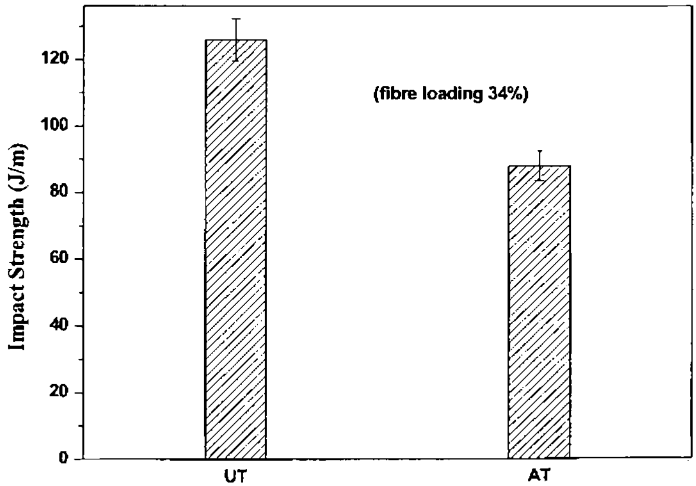


Figure 7.8. Effect of alkali treatment on the impact strength of randomly oriented isora-epoxy composite

Alkali treatment of fibre lowered the impact strength of the composite by 30% compared to untreated fibre composite. This lowering of impact strength of the alkali treated fibre composite may be attributed to the stronger interfacial bonding between the fibre and the resin. A weak interface will not facilitate efficient stress transfer resulting in a weak but tough composite. But the composites having strong interface will have low toughness value compared to the one having weaker interface. The low impact strength of the alkali treated fibre composite is assumed to be due to the strong interface as evidenced from the mechanical properties of the composite.

7.2.2. Oriented long isora fibre reinforced epoxy composites

7.2.2.1. Tensile properties

a) Effect of fibre loading on untreated fibre composite

The effect of fibre loading on the tensile properties of the untreated, oriented long isora fibre-epoxy composite with standard deviation are given in the Table 7.3. The variation of tensile strength and Young's modulus of the composite with fibre loading is shown in the Figure 7.9.

Table 7.3. Effect of fibre loading on the tensile properties of oriented long isora-epoxy composites

Fibre loading (% v/v)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
0 (neat resin)	45 ± 2.2	1.50 ± 0.06	4.46 ± 0.18
31	109 ± 4.3	3.8 ± 0.17	3.26 ± 0.13
36	151 ± 6.3	5.15 ± 0.23	3.41 ± 0.14
40	178 ± 7.8	5.99 ± 0.28	3.56 ± 0.16
49	200 ± 8.0	6.55 ± 0.30	4.42 ± 0.20
53	198 ± 7.9	6.48 ± 0.29	4.07 ± 0.18

Tensile strength and modulus of the composite increased regularly with fibre loading and reached maximum at 49% loading. The increase in tensile strength is

344% and increase in Young's modulus is 337%, compared to neat epoxy resin. The increase in tensile strength and modulus are not significant at higher fibre loadings.

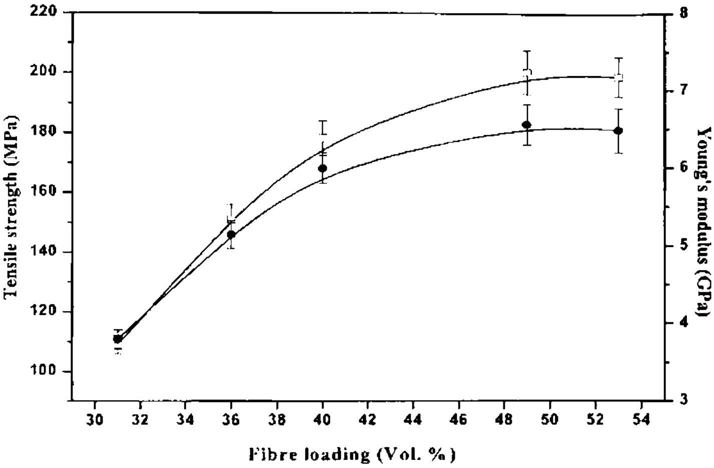


Figure 7.9. Variation of tensile strength and Young's modulus with fibre loading of untreated oriented long isora-epoxy composites.

So the optimum fibre loading for the tensile properties of the composite is 49% by volume at which there is maximum wetting of the fibre and effective stress transfer at the fibre/matrix interface. The decrease in tensile properties at higher fibre loadings may be due to improper wetting and adhesion. EB values of the composite are lower than that of neat resin and increase regularly with fibre loading, reached maximum at the optimum fibre loading of 49 vol. %.

b) Effect of fibre treatments

The effect of various surface modifications of the fibre on the tensile properties of the oriented long isora fibre-epoxy composites, with standard deviation is given in the Figures 7.10, 7.11and 7.12. The effect of fibre treatment on the tensile strength of the composites is given in Figure 7.10. All fibre treatments resulted in improvement in tensile properties. The tensile strength increased in the order UT < US < DT < AT < TT. The percentage increase in tensile strength of the treated fibre composites compared to untreated fibre composite is as follows: TT-10, AT-5.5, DT-5 and US-2.5.

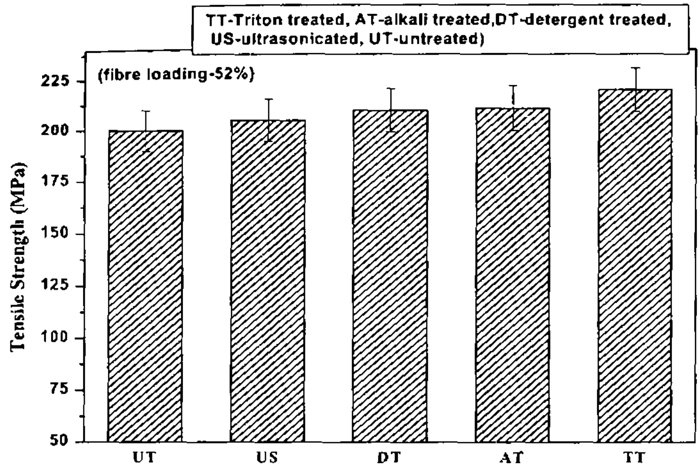


Figure 7.10. Effect of various fibre treatments on the tensile strength of oriented long isora-epoxy composites

Figure 7.8 shows the effect of fibre treatment on the Young's modulus of the composites. The increase in Young's modulus values of the composites on surface modification of the fibre follows the same trend as in the case of tensile strength. The percentage increase in the property compared to UT fibre composite is: TT-26.9, AT-12.3, DT-10.5 and US-9. It can be observed that fibre treatments have more effect on stiffness of the composite than on tensile strength.

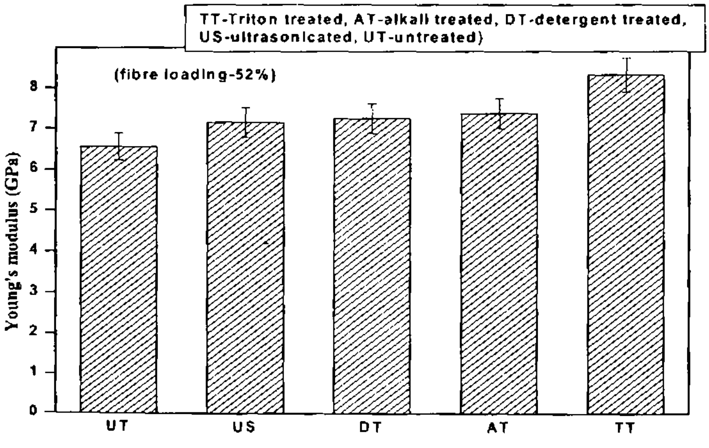


Figure 7.11. Effect of various fibre treatments on Young's modulus of oriented long isora-epoxy composites

The effect of fibre treatment on % elongation at break of the composite is given in Figure 7.12. The EB values of the treated fibre composites are lower than that of untreated fibre composite, supported by the high modulus values of the treated fibre composites.

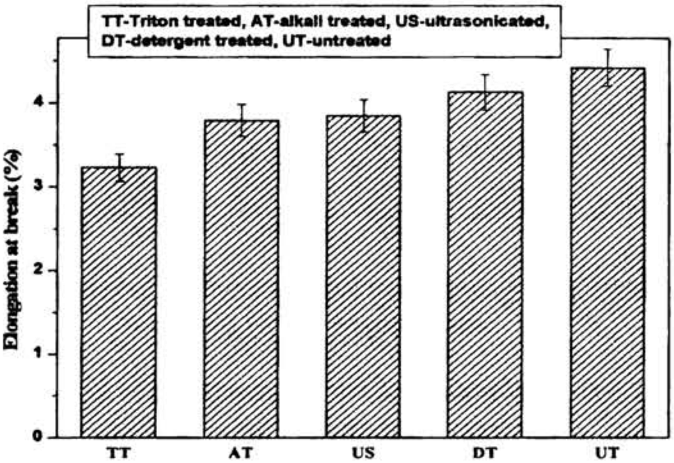
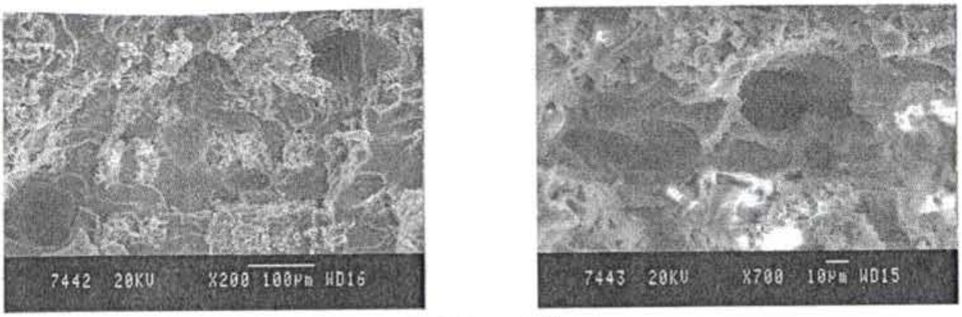


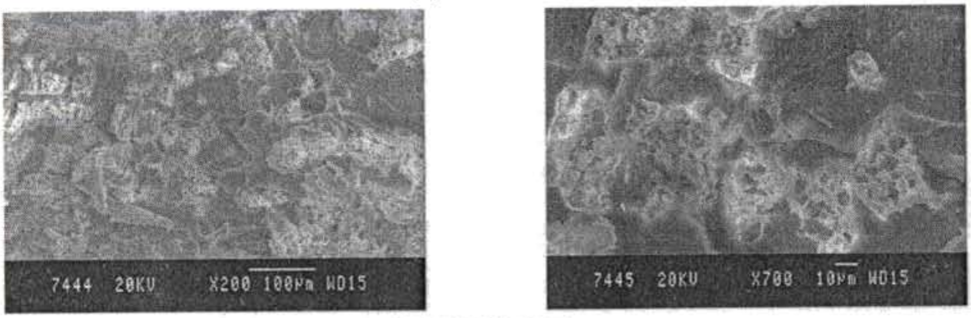
Figure 7.12. Effect of various fibre treatments on % elongation at break of oriented long isora-epoxy composites

The improvement in tensile properties can be attributed to the improved adhesion between the fibre and the resin after chemical treatment of fibre. Fibre treatment washes away the surface impurities and develops micro porosity with many pits and holes on the fibre surface by the removal of globular protrusions of fibre surface present in the untreated fibre. This leads to a larger area of contact and greater mechanical interlocking between fibre and matrix, making the interfacial adhesion stronger and the mechanical properties higher. The decrease in tensile strength and Young's modulus at higher fibre loadings is due to improper wetting and poor adhesion between the fibre and matrix resin.

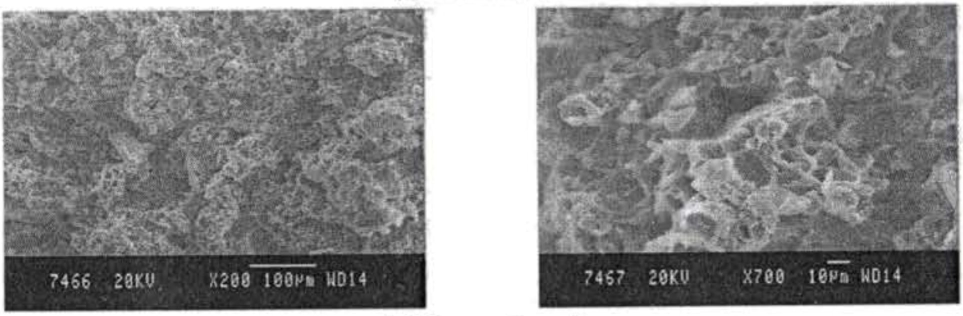
The Scanning electron photographs of the tensile fracture surface of oriented long isora-epoxy composites are given in the Figures 7.13 (a) to (d)



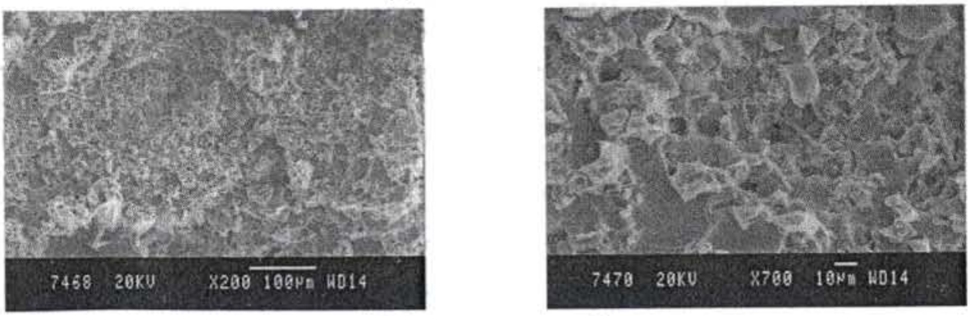
(a) Untreated



(b) Alkali treted



(c) Ultrasonicated



(d) Detergent treated

Figure 7.13. **(a)-(d)** Tensile fracture surface of treated, oriented long isora-epoxy composites at magnifications × 200 and × 700

Fibre pull out and debonding are clear in the SEM photograph of untreated fibre composite whereas improved fibre-matrix adhesion is evident in the SEM photographs of various treated fibre composites.

7.2.2.2. Flexural properties

a) Untreated fibre composite

The effect of fibre loading on the flexural properties of untreated fibre composites, with standard deviation is given in Table 7.4. The variation of flexural strength and flexural modulus of the composite are shown in Figure 7.14. The flexural strength and flexural modulus of the composites are higher than that of neat resin. The flexural strength and flexural modulus of the composite increased regularly with fibre loading, reached maximum at a fibre loading of 45% by volume, then decreased for higher loadings.

Table 7.4. Effect of fibre loading on the flexural properties of untreated oriented long isora-epoxy composites

Fibre loading (% v/v)	Flexural strength (MPa)	Flexural modulus (GPa)	Strain (%)
0 (neat resin)	87 ± 3.5	2.32 ± 0.09	4.31 ± 0.18
33	162 ± 6.8	7.85 ± 0.34	3.11 ± 0.13
37	180 ± 7.9	10.3 ± 0.0.45	3.20 ± 0.14
41	195.5 ± 8.4	11.62 ± 0.53	3.29 ± 0.15
45	200 ± 9	12.64 ± 0.57	3.39 ± 0.17
50	190 ± 8.3	11.42 ± 0.50	3.17 ± 0.13

Compared to neat resin, the increase in flexural strength of the composite is 86% at a fibre loading of 33% and 131% at 45% fibre loading. The corresponding increase in flexural modulus is 238% at 33% fibre loading and 453%, at 45% fibre loading. So the optimum fibre loading for flexural properties of the untreated fibre composite is 45% by volume. Increase in flexural strength with increasing fibre loading is due to increased interaction between fibre and matrix whereas the decrease of flexural strength at higher fibre loading is due to increased fibre-to-fibre interaction and dispersion problems.

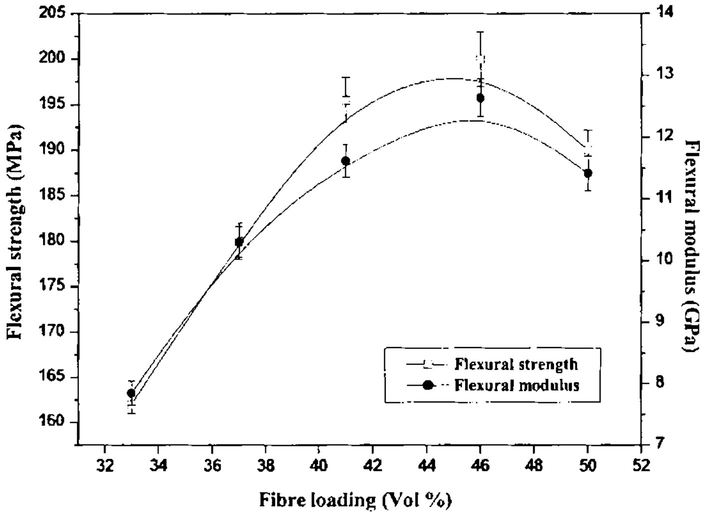


Figure 7.14. Effect of fibre loading on the flexural strength and flexural modulus of untreated oriented long isora-epoxy composites

b) Effect of fibre treatments

The effect of various surface modifications of the fibre on the flexural properties of the oriented long isora fibre-epoxy composites, with standard deviation is given in the Figures 7.15, 7.16 and 7.17. Figure 7.15 shows the effect of fibre treatment on the flexural strength of the composites compared to untreated fibre composite. Flexural properties of the composite are found to be improved by all fibre treatments. The flexural strength increased in the order UT < AT < DT < TT < US. The percentage increase in flexural strength of the treated fibre composites compared to UT fibre composite is as follows: AT-38, DT-41.5, TT-50.3 and US-59.

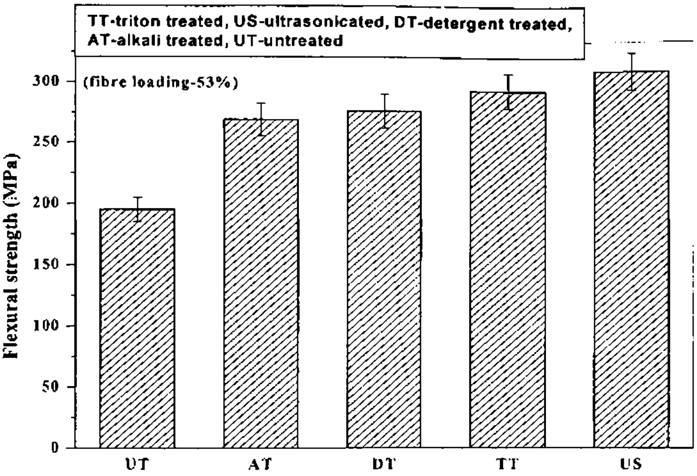


Figure 7.15. Effect of various fibre treatments on flexural strength of oriented long isora-epoxy composites

The effect of fibre treatment on the flexural modulus of the oriented long isora-epoxy composites, with standard deviation is given in the Figure 7.16. Flexural modulus of the composite varied in the same manner as that of flexural strength, on fibre treatment. Compared to untreated fibre composite the percentage increase in flexural modulus of the treated fibre composite is: AT-35, DT-36.4, TT-70.7 and US-80.

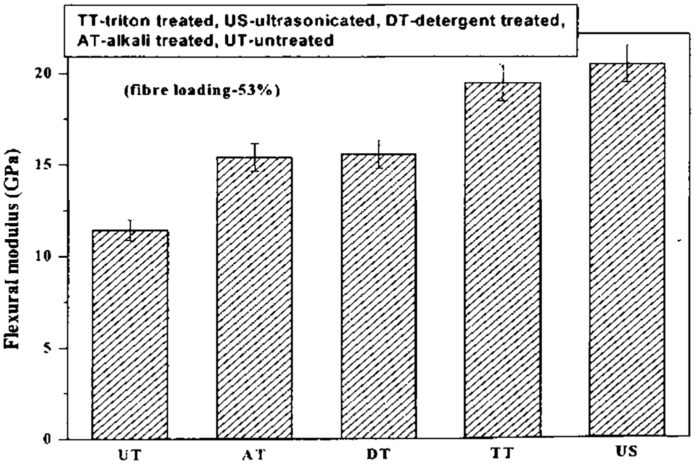


Figure 7.16. Effect of various fibre treatments on flexural modulus of oriented long isora-epoxy composites

On fibre treatment, flexural strain of the composite varied in the order: TT < US < DT< AT < UT. (Figure 7.17). The decrease in percentage strain of the treated fibre composites compared to the untreated fibre composite is TT-42.4, US-37.5, DT-35.9 and AT-7.7.

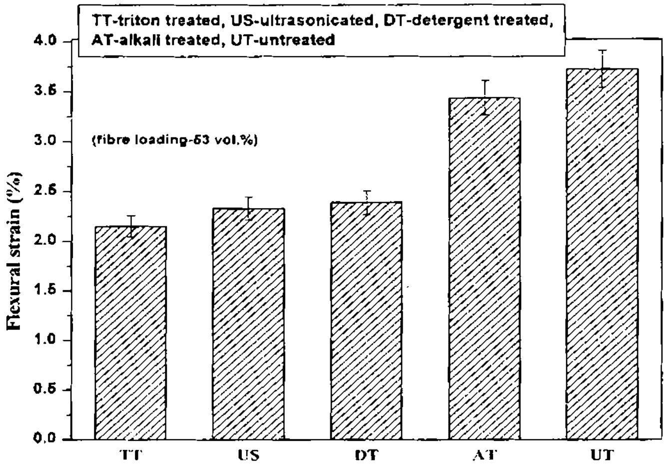


Figure 7.17. Effect of various fibre treatments on the flexural strain of oriented long isora-epoxy composites

7.2.2.3. Impact properties

a) Untreated fibre composite

Figure 7.18 shows the variation of impact strength of the untreated oriented long isora-epoxy composites with fibre loading. Impact strength increased with fibre loading, reached a maximum value at 55% by volume of fibre. Compared to neat resin, the increase in impact strength is 166%. With further increase in fibre loading, there is no significant increase in impact strength. The fibres play an important role in the impact resistance of the composites as they interact with the crack formation in the matrix and act as stress transferring medium.

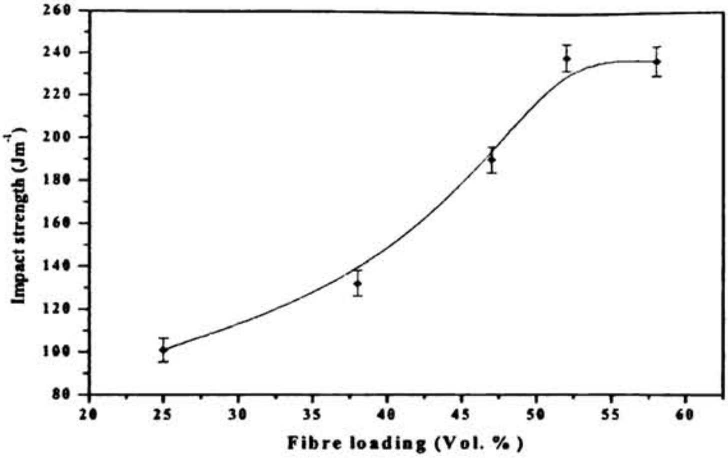


Figure 7.18. Variation of impact strength with fibre loading of untreated, oriented long isora-epoxy composites

b) Treated fibre composite

The effect of various fibre modifications on the impact strength of oriented long isora-epoxy composite is given in the Figure 7.19. On fibre treatment, impact strength of the composites improved, the improvement followed the order: TT > AT > US > DT > UT. Compared to untreated fibre composite the percentage increase in impact strength is: DT-29.6, US-32.5, AT-33.7 and TT-36.2.

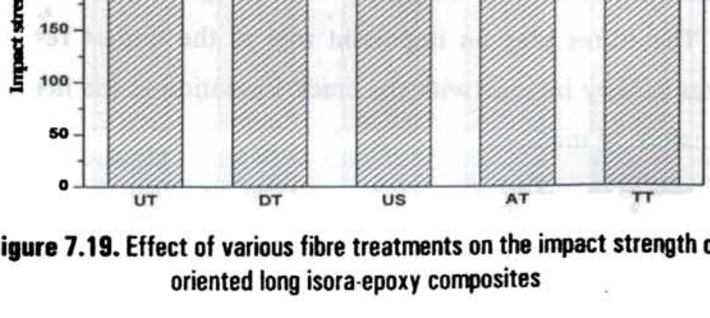


Figure 7.19. Effect of various fibre treatments on the impact strength of oriented long isora-epoxy composites

The impact failure of a composite occurs by factors like matrix fracture, fibre/matrix debonding and fibre pull out. Fibre pull out is found to be an important energy dissipation mechanism in fibre reinforced composites [29].

Figure 7.20. Optical photograph of the impact fracture surface of oriented isora-epoxy composite

The applied load transferred by shear to fibres may exceed the fibre/matrix interfacial bond strength and then debonding occurs. When the stress level exceeds the fibre strength, fibre fracture occurs. The fractured fibres may be pulled out of the matrix, which involves energy dissipation [30]. The impact fracture of the composites was brittle as evident from Figure 7.20 and not hinge type like their polyester counterpart (Figure 6.12). This indicates stronger interfacial adhesion in the epoxy composite. This is supported by the lower impact strength of oriented isora-epoxy composites compared to oriented isora-polyester composites (compare Figures 6.10 and 7.18). Fibre breakage is the main energy dissipating mechanism here.

7.3. Theoretical modeling

7.3.1. Randomly oriented isora-epoxy composites

The theoretical values of tensile strength calculated using Series and Hirsch model are found to be higher than the experimental tensile strengths of untreated randomly oriented isora-epoxy composites, shown in Figure 7.21. But the theoretical and experimental Young's modulus values are in good agreement which is evident in Figure 7.22, indicating effective stress transfer between isora fibre and epoxy resin.

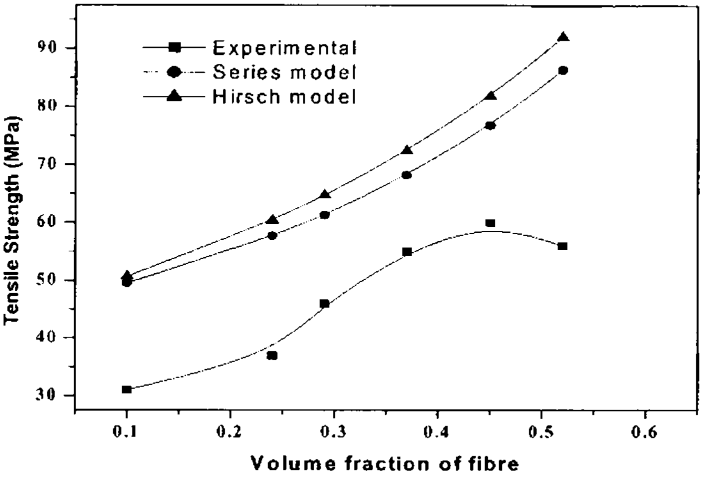


Figure 7.21. Comparison of experimental and theoretical tensile strengths of untreated randomly oriented isora-epoxy composites

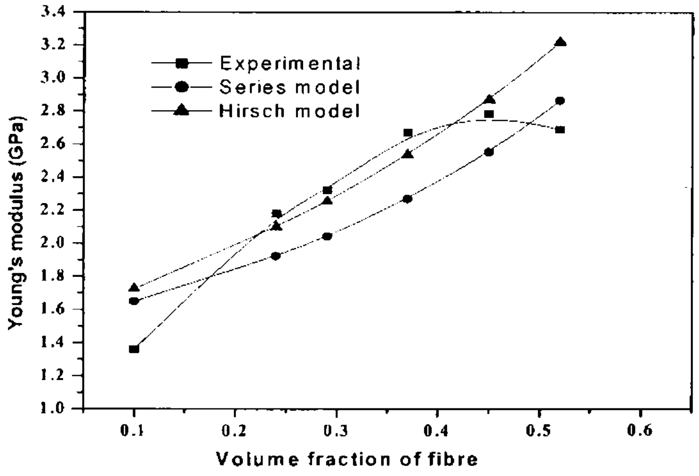


Figure 7.22. Comparison of experimental and theoretical Young's modulus of untreated randomly oriented isora-epoxy composites

7.3.2. Oriented isora-epoxy composites

The theoretical and experimental values of tensile strength and Young's modulus of the composite are plotted in Figures 7.23 and 7.24 respectively. In both cases, there is better agreement between Hirsch model values and the experimental ones whereas the ROM values are higher than experimental values.

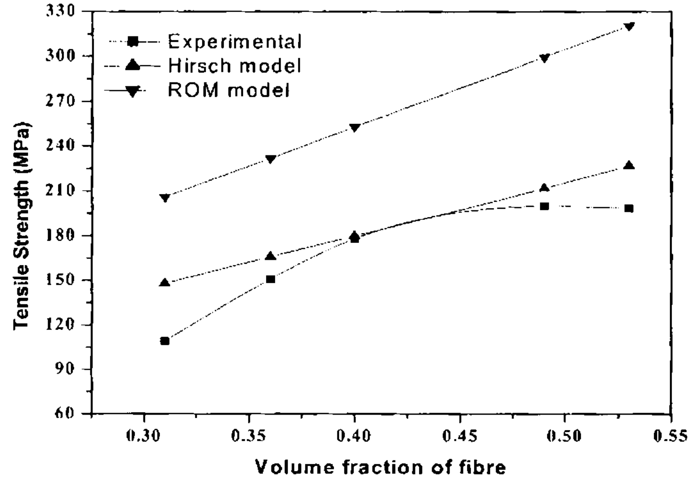


Figure 7.23. Comparison of experimental and theoretical tensile strengths of untreated oriented long isora-epoxy composites

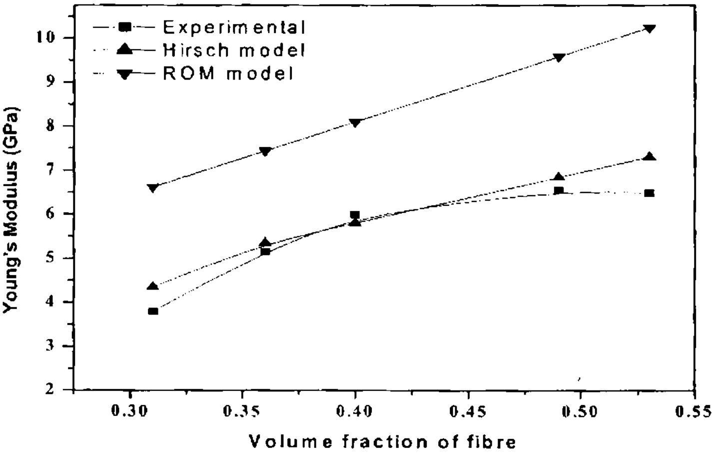


Figure 7.24. Comparison of experimental and theoretical Young's modulus of untreated oriented long isora-epoxy composites

7.4. Conclusion

Randomly oriented untreated isora-epoxy composites showed maximum properties at 45% fibre loading. Alkali treatment of fibre improved tensile and flexural properties of the composite but decreased the impact strength.

The tensile properties of oriented long isora-epoxy composites were maximum at 49% fibre loading and the flexural properties at 45% fibre loading. All fibre treatments resulted in enhancement of properties. Triton treatment showed maximum improvement in tensile and flexural properties. The tensile fractographs of the composites were studied by SEM and it further showed improved fibre-matrix interaction for the samples which showed high strength and moduli.

Impact strength of the composite was maximum at 55% fibre loading. Fibre treatments resulted in improved impact strength, which was maximum for triton treatment.

References

[1] Collyer A., Ed. 'Rubber toughened engineering Plastics', Ch. 6; 1994, Chapman & Hall, London.

[2] Carfagna, D. Acierno, V. D. Palma, E. Amendola, M. Giamberini, *Macromol. Chem. Phys.*, (2000) **201:** 2631-2638.

[3] Rong M. Z., Zhang M. Q., Liu Y., Yang G. C., Zeng H. M., *Comp. Sci. Technol.*, (2001) **61:** 1437-1447.

[4] Van de Weyenberg, Chi Truong T., Vangrimde B., Verpoest I., *Composites: Part A.*, (2006) **37(9):** 1368-1376.

[5] Gassan J., Bledzki A. K., *Comp. Sci. Technol.*, (1999) **59:** 1303-1309.

[6] Bledzki K., Fink H. P., Specht K., *J. Appl. Polym. Sci.*, (2004) **93:** 2150-2156.

[7] Bisanda E. T. N., Ansell M. P., *Comp. Sci. Technol.*, (1991) **41:** 165-178.

[8] Van de Weyenberg, Ivens J., De Coster A., Kino B., Baetens E., Verpoest I., *Comp. Sci. Technol.,* (2003) **63:** 1241-1246.

[9] Hepworth P., Vincent J. F. V., Jeronimidis G., Bruce D. M., *Composites: Part A.,* (2000) **31:** 599-601.

[10] Gassan J., Gutowski V. S., *Comp. Sci. Technol.,* (2000) **60:** 2857-2863.

[11] Jindal U. C., *J. Comp. Mater.,* (1986) **20:** 19.

[12] Zimmerman J. M. and Losure N. S., *J. Adv. Mater.,* (1998) **30,** 32.

[13] George J., Van De Weyenberg., Ivans J. and Verpoest I., 2^{nd} *International Wood and Natural Fibre Composites Symposium* June 28-29, 1999 in Kassel/Germany.

[14] Low M., Schmidt P. and Lane J., *J. Mater. Sci. Lett.* (1995) **14:** 170-172.

[15] Kandola B. K., Horrocks A. R., Myler P., Blair D., *J. Appl. Polym. Sci.,* (2003) **88:** 2511-2521.

[16] Andreopoulos G., Tarantili P. A., *J. Appl. Polym. Sci.,* (1998) **70:** 747-755

[17] Siddaramaiah, Suresh S. V., Atul V. B., Srinivas D., Girish S., *J. Appl.Polym. Sci.,* (1999) **73:** 795-799.

[18] Wan Y. W., Wang Y. L., Zhou F. G., Cheng G. X., Han K. Y., *J. Appl. Polym. Sci.,* (2002) **85:** 1040-1046.

[19] Raval K., Patel R. B., Vyas S. K., *Macromol. Mater. Eng.* (2002) **287:** 133-138.

[20] Liu L., Huang Y. D., Zhang Z. Q., Jiang B., Nie J., *J. Appl. Polym. Sci.,* (2001) **81:** 2764-2768.

[21] Wei Q., Lazzeri A., Cuia F. D., Scalari M., Galoppini E., *Macromol. Chem. Phys.,* (2004) **205:** 2089-2096.

[22] Chang-Lun Lee, Kung-Hwa-Wei, *J. Appl. Polym. Sci.,* (2000) **77:** 2149-2156.

[23] Kulkarni S. M., Kishore, *J. Appl. Polym. Sci.,* (2003) **87:** 836-841.

[24] Amdouni N., Sautereau H., Gerard J. F., *J. Appl. Polym. Sci.,* (1992) **45:** 1799-1810.

[25] Sapuan S. M., Maleque M. A., *Materials and Design,* (2005) **26:** 65-71.

[26] Milewski J. V. and Katz H. S., *Handbook of Reinforcements for Plastics,* Van Nostrand Reinhold, N. Y., (1987).

[27] Prasad S. V., Pavithran C., Rohatgi P. K., *J. Mater. Sci.* (1983) **18:** 1443.

[28] Bledzki A.K., Gassan J., *Prog. Polym. Sci.* (1999) **24:** 221–274.

[29] Wells J. K., Beaumont P. W., *J. Mat. Sci.* (1985) **20:** 1275.

[30] Thomason J. L., Vlung M. A., *Comp. Part A,* (1997) **28A:** 277.

Chapter 8

DYNAMIC MECHANICAL ANALYSIS OF ISORA FIBRE REINFORCED POLYESTER AND EPOXY COMPOSITES

Abstract

The dynamic mechanical properties of the composites were studied with special reference to fibre loading and fibre surface .modifications. The storage moduli of the composites were found to increase with fibre loading and with fibre surface modifications. The damping properties of the composites were found to decrease with fibre loading and with fibre surface modifications indicting enhanced fibre/matrix adhesion. The storage modulus and damping factor of the composites were compared with theoretical predictions.

8.1. Introduction

Dynamic mechanical analysis (DMA) is a sensitive technique [1-5] that is used for studying the effect of temperature on the mechanical properties of materials. DMA has been mainly used for evaluating the interfacial interactions in composite materials. Dynamic tests, over a wide range of temperature and frequency, are especially sensitive to all kinds of transitions and relaxation processes of matrix resin and also to the morphology of the composites [6]. The dynamic behaviour of the composites plays important roles in the applications because there are always repeated loading and fatigue loading on the composite materials. DMA is a versatile thermal analysis technique, which measures the modulus (stiffness) and damping properties (energy dissipation) of materials, as the materials are deformed under periodic stress. The technique separates the dynamic modulus $|E|$ of materials into two distinct parts: an elastic (storage) part (E') and viscous (loss) component (E''). Storage modulus is the most important property to assess the load bearing capacity of a composite material. The ratio of the loss modulus to the storage modulus is known as the mechanical loss factor ($\tan \delta$), is a measure of energy dissipation (damping parameter) [7]. Since the fibre-reinforced materials undergo various types of dynamic stressing during service, studies of viscoelastic behaviour of these materials are of great importance.

The principal use of natural fibre reinforced composites is for the interior lining of cars and commercial vehicles. For these applications they should have strength and stiffness properties retaining up to 100°C. In dynamic mechanical thermal analysis, the performance of material over a wide range of temperatures is analysed. Several studies have been reported on the dynamic mechanical properties of various natural/synthetic fibre reinforced composites [8-11]. Several researchers have done interface characterization using DMA [12-15]. Rana *et al.* [16] reported on the effect of acetylation on dynamic properties of jute board. They found that E' of acetylated boards was much higher than that of the non-acetylated one at a particular temperature. Also E" and tan δ peaks were lowered due to increased bulkiness of the fibre after acetylation. Kaliske and Rothert have done modelling of material damping of unidirectional fibre reinforced composites [17]. Pedroso *et al.* [18] in the study of the role of additives in the manufacture of sheets of unsaturated polyester and post consumer unsaturated polyester/glass fibre composites found that when silane was directly added to resin and the ground material was previously treated with silane, there was an increase of E′ and a shift toward higher temperatures of the inflection point, indicating that there was an improvement in interfacial adhesion. Saha *et al.* [6] observed that when jute fibre was cyanoethylated, the storage modulus and thermal transition temperature of the composites with polyester, shifted to higher values. Aziz *et al.* [7] studied the effect of alkalization and fibre alignment of long and random hemp and kenaf fibre reinforced polyester resin and reported that the alkalized fibre composites have higher E′ and lower tan δ indicating greater interfacial bond strength and adhesion between the matrix resin and the fibre. Thomas and co-workers have reported the dynamic mechanical response of various natural fibre filled polymer composites [19-22]. It was observed that introduction of natural fibres into the polymer matrix improved the viscoelastic properties to a greater extent.

Gassan [23] observed that natural fibre reinforced plastics with higher fibre strength and modulus; strong fibre/matrix adhesion and fibre volume fractions possess higher critical loads for damage initiation and higher failure loads. Ghosh *et al.* [24] found that the storage modulus of hybrid fibre reinforced epoxy composites of glass and jute showed intermediate modulus values compared to individual composites.

The effect of surface treatments of glass fibre on the dynamic mechanical properties of epoxy resin based composites were analysed by Keusch and Haessler [25]. They also compared the values with mechanical measurements of adhesion. It was found that the storage modulus of composite increased with increasing interfacial adhesion and a decrease in the value tan δ at relaxation revealed a better interfacial adhesion.

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.

Characterization and evaluation of the viscoelastic response of a series of oriented and randomly oriented isora fibre reinforced polyester and epoxy composites are proposed to be undertaken in this chapter. The effect of fibre loading, fibre orientation, chemical treatments and temperature on the dynamic mechanical properties of isora fibre reinforced polyester and epoxy composites will also be analysed.

8.2. Results and discussion

8.2.1. Randomly oriented isora-polyester composites

8.2.1.1. Effect of fibre loading

The damping mechanism in composites mainly results from the viscoelastic nature of matrix and fibre, the thermo elastic damping, the coulomb friction damping due to slip between the unbonded, debonded and bonded regions of fibre-matrix interface and the energy dissipation occurring at cracks or delaminations [26].

Figure 8.1 illustrates the variation of storage modulus (E′) with fibre loading of randomly oriented isora-polyester composite as a function of temperature. It is found that the storage modulus of the composites increased with increase in fibre content and it is more pronounced at low temperatures. This increase in E′ of the composites at higher fibre loading is due to greater interfacial adhesion and bond strength between matrix resin and fibre as reported by several authors [27, 7]. The E′ values of the composites fell steeply around the glass transition temperature at 60-80°C. T_g values are often determined by constructing a straight line through the linear viscoelastic part of the E' characteristic and a tangent to the elastic portion of the E' characteristic. Where these lines cross corresponds to the T_g value. On fibre loading T_g values of the composites increased. The E' value is maximum at 34% fibre loading and then decreased at 41% fibre loading which may be caused by the increase in fibre-to-fibre interaction resulting in poor dispersion.

The decrease in modulus at higher temperature is associated with the chain mobility of the matrix [28] and the thermal expansion occurring in the matrix resulting in reduced intermolecular forces [29].

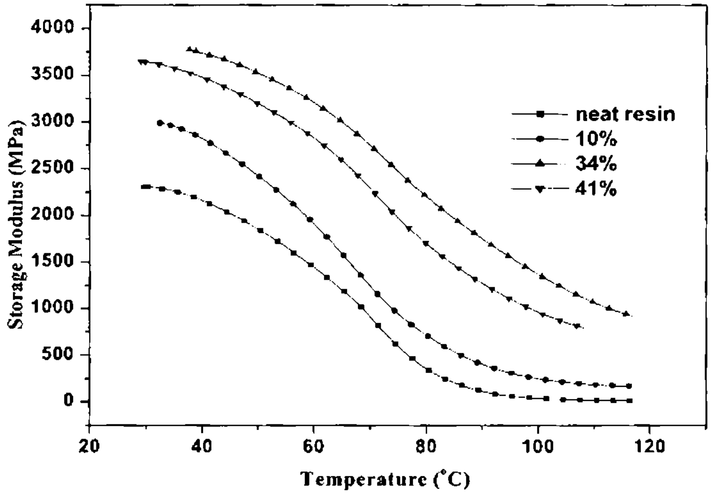


Figure 8.1. Variation of storage modulus of randomly oriented isora-polyester composite with fibre loading at different temperatures

Table 8.1. shows the storage modulus and relative (normalized) storage modulus (E'_c/E'_m where E'_c and E'_m are the storage moduli of composite and matrix respectively) values of untreated randomly oriented isora/polyester composites at temperatures 50°C (below T_g), 75°C (around T_g) and 100°C (above T_g).

Table 8.1. Variation of storage modulus and normalized storage modulus of untreated randomly oriented isora-polyester composites with fibre loading at 50, 75 and 100°C

Isora fibre loading (% v/v)	Storage modulus (MPa)			Normalized storage modulus		
	50°C	75°C	100°C	50°C	75°C	100°C
(0) Cured resin	1849	598	34.7	1	1	1
10%	2424	935	241	1.31	1.56	6.95
34%	3542	2489	1382	1.91	4.16	39.8
41%	3215	1977	969.7	1.74	3.3	27.9

The storage modulus and the normalized storage modulus of the composites increased uniformly with increase in fibre loading up to 34% at all temperatures, but at 41% fibre loading, there is a lowering of these values at all temperatures. The normalized modulus values at 50°C and 75°C do not show considerable variation, but at 100°C very high normalized modulus values are obtained at high fibre loading, compared to the neat resin.

The variation of tan δ of the cured resin and untreated randomly oriented isora-poyester composites with fibre loading, as a function of temperatures is shown in Figure 8.2. Incorporation of stiff fibres reduces the tan δ peak of the composite by restricting the movement of polymer molecules, and also due to the reduction in the viscoelastic lag between the stress and the strain [6, 27]. The tan δ values were lowered in the composites compared to the resin also because there was less matrix by volume to dissipate the vibrational energy. Figure 8.2 clearly indicates that the relatively high viscoelastic damping character (tan δ value) for the cured unsaturated polyester resin becomes substantially lowered on reinforcement with isora fibre. The height of tan δ peaks of the composites is lowered with increase in fibre loading up to the optimum loading of 34%, as expected. Above this fibre loading there is only a marginal increase in tan δ. The lowering of the tan δ peak height is a measure of enhanced interfacial bond strength and adhesion between the fibre and the resin matrix.

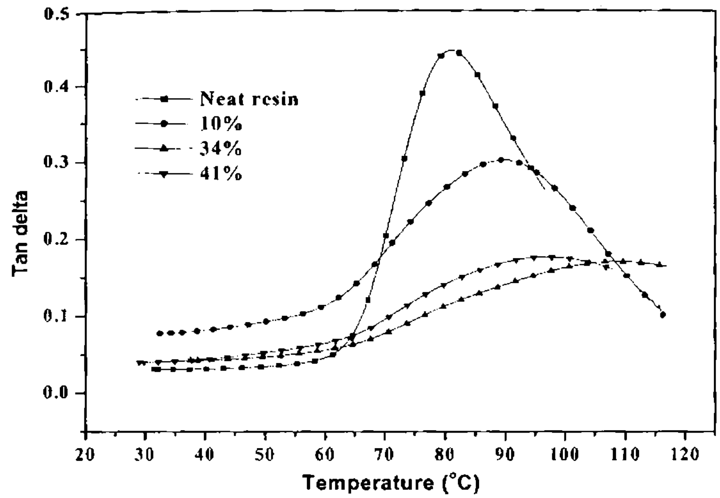


Figure 8.2. Variation of tan δ of untreated randomly oriented isora-polyester composite as a function of fibre loading, at different temperatures.

The tan δ_{max} values and glass transition temperatures of randomly oriented isora fibre-polyester composite containing different fibre volume fractions are given in Table 8.2. The tan δ_{max} value is maximum for the neat resin and the value decreased with fibre loading up to 34% and a marginal increase is observed for 41% loading. The increased glass transition temperature of the composites suggests an increase in rigidity at the fibre-matrix interfacial zone due to improved fibre-matrix interaction [30] which reduces molecular mobility at the interfacial zone. The decrease at 41% loading may be due to high fibre-fibre interaction resulting in lower matrix-fibre bonding as observed for other properties also.

Table 8.2. tan δ_{max} and T_g values of untreated randomly oriented isora-polyester composite as a function of fibre loading. (frequency 1Hz)

Isora fibre loading (% v/v)	tan δ_{max}	Glass transition temperature(T_g) °C
0 (Cured resin)	0.4472	81.05
10%	0.3027	90.93
34%	0.1713	110.41
41%	0.1775	97.02

8.2.1.2. Effect of concentration of alkali

Figure 8.3 shows the effect of concentration of alkali on the storage modulus of randomly oriented isora-polyester composite as a function of temperature. It is found that the storage modulus of the composite containing fibre treated with 1% alkali showed the maximum value which is an indication of the enhanced interfacial adhesion between the fibre and the matrix. The increase in modulus of the alkalized fibre is associated with the fibrillar and porous nature of the fibre after alkali treatment. This makes the penetration of the resin matrix well into the fibre and hence the stiffness of the composite increased. This is in good agreement with the results obtained for the mechanical properties of the composite. The increase in the E′ values is more pronounced at low temperatures.

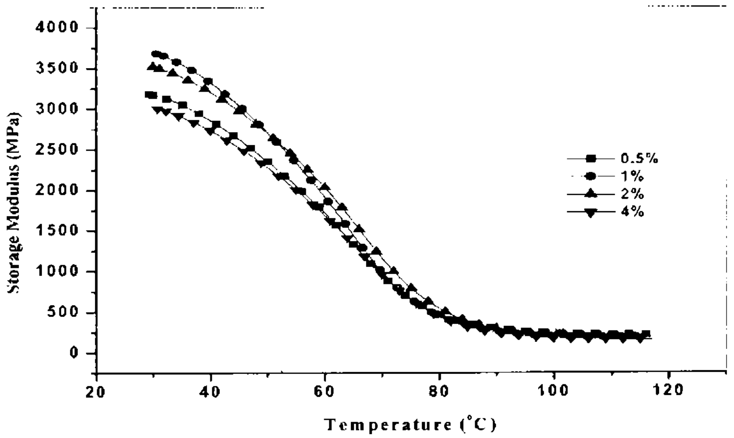


Figure 8.3. Variation of storage modulus of randomly oriented isora -polyester composite with concentration of alkali at different temperatures (fibre loading 22% v/v)

The effect of concentration of alkali on the tan δ values of the composites as a function of temperatures is shown in Figure 8.4 and in Table 8.3, the tan δ_{max} values and glass transition temperatures of the composite are given. The tan δ_{max} value is minimum for the composite containing 1% alkali treated fibre composite and maximum for the composite containing 0.5% alkali treated fibre. The T_g value is maximum for the composite containing 2% alkali treated fibre composite and minimum for the composite containing 0.5% alkali treated fibre.

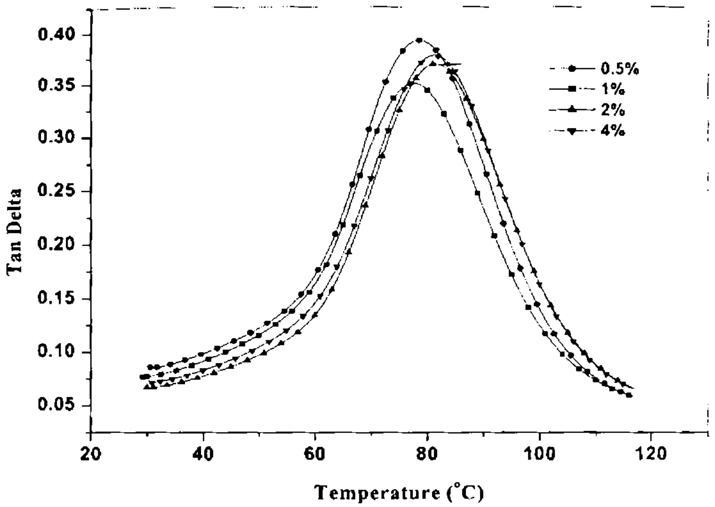


Figure 8.4. Variation of tan δ of randomly oriented isora-polyester composite as a function of concentration of alkali at different temperatures (Fibre loading 22% v/v)

Table 8.3. Effect of alkali concentration on the tan δ_{max} and T_g values of randomly oriented isora-polyester composite (fibre loading 22% v/v)

Con. of alkali (% w/v)	tan δ_{max}	Glass transition temperature (T_g)°C
0.5	0.3923	79.21
1	0.3514	80.86
2	0.3696	82.18
4	0.3782	81.62

8.2.1.3. Effect of duration of alkali treatment (con. of alkali=1%)

Figure 8.5 shows the effect of duration of alkali treatment on the storage modulus of randomly oriented isora-polyester composite as a function of temperature. It can be observed that the storage modulus of the composite containing 4 hour-alkali treated fibres showed maximum value which is an indication of the enhanced interfacial adhesion between the fibre and the matrix. These results are also in good agreement with that obtained for the mechanical properties of the composite.

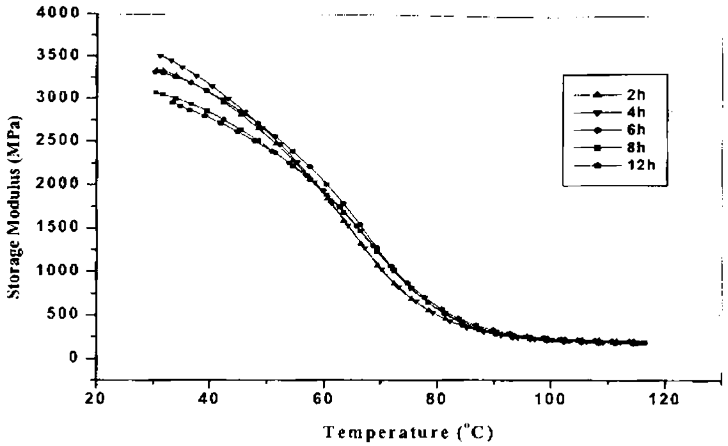


Figure 8.5. Variation of storage modulus of randomly oriented isora-polyester composite with duration of alkali treatment at different temperatures (fibre loading 22% v/v)

The effect of duration of alkali treatment on the tan δ values of the composites as a function of temperature is shown in Figure 8.6. The tan δ_{max} values and glass transition temperatures of the composite are given in Table 8.4. The tan δ_{max} value is minimum for the composite containing 4h-alkali treated fibres and maximum for the composite containing 12h-alkali treated fibres. The T_g values showed moderate increase with increase of fibre treatment time. This may be due to increase in cross-linking.

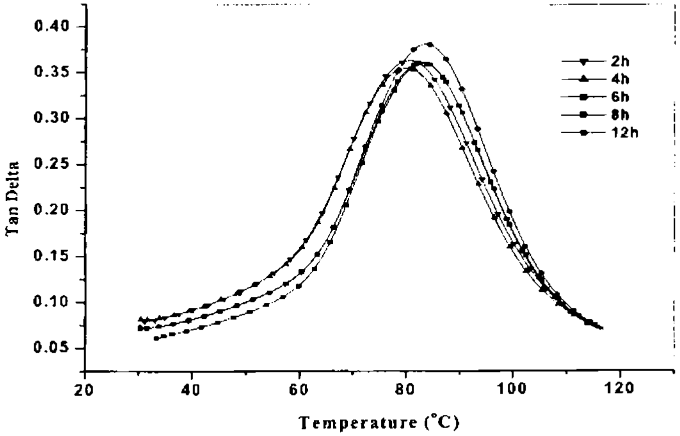


Figure 8.6. Variation of tan δ of randomly oriented isora-polyester composite as function of duration of alkali treatment at different temperatures. (fibre loading 22% v/v)

Table 8.4. Effect of duration of alkali treatment on the tan δ_{max} and T_g values of randomly oriented isora-polyester composite (fibre loading = 22% v/v)

Duration (hours)	tan δ_{max}	Glass transition temperature(T_g)°C
2	0.3617	80.4
4	0.3514	80.86
6	0.3554	83.18
8	0.3605	83.46
12	0.3638	84.06

8.2.1.4. Effect of chemical treatment

A clear understanding of the storage modulus-temperature curve obtained during dynamic mechanical analysis provides valuable insight into the stiffness of the material as a function of temperature. Dynamic mechanical analysis provides a sensitive detection of the interfacial bonding. Our studies have shown that the surface modification of isora fibre by alkalization, silane treatment, benzoylation, acetylation and triton treatment can improve the strength and stiffness (evidenced from Young's modulus) of the isora fibre reinforced composites (Chapters 3 and 4). Earlier works on natural fibre-reinforced composites revealed that the presence of compatibilizers develops a bond between the matrix and fibre and hence increases the storage modulus value of the composites [31-33].

The effect of chemical treatment of the fibre on the storage modulus of randomly oriented isora-polyester composite as a function of temperature is shown in Figure 8.7. It is observed that chemical treatments of fibre enhanced the storage modulus of the composites compared to the untreated fibre composite, at low temperatures. The increase in storage modulus follows the order: Triton treated >> acetylated > benzoylated > silane treated > untreated.

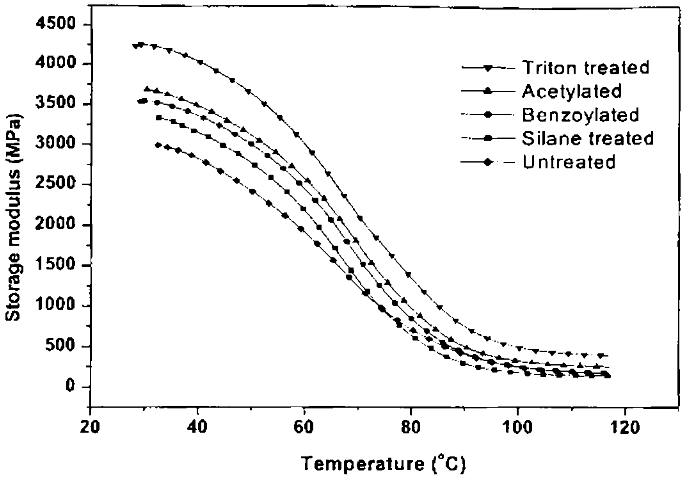


Figure 8.7. Storage modulus v/s temperature curves of chemically treated randomly oriented isora-polyester composites. (fibre loading 22% v/v)

The highest value of storage modulus is obtained for the triton treated fibre composite, which is assumed to be due to the easy dispersability of the treated fibre and increase in aspect ratio of the fibre.

Acetylated fibre composites showed improvement in properties, next to triton treated fibre composites. The improvement in interfacial bonding can be attributed to the mechanical interlocking between the polyester resin and the caved fibre surface due to the alkali pretreatment. Rong *et al.* [34] noted increase in mechanical properties of acetylated sisal fibre reinforced epoxy composites. Another important contributing factor is the reduction in the hydrophilicity of the fibre as a result of acetylation, which makes the fibre more compatible with hydrophobic polyester. The improvement in stiffness of benzoylated fibre composite is attributed to the improvement in the thermodynamic compatibility between the fibre and the matrix and reduction in hydrophilicity of the fibre on benzoylation. Also benzoylation makes the surface of the fibre very rough and provides better mechanical interlocking to the polyester matrix.

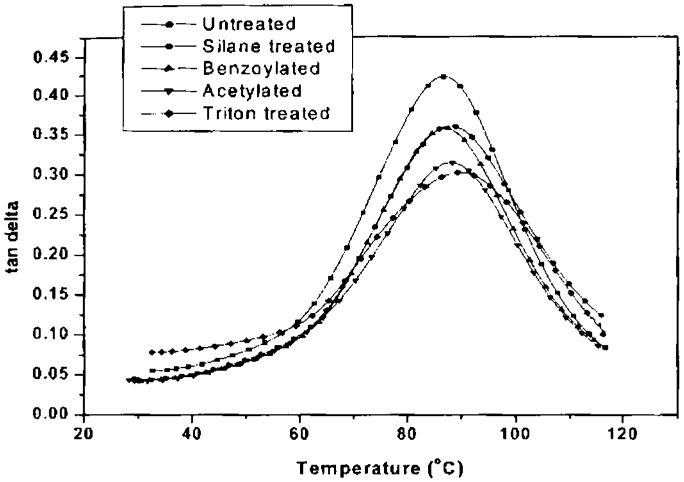


Figure 8.8. Effect of chemical treatment on tan δ of randomly oriented isora-polyester composite at different temperatures. (fibre loading 22% v/v)

Silane treatment also showed increase in modulus values compared to that of untreated fibre composites due to improved physical interfacial interactions (Van der Waals) by forming a bridge at the interface.

The effect of chemical treatments of fibre on the tan δ values of randomly oriented isora-polyester composites as a function of temperature is given in the Figure 8.8. The tan δ is a damping term, which can also be related to the impact resistance of the material [35]. Since the damping peak occurs in the region of glass transition where the material changes from rigid to a more rubbery state, it is associated with the segmental mobility of the chains, which are initially in the frozen state. The higher the peak tan δ value, the greater is the degree of molecular mobility. On comparing the peak tan δ values of the different composites (Table 8.5), untreated fibre composite is having the maximum value followed by silane treated, benzoylated, acetylated and triton treated. So the fibre-matrix adhesion is the strongest in the triton treated fibre composite and the damping characteristic is maximum in the untreated fibre composite.

Table 8.5. Effect of chemical treatment of fibre on the tan δ_{max} and T_g values of randomly oriented isora-polyester composite (fibre loading 22% v/v)

Fibre treatment	tan δ_{max}	Glass transition temperature (T_g) °C
Untreated	0.4242	86.6
Silane	0.4231	87.0
Benzoylation	0.3618	87.6
Acetylation	0.3593	88.3
Triton	0.3160	88.5

The T_g values of the composites also are shown in Table 8.5. The increased glass transition temperature of the composites prepared from treated fibres over the untreated fibre composites suggests an increase in rigidity of the interface due to increased fibre/matrix interaction, which reduces the molecular mobility in the interfacial zone.

8.2.2. Oriented long isora fibre reinforced polyester composites

8.2.2.1. Effect of fibre loading

Figure 8.9 illustrates the variation of storage modulus (E′) of oriented long isora-polyester composite with fibre content as a function of temperature. It is found that the storage modulus of the composites increased with increase in fibre content and it is more pronounced at low temperatures as in the case of randomly oriented isora-polyester composites (Figure 8.1). As already discussed, this increase in E′ of the composites at higher fibre loading is due to greater interfacial adhesion and bond strength between the resin and fibre. The E′ values of the composites fell steeply around the glass transition temperature at 60-80°C. Also on fibre loading, T_g values of the composites increased and the E′ value is maximum for 47% fibre loading. As the fibre loading is increased to 57%, E′ decreased, which may be caused by the increase in fibre-to-fibre interaction resulting in poor dispersion.

The decrease in modulus at higher temperature is associated with the chain mobility of the matrix and the thermal expansion occurring in the matrix resulting in reduced intermolecular bonding.

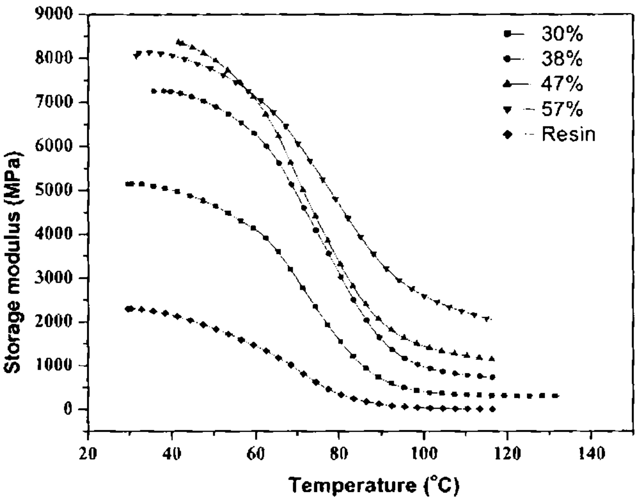


Figure 8.9. Variation of storage modulus of untreated oriented long isora-polyester composite as a function of fibre loading at different temperatures

Table 8.6. shows the storage modulus and relative (normalized) storage modulus values of untreated oriented long isora-polyester composites at temperatures 50°C, 75°C and 100°C.

Table 8.6. Variation of storage modulus and normalized storage modulus of untreated oriented long isora-polyester composites with fibre loading at 50, 75 and 100°C

Isora fibre loading (% v/v)	Storage modulus (MPa)			Normalized storage modulus		
	50°C	75°C	100°C	50°C	75°C	100°C
0 (Cured resin)	1849	598	34.7	1	1	1
30%	4667	2214	426	2.52	3.70	12.27
38%	6884	4034	957	3.72	6.74	27.57
47%	8006	4270	1419	4.32	7.14	40.89
57%	7729	5451	2616	4.18	9.11	75.38

The storage modulus and the normalized storage modulus of the composites increased uniformly with increase in fibre loading at all temperatures except at 50°C, at which there is a lowering of these properties for 57% loading. The normalized modulus values at 50°C and 75°C do not show considerable variation, but at 100°C very high normalized modulus values are obtained at high fibre loading, compared to the neat resin.

The variation of tan δ of the cured polyester resin and the composites with fibre loading as a function of temperatures is shown in Figure 8.10. Incorporation of isora fibres reduced the tan δ peak height of the composites, compared to cured unsaturated polyester resin as expected. The height of tan δ peaks of the composites is lowered with increase in fibre loading. The lowering of the tan δ peak height is a measure of enhanced interfacial bond strength and adhesion between the fibre and the resin.

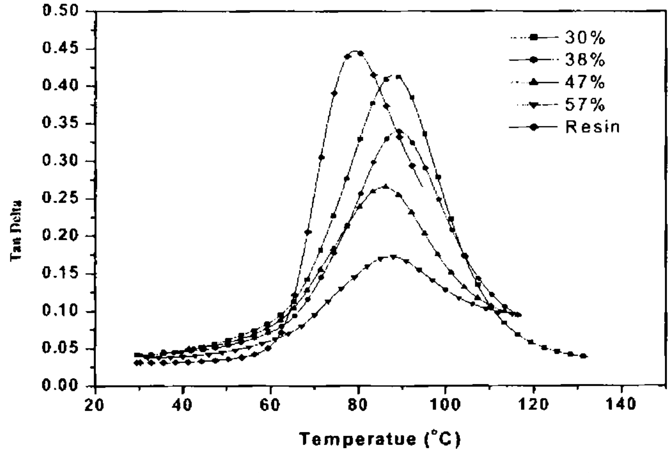


Figure 8.10. Variation of tan δ of untreated oriented long isora-polyester composite as a function of fibre loading at different temperatures

The tan δ_{max} values and glass transition temperatures of oriented long isora fibre-polyester composite containing different volume fractions of fibre are given in Table 8.7. The tan δ_{max} value is maximum for the neat resin and the value decreased with increase in fibre loading. The glass transition temperature of the composites also generally increased with fibre loading. This suggests an increase in rigidity of the fibre-matrix interface due to improved fibre-matrix interaction, which reduces molecular mobility in the interfacial zone.

Table 8.7. Effect of fibre loading on the tan δ_{max} and T_g values of untreated oriented long isora-polyester composite

Isora fibre loading (% v/v)	tan δ_{max}	Glass transition temperature (T_g) °C
0 (Cured resin)	0.4472	81.05
30%	0.4146	88.02
38%	0.3401	89.01
47%	0.2655	85.63
57%	0.1725	86.8

8.2.2.2. Effect of fibre treatment

The effect of various fibre treatments on the storage modulus of oriented long isora fibre-polyester composite as a function of temperature is shown in Figure 8.11. It can be observed that all fibre treatments enhanced the storage modulus of the composites compared to the untreated fibre composite at all temperatures.

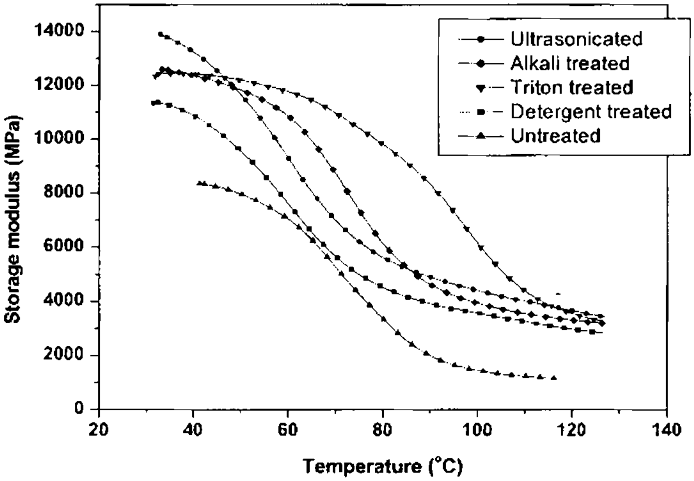


Figure 8.11. Effect of fibre treatment on the storage modulus of oriented long isora-polyester composite at different temperatures. (fibre loading 52% v/v)

The storage modulus of the composites at 50, 75 and 100°C are given in Table 8.8. The increase in storage modulus of the composites at 50°C and 75°C are in the following order: Triton treated >Alkali treated > Ultrasonicated > detergent treated > untreated. At 100°C the ultrasonicted fibre composite showed higher storage modulus than alkali treated fibre composite. It is also observed that from 60°C to 100°C the storage modulus of triton treated fibre composite is significantly higher than that of other composites.

Table 8.8. Effect of fibre treatment on the storage modulus of oriented long isora-polyester composite at different temperatures (fibre loading 52% v/v)

Fibre treatment	Storage modulus (MPa)		
	50°C	75°C	100°C
Untreated	7922	4283	1462
Detergent	9637	5031	3604
Ultrasonication	11674	6207	4422
Alkali	11778	7391	3926
Triton	12205	10385	6137

The effect of chemical treatments of fibre on the damping characteristics (tan δ) of the oriented long isora-polyester composites as a function of temperature is given in the Figure 8.12. On comparing the peak tan δ values of the different composites given in Table 8.9, untreated fibre composite is having the maximum value followed in order by detergent treated, ultrasonicated, triton treated and alkali treated fibre composites. So the damping property is maximum for the untreated fibre composite and minimum for the alkali treated fibre composite.

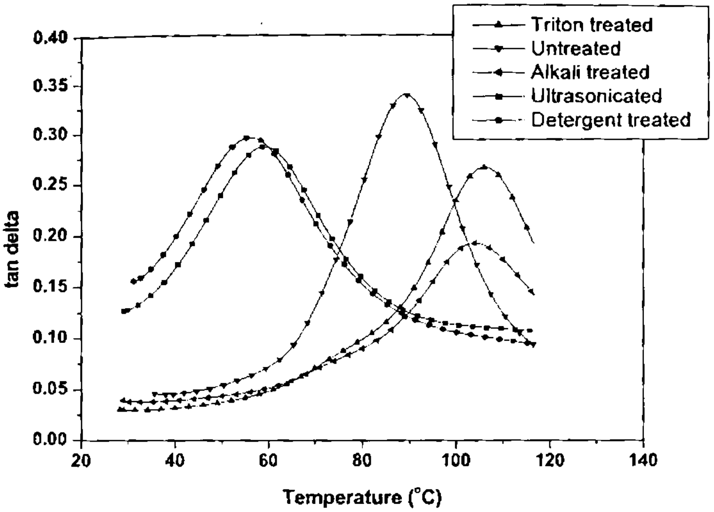


Figure 8.12. Effect of fibre treatment on the tan delta values of oriented long Isora-polyester composite at different temperatures (fibre loading 52% v/v)

The T_g values of the detergent treated and ultrasonicated fibre composites are lower than that of untreated fibre composite whereas enhancement in T_g values is observed for triton treated and alkali treated fibre composites.

Table 8.9. Effect of fibre treatment on the tan δ_{max} and T_g values of oriented long isora-polyester composite (fibre loading 52% v/v)

Fibre treatment	tan δ_{max}	Glass transition temperature (T_g)°C
Untreated	0.3398	89
Detergent	0.296	56
Ultrasonication	0.288	59
Triton	0.2669	105
Alkali	0.1926	103

8.2.3. Randomly oriented isora-epoxy composites

8.2.3.1. Effect of fibre loading

Figure 8.13 illustrates the variation of storage modulus with fibre content of randomly oriented isora-epoxy composites as a function of temperature. It is found that the storage modulus of the composites increased with increase in fibre content, which is due to greater interfacial adhesion and bond strength between the resin and fibre. The E′ values of the composites fell steeply around the glass transition temperature at 60-80°C. On fibre loading T_g values of the composites increased. The decrease in modulus at higher temperature is associated with the chain mobility of the matrix and the thermal expansion occurring in the matrix resulting in reduced intermolecular forces

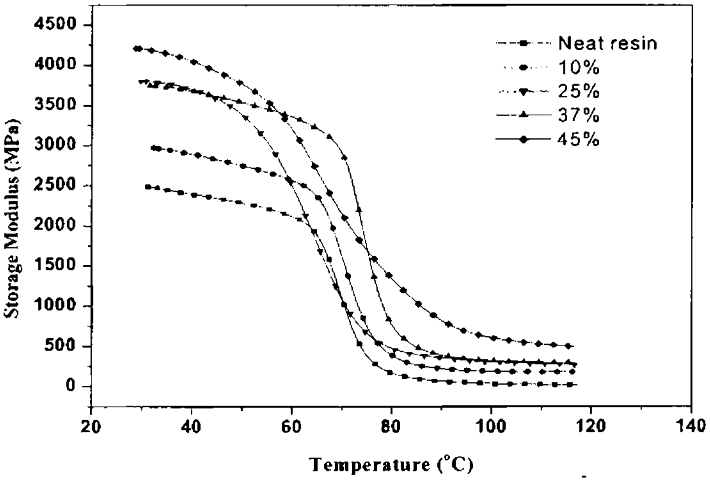


Figure 8.13. Variation of storage modulus of untreated randomly oriented isora-epoxy composites as a function of fibre loading at different temperatures

Table 8.10. shows the storage modulus and normalized storage modulus values of randomly oriented isora-epoxy composites at temperatures 50°C (below T_g), 75°C (around T_g) and 100°C (above T_g)

Table 8.10. Variation of storage modulus and normalized storage modulus of untreated randomly oriented isora/epoxy composites with fibre loading at 50, 75 and 100°C

Isora fibre loading (% v/v)	Storage modulus (MPa)			Normalized storage modulus		
	50°C	75°C	100°C	50°C	75°C	100°C
0 (Cured resin)	1938	585	31.4	1	1	1
10%	2744	733	176.5	1.41	1.25	5.62
25%	3420	646	307	1.76	1.10	9.77
37%	3531	1697	309	1.82	2.90	9.84
45%	3783	1708	585	1.95	2.91	18.63

The storage modulus and the normalized storage modulus values of the composites increased uniformly with increase in fibre loading at all temperatures, except for 25% loading at 75°C. The normalized modulus values at 50°C and 75°C do not show considerable variation, but at 100°C, high normalized modulusvalues are obtained for high fibre loading, compared to the values of neat resin.

Variation of tan δ of the cured resin and randomly oriented untreated isora-epoxy composites with fibre loading as a function of temperature is shown in Fig. 8.14. Incorporation of stiff fibres reduced the tan δ peak of the composites as expected. It is observed that the relatively high tan δ of the cured resin is substantially lowered on reinforcement with the fibre. The height of tan δ peaks of the composites is lowered with increase in fibre loading. The lowering of the tan δ peak height is a measure of enhanced interfacial bond strength and adhesion between the fibre and the resin.

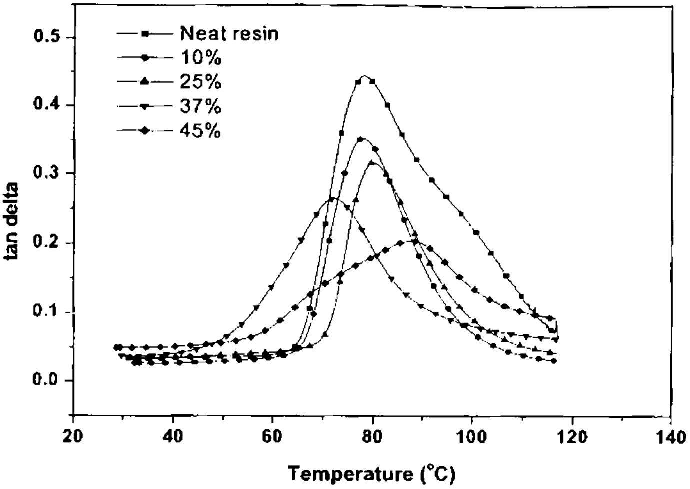


Figure 8.14. Variation of tan δ of untreated randomly oriented isora-epoxy composite as a function of fibre loading, at different temperatures

The tan δ_{max} values and glass transition temperatures of randomly oriented isora-epoxy composite containing different fibre volume fractions are given in Table 8.11. The tan δ_{max} value is maximum for neat resin and the value decreased with increase in fibre loading. The increased glass transition temperature of the composites suggests an increase in rigidity of the fibre-matrix interfacial zone due to improved fibre-matrix interaction, which reduces molecular mobility in the interfacial zone.

Table 8.11. Effect of fibre loading on the tan δ_{max} and T_g values of untreated randomly oriented isora-epoxy composite

Isora fibre loading (% v/v)	tan δ_{max}	Glass transition temperature (T_g) °C
0 (cured resin)	0.4427	78.55
10%	0.3530	77.88
25%	0.3178	80.12
37%	0.2654	72.25
45%	0.2038	87.82

8.2.3.2. Effect of alkali treatment

Figure 8.15 illustrates the effect of alkali treatment on the storage modulus of randomly oriented isora fibre reinforced epoxy composites as a function of temperature. It is found that on alkali treatment, the storage modulus of the composite increased, which is due to greater interfacial adhesion and bonding between resin and fibre.

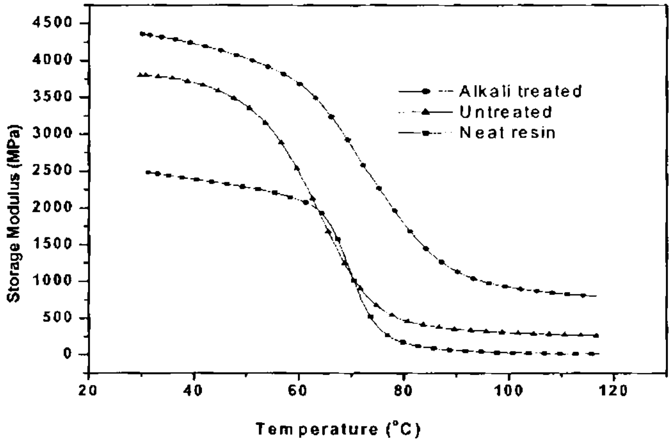


Figure 8.15. Effect of alkali treatment on storage modulus of randomly oriented isora-epoxy composite as a function of temperature (fibre loading 35% v/v)

Effect of alkali treatment on the storage modulus and normalized storage modulus values of randomly oriented isora-epoxy composites at 50, 75 and 100°C is given in Table 8.12. The storage modulus and the normalized storage modulus values of the composites increased on alkali treatment of the fibre at all temperatures. On alkali treatment the increase in storage modulus when compared to untreated fibre composite is 19.6% at 50°C, 262% at 75°C and 202% at 100°C. The normalized modulus values at 50°C and 75°C do not show considerable variation, but at 100°C, high normalized modulus values are obtained, compared to neat resin.

Table 8.12. Effect of alkali treatment on the storage modulus and normalized storage modulus of randomly oriented isora-epoxy composites at 50, 75 and 100°C

Material	Storage modulus (MPa)			Normalized storage modulus		
	50°C	75°C	100°C	50°C	75°C	100°C
Cured resin	1938	585	31.4	1	1	1
UT composite (37%)	3531	1697	309	1.82	2.9	9.8
AT composite (37%)	4050	2300	936	2.08	3.93	29.8

Figure 8.16 shows tan δ versus temperature plots of neat epoxy resin (cured) and composites containing untreated and alkali treated fibres. It is observed that the height of the tan δ peaks of the composites lie far below that of the neat resin. It can also be noted that the peak height of the alkali treated fibre composite is lower than that of untreated fibre composite indicating improved interfacial adhesion between the fibre and the matrix in the former.

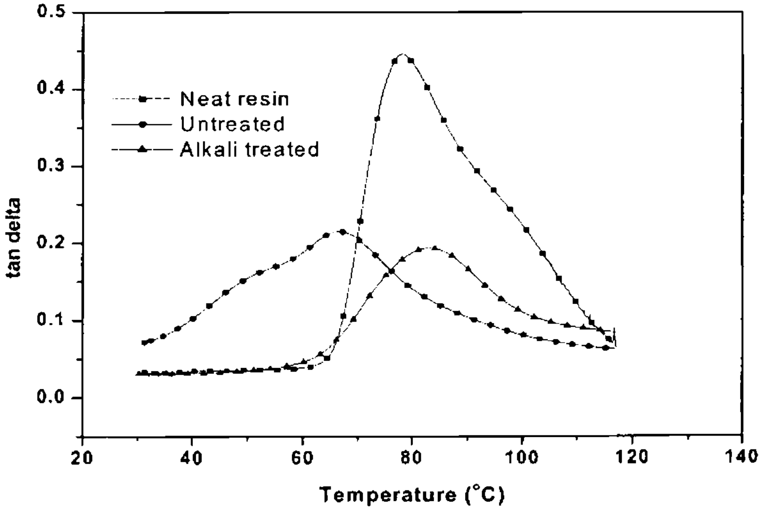


Figure 8.16. Effect of alkali treatment on tan δ of randomly oriented isora-epoxy composite as a function of temperature (fibre loading=45%)

The tan δ_{max} and T_g values of the resin and the untreated and alkali treated fibre composites are given in Table 8.13. The T_g value of the untreated fibre composite is lower than that of the cured resin whereas it is higher for alkali treated fibre composite. The increase in glass transition temperature of the alkali treated fibre composite suggests an increase in rigidity of the fibre-matrix interfacial zone due to improved fibre-matrix interaction which reduces molecular mobility at the interfacial zone.

Table 8.13. Effect of fibre treatment on the tan δ_{max} and T_g values of randomly oriented isora-epoxy composite

Material	tan δ_{max}	Glass transition Temperature (T_g)°C
Cured resin	0.4427	78.55
UT composite (37%)	0.2654	72.25
AT composite (37%)	0.1937	83.72

8.2.4. Oriented long isora-epoxy composites

8.2.4.1. Effect of fibre loading

The variation of storage modulus of oriented long isora-epoxy composites with fibre content as a function of temperature is given in Figure 8.17. As expected the storage modulus of the composites increased with increase in fibre content. As already discussed, this increase in E′ of the composites at higher fibre loading is due to greater interfacial adhesion and bond strength between the resin and fibre. The E′ values of the composites fell steeply around the glass transition temperature at 60-90°C. E′ value is maximum for the composite at 46% fibre loading. At a higher fibre loading of 52%, E′ decreased, which may be caused by the increase in fibre-to-fibre interaction resulting in poor dispersion.

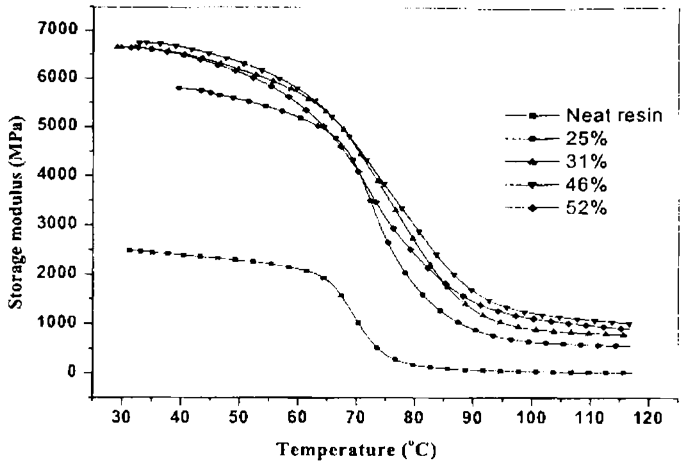


Figure 8.17. Variation of storage modulus of untreated oriented isora-epoxy composite as a function of fibre loading at different temperatures

Table 8.14 shows the effect of fibre loading on the storage modulus and normalized storage modulus values of oriented long isora-epoxy composites at temperatures 50°C (below T_g), 75°C (around T_g) and 100°C (above T_g). The storage modulus and the normalized storage modulus values of the composites increased with fibre loading up to 46% at all temperatures and at 52% fibre loading a decrease in the values for these properties was observed. The normalized modulus values at 50°C and 75°C do not show considerable variation, but at 100°C, high normalized modulus values are obtained, compared to the neat resin.

Table 8.14. Effect of fibre loading on the storage modulus and normalized storage modulus of untreated oriented long isora-epoxy composites at 50, 75 and 100°C

Isora fibre loading (% v/v)	Storage modulus (MPa)			Normalized storage modulus		
	50°C	75°C	100°C	50°C	75°C	100°C
0 (Cured resin)	1938	585	31.4	1	1	1
25%	5568	2768	642	2.87	4.73	20.4
31%	6223	3655	916	3.21	6.24	29.1
46%	6320	3850	1222	3.26	6.58	38.9
52%	6125	3209	1125	3.16	5.48	35.8

Figure 8.18 shows tan δ versus temperature plots of neat resin (cured) and oriented long isora-epoxy composites containing varying volume fractions of untreated fibres. It is observed that the height of the tan δ peaks of the composites lie far below that of the neat resin. It can also be noted that the peak height of the composites decreased with increase in fibre loading indicating improved interfacial adhesion between the fibre and the resin with fibre loading.

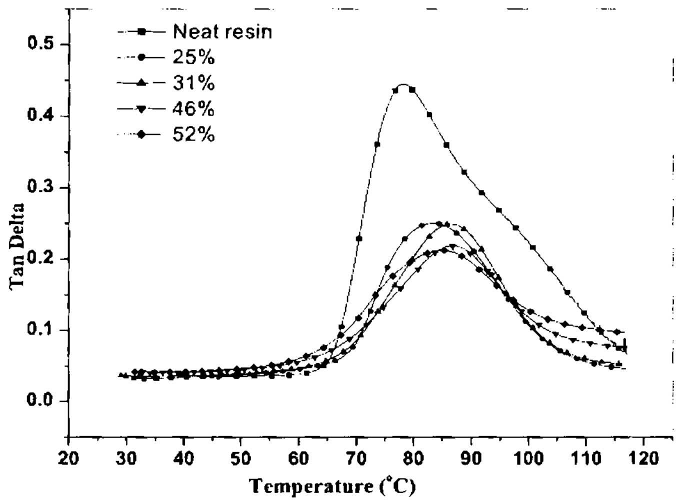


Figure 8.18. Variation of tan δ of untreated oriented long isora-epoxy composite as a function of fibre loading at different temperatures

The tan δ_{max} and T_g values of the cured resin and the composites are given in Table 8.15. tan δ_{max} values of the composites decreased with increase in fibre loading up to 46% fibre loading and at 52% loading, a marginal increase is observed. The T_g values of the composites shifted to higher temperatures as expected. The increase in glass transition temperature of the composites is due to an increase in rigidity of the fibre-matrix interfacial zone due to improved fibre-matrix interaction, which reduces molecular mobility in the interfacial zone.

Table 8.15. Effect of fibre loading on the tan δ_{max} and T_g values of untreated oriented long isora-epoxy composite

Isora fibre loading (% v/v)	tan δ_{max}	Glass transition Temperature (T_g)°C
0 (Cured resin)	0.4427	78.55
25%	0.2509	83.26
31%	0.2498	86.17
46%	0.2188	87.05
52%	0.2238	85.27

8.2.4.2. Effect of fibre treatment

The effect of various fibre treatments on the storage modulus of oriented long isora-epoxy composites as a function of temperature is shown in Figure 8.19. It can be observed that all fibre treatments enhanced the storage modulus of the composites compared to the untreated fibre composite at all temperatures.

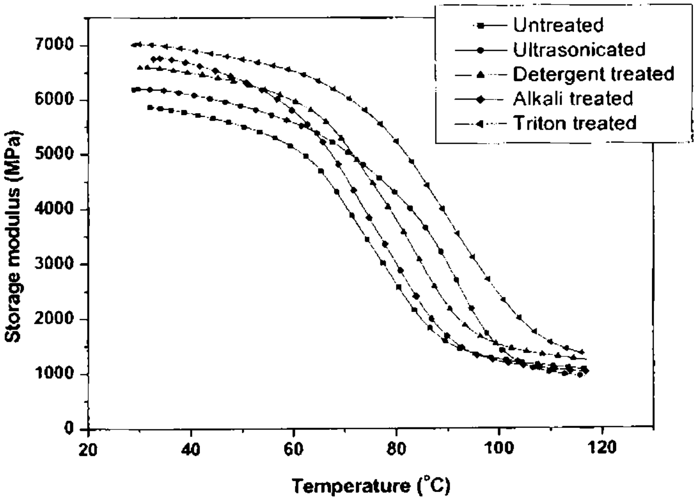


Figure 8.19. Effect of fibre treatment on the storage modulus of oriented long isora-epoxy composite at different temperatures.

The storage modulus of the composites at 50, 75 and 100°C are given in Table 8.16. The increase in storage modulus of the composites at 50°C are in the order: Triton treated >Alkali treated > detergent treated > Ultrasonicated > untreated. At 75°C and 100°C the variation is not regular. It is observed that from 60°C to 100°C the storage modulus of triton treated fibre composite is significantly higher than that of other composites as in the case of oriented isora -polyester composites. (Section 8.2.2.2.)

Table 8.16. Effect of fibre treatment on the storage modulus of oriented long isora-epoxy composite at different temperatures (fibre loading 52% v/v)

Fibre treatment	Storage modulus (MPa)		
	50°C	75°C	100°C
Untreated	6125	3209	1125
Ultrasonication	6250	4344	1506
Detergent	6320	4492	1507
Alkali	6337	3843	1253
Triton	6738	5689	2428

The effect of chemical treatments of fibre on the damping characteristics (tan δ) of the oriented long isora-epoxy composites as a function of temperature is given in the Figure 8.20. On comparing the peak tan δ values of the different composites ultrasonicated fibre composite is having higher damping value compared to untreated fibre composite (Table 8.17). Alkali treated and detergent treated fibre composites have comparable damping values slightly lower than the untreated fibre composite. Triton treated fibre composites showed minimum damping value.

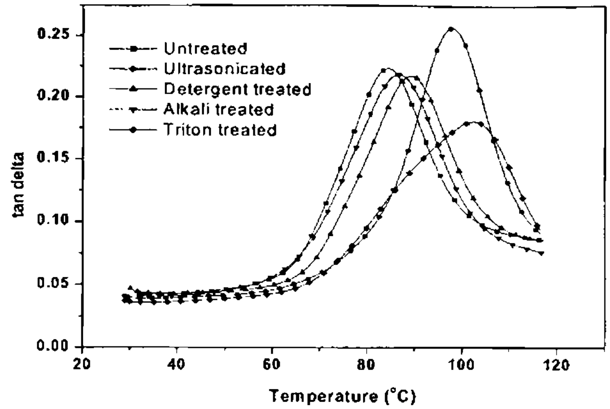


Figure 8.20. Effect of fibre treatment on tan delta of oriented long isora-epoxy composite at different temperatures (fibre loading 52% v/v)

Fibre treatments improved glass transition temperature of the composite in all cases and followed the order: Triton treated > Ultrasonicated > detergent treated > Alkali treated > untreated.

Table 8.17. Effect of fibre treatment on the tan δ_{max} and T_g values of oriented long isora-epoxy composite (fibre loading 52% v/v)

Fibre treatment	tan δ_{max}	Glass transition Temperature (T_g)°C
Untreated	0.2238	85.27
Ultrasonication	0.2569	97.9
Alkali	0.2191	86.9
Detergent	0.2178	89
Triton	0.1813	102

8.3. Theoretical modelling of storage modulus

8.3.1. Randomly oriented isora-polyester composites

The storage modulus of the randomly oriented isora-polyester composite was calculated theoretically using the equation proposed by Einstein [36].

$$Ec = E_m(1+V_f) \qquad \text{.......................................} \quad 8.1$$

Where Ec is the storage modulusof the composite, E_m, the modulus of the matrix and V_f, the volume fraction of the fibre in the composite.

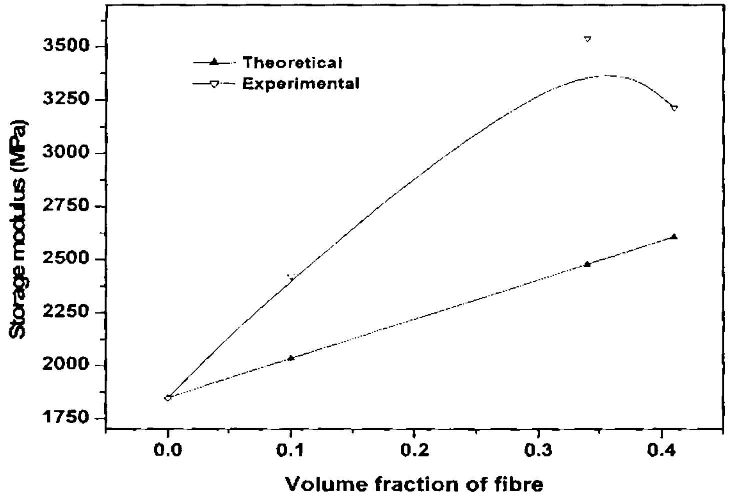


Figure 8.21. Experimental and theoretical storage modulus values of randomly oriented isora-polyester composites at 50°C.

The experimental and theoretical storage modulus of randomly oriented isora-polyester composite at 50°C for different fibre loadings are given in Figure 8.21.

The experimental values of the composites are found to be much higher than theoretical values. Higher modulus values of the composites indicate the enhanced reinforcing effect of the fibres with the polyester resin.

8.3.2. Randomly oriented isora-epoxy composites

The theoretical storage modulus values calculated using Einstein's equation is compared with the experimental values at 50°C, of the randomly oriented isora-epoxy composite for different fibre loadings, which is given in Figure 8.22.

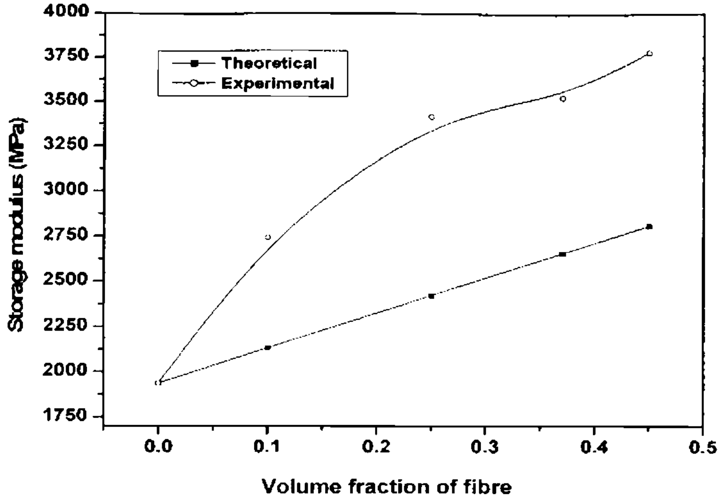


Figure 8.22. Experimental and theoretical storage modulus values of randomly oriented isora-epoxy composites at 50°C.

As in the case of isora-polyester composite, the experimental storage modulus values of the randomly oriented isora-epoxy composite were also found to be higher than the theoretical values, indicating the enhanced reinforcing effect of the fibres with the epoxy resin.

8.4. Theoretical modeling of tan delta

8.4.1. Randomly oriented isora-polyester composites

The damping factor ($\tan\delta_c$) of an ideal composite can be represented by the rule of mixtures as suggested by Nielsen [37]. In the case of a low damping reinforcement (($\tan\delta_f = 0$), the damping factor ($\tan\delta_c$) is given by

$$(\tan\delta_c) = (1 - V_f)(\tan\delta_m) \qquad \text{..} \; 8.2$$

Where V_f is the volume fraction of fibre and the subscripts *c* and *m* refer to the composite and the matrix respectively. Around T_g of the matrix, the molecular chains of the matrix have high mobility and hence the damping of the composite is primarily due to the matrix. Therefore the damping is simply related to the matrix content as given by equation 8.2. The theoretical and experimental damping values of randomly oriented isora-polyester composite as a function of fibre loading are given in Figure 8.23.

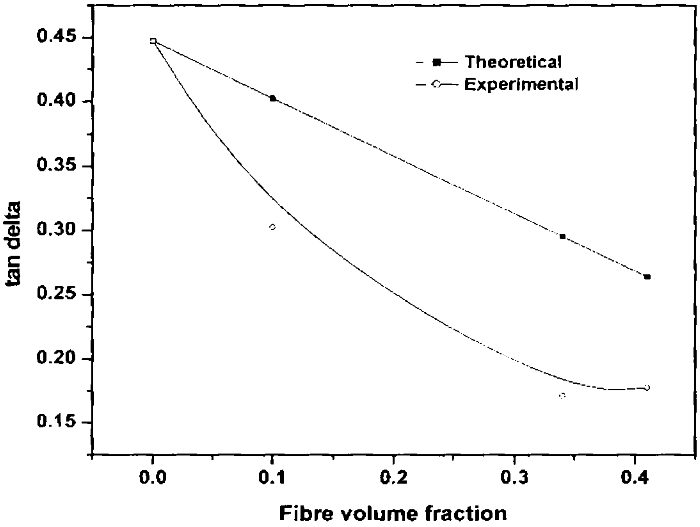


Figure 8.23. Experimental and theoretical tan delta values of randomly oriented isora-polyester composites

The values clearly show that the damping behaviour of the composites does not follow the prediction from equation 8.2 and that all values are lower than the predicted. The smaller values of experimental damping than the prediction indicate better interfacial interactions and suggest an immobilized layer at the interfacial region [38].

8.4.2. Randomly oriented isora-epoxy composites

The theoretical damping values calculated using Nielsen's equation is compared with the experimental values of the randomly oriented isora-epoxy composite for different fibre loadings and is given in Figure 8.24.

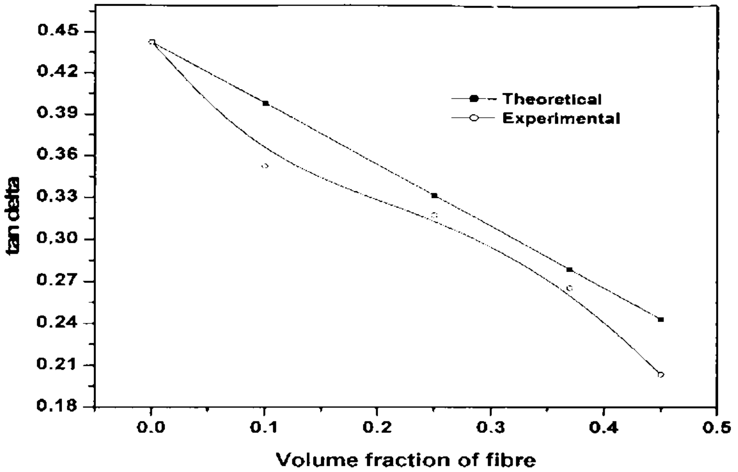


Figure 8.24. Experimental and theoretical tan delta values of randomly oriented isora-epoxy composites

It is observed that the experimental damping values of the composites are lower than the predicted values (Figure 8.24), but the agreement between the theoretical and experimental values are better, compared to the isora-polyester composites (Figure 8.23). The smaller values of experimental damping than the prediction indicate better interfacial interactions.

8.5. Conclusion

The storage moduli of isora-polyester and isora-epoxy composites were found to increase with increase in fibre loading. All the composites showed decrease in modulus values with increase in temperature. The dynamic properties are strongly influenced by the fibre orientation. Oriented fibre composites showed higher values of storage modulus than randomly oriented fibre composites. Modified fibre composites showed higher storage modulus than that of untreated fibre composites and can be explained on the basis of better fibre-matrix adhesion.

The damping factor (tan δ) of the matrices decreased by the addition of the fibres and the area and height of the damping peak of the composites were lower and broader than that of the neat matrices. Fibre modification decreased the height and increases the width of the damping peak.

The experimental values of the composites are found to be much higher than the theoretical predictions. Higher modulus values of the composites indicate the enhanced reinforcing effect of the fibres with the matrices.

The theoretical and experimental damping values of the composites showed that the damping behaviour of the composites does not follow the theoretical predictions and that all values are lower than the predicted values. The smaller values of experimental damping than the prediction indicate better interfacial interactions.

References

[1] Milios J., Kefalas V., Sidridis and Spathis G. *Handbook of Ceramic and Composites*, N. P. Cheremisinoff, Ed., Vol. 1, Ch. 6, Marcel Dekker, N. Y., 1990.

[2] Harris B., Braddel O. G., Almond D. P., Lefebvre C. and Verbist J., *J. Mater. Sci.* (1993) **28:** 3353.

[3] Akay M., *Comp Sci Technol*, (1988) 33: 1.

[4] Das J., Bandyopadhyay S., Blairs S., *J. Mater. Sci.* (1994) **29:** 5680.

[5] Wingard C. D., Beatty C. L., *J. Appl. Polym. Sci.* (1990) **71**: 2539.

[6] Saha A. K., Das S., Bhatta D., Mitra B. C. *J. Appl. Polym. Sci.* (1999) **71**:1505-13.

[7] Aziz S. H., Ansell M. P., *Comp. Sci. Technol.* (2004) **64:** 1219-30.

[8] Wielage B., Th. Lampke, Utschick H., Soergel F. *J. Mat. Process Technol.* (2003) **39:** 140-146.

[9] Gassan J., Bledzki A.K., *Appl. Comp. Mat.* (2000) **7:** 373.

[10] Qui W., Zhang F., Endo T., Hirotsu T., *J. Appl. Polym. Sci.* (2003) **87**: 337.

[11] Idicula M., Malhotra S. K., Joseph K., Thomas S., *Comp. Sci. Technol.* (2005) **65:** 999.

[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] Rana A. K., Mitra B.C., Bannerjee A. N., *J. Appl. Polym. Sci.*, (1999) **72:** 935-944.

[17] Kaliske M., Rothert H., *Comp. Engg.*, (1995) **5:** 551.

[18] Pedroso A. G., Rosa D. S., Atvars T. D. Z. *J. Appl. Polym. Sci.* (2004) **92**: 1834-1839.

[19] George J., Bhagawan S.S., Thomas S., *J. Thermal Analysis*,.(1996) **47:**1121.

[20] Varghese S., Kuriakose B., Thomas S., *J. Adh. Sci. Technol.*, (1994) **8:** 235.

[21] Sreekala M.S., Bhagawan S.S., Thomas S., *J. Reinf.Plast. Comp.*, (1998) **17:** 1471.

[22] Pothan L.A., Oommen Z., Thomas S., *Comp. Sci. Technol.*,(2003) **63:** 283.

[23] Gassan J., *Comp. Part A* (2002) **33:** 369.

[24] Ghosh P., Bose N.R., Mitra B.C., Das S*J. Appl. Polym. Sci.*(1997) 2467-72.

[25] Keusch S., Haessler R., *Comp. Part A* (2002) **30:** 997.

[26] Rozman H., Tay G. S., Kumar R. N., Abusamah A., Ismail H., Ishak Z. A. M., *Euro. Polym. J.*, (2001) **37:** 12831.

[27] Ray D., Sarkar B. K., Das S., Rana A. K., *Comp. Sci. Technol.*, (2002) **62:** 911-917.

[28] Joseph P. V., Mathew G., Joseph K., Groeninckx G., Thomas S., *Comp. Part A* (2003) **34:** 275.

[29] George J., Bhagavan S. S., Thomas S., *J. Thermoplastic Comp. Mat.*, (1999) **12:** 443.

[30] Chua P. S., *Polym. Comp.* (1987) **11:** 105.

[31] Hedenberg P., Gatenholm P., *J. Appl. Polym. Sci.* (1995) **56:** 641.

[32] Felix J. M., Gatenholm P., *J. Appl. Polym. Sci.* (1991) **42:** 609.

[33] Raj K. G., Kokta B. V., Maldas D., Deneault C., *J. Appl. Polym. Sci.* (1989) **37:** 1089.

[34] Rong M. Z., Zhang M. Q., Liu Y., Yang G. C., Zeng H. M.: *Comp. Sci. Technol.*, (2001) **61:** 1437-1447.

[35] Sepe M. P., *Adv Mater Processes*, (1992) **4:** 32.

[36] Einstein A., Investigation on theory of Brownian motion, New York, Dover, 1956.

[37] Nielsen L. E., *Mechanical properties of Polymers and Composites*, Vol. 2, Dekker, New York.

[38] Dong S. and Gauvin R., Polym. Comp. (1993) **14:** 414.

Chapter 9

WATER ABSORPTION AND THERMAL AGING STUDIES OF ISORA FIBRE REINFORCED POLYESTER AND EPOXY COMPOSITES

Abstract

Water sorption kinetics and the effect of thermal aging on the properties of isora fibre reinforced polyester and epoxy composites are presented in this chapter. It is observed that the rate of water absorption depends on the fibre content and there is a steady increase with fibre loading. Different surface modifications were performed on the fibres and the effect of interface on the water sorption behaviour of the composites has been analysed. All fibre treatments decreased the water absorption of the composites. The diffusion coefficient, sorption coefficient and permeation coefficient of the composites have been calculated from diffusion experiments. The effect of hot air oven aging on the tensile and flexural properties of the composites has also been evaluated.

9.1. Introduction

There has been a tremendous growth in the use of composite materials in various fields of application nowadays, ranging from sporting goods to structural materials for the automotive and aerospace industries, where the long-term properties are of primary importance [1, 2]. Such applications almost invariably entail contacts with liquids or vapours, either aqueous or organic, affecting the immediate or the long-term performance of the material [3-6]. Hence when composite materials are used, the environmental aspects have to be carefully considered [7]. One of the most important issues in the design of natural fibre composites is the degradation behaviour of the composites when exposed to environmental conditions such as humidity, sunlight or microorganisms. The important factors that affect water absorption of composites are the hydrophilicity of the individual components and the structural arrangement of the fibres within the matrix. The rate of water absorption by composites depends on many variables including chemical composition and microstructure of polymers, temperature, the difference in water distribution within the composite and reaction between water and the matrix. The poor resistance of the fibres to water absorption can have undesirable effects on the mechanical properties and the dimensional stability of the composites [8-10]. Fibre/resin debonding may be initiated by the development of osmotic pressure pockets at the surface of fibres due to the leaching of water soluble substances from the fibre surface [11].

Moisture penetration into composite materials occurs by three different mechanisms [12]. The main process consists of diffusion of water molecules inside the micro gaps between polymer chains. The other common mechanisms are capillary transport into the gaps and flaws at the interfaces between fibres and polymer, because of incomplete wettability and impregnation and transport by micro cracks in the matrix, formed during the compounding process [13, 14]. Moisture absorption may induce irreversible changes to polymers and composites such as chemical degradation, cracking and debonding. These damages to the material will also change the weight gain behaviour of the material correspondingly [15].

Lignocelluluosic natural fibres are highly hydrophilic due to the presence of hydroxyl groups in cellulose and lignin and are permeable to water. Incorporation of cellulose fibres into polymeric matrices increases the water uptake. It is known that a lignocellulosic material absorbs water by forming Hydrogen bonds between water and hydroxyl groups of cellulose, hemi cellulose and lignin [16]. The absorption of water occurs mainly through the cross sectional area of composites. The resin matrix in the completely cross linked state cannot penetrate water. But the absorption of water occurs through the interface and the cross sectional region of fibre by capillary mechanism [17].

Pothen *et al.*[18] have shown that when short banana fibre reinforced polyester composites were subjected to accelerated water ageing, a decrease of 32% in tensile strength was observed. Uma Devi *et al.*[19] conducted aging studies of Pine apple leaf fibre-reinforced polyester composites and concluded that aging studies showed a decrease in tensile strength of about 6% for samples subjected to thermal aging, whereas the composite specimens subjected to water aging showed 34% loss in tensile strength. Also the water uptake of the composites was found to increase with fibre loading and levelled off at longer times. Siddaramaiah *et al.*[20] studied the effect of aggressive environments on glass fibre reinforced epoxy and unsaturated polyester composites. Their studies revealed that the epoxy laminates have superior mechanical properties over polyester composites and there was a reduction in the mechanical properties of composites after subjecting them to aggressive environments like 120°C, lubricating oil, 95% relative humidity etc. Joseph et al [11] reported the influence of various ageing conditions like water and UV radiation on the mechanical properties of sisal/PP composites. They found that water uptake of the composite increased with fibre content and with temperature but chemical modification showed a reduction in water uptake. Nash *et al.*[21] investigated the weathering and thermal behaviour of jute-polyester composites and found that the tensile strength of the composites decreased while the tensile modulus increased after weathering. Sreekala *et al.* [22] made a detailed study on the effect of chemical treatments and hybridization with glass fibres on the water sorption kinetics of oil palm fibre reinforced phenolic composites. The effect of hygrothermal history on water sorption and interlaminar shear strength of glass/polyester composites with different interfacial strength was studied by Pavlindou *et al.*[15]. Karmaker *et al.*[23] investigated the influence of water uptake on the mechanical properties of jute/PP composites and concluded that swelling of jute fibres in a composite material can have positive effects on mechanical properties. Bessadok et al have carried out a detailed investigation on the water sorption characteristics of Alfa fibres [24]. Albuquerque *et al.*[25] studied the effect of wettability and aging conditions on the physical and mechanical properties of uniaxially oriented jute-roving-reinforced polyester composites. Rout *et al.*[26] reported that water absorption studies of coir/polyester and hybrid composites showed significant reduction in water absorption due to surface modifications of coir fibres. Hill *et al.*[27] conducted water exposure tests on the mass loss, tensile and flexural properties of coir and oil palm reinforced polyester composites.

In this chapter a detailed study of the water sorption behaviour of isora-polyester and isora-epoxy composites as a function of fibre loading and fibre modification are proposed to be carried out. The effect of thermal aging on the tensile and flexural properties of these composites is also proposed to be done.

9.2. Results and discussion

Water uptake in a fibrous composite is dependent on temperature, fibre loading, orientation of fibres, permeability of the fibre, surface protection, area of the exposed surfaces, diffusivity etc.

9.2.1. Randomly oriented isora-polyester composites

9.2.1.1. Effect of fibre loading on water uptake

Figure 9.1 shows the effect of fibre loading on water sorption behaviour of randomly oriented isora-polyester composites at two temperatures

(30 and 50°C) for an immersion time of 24 hours. At 30°C, it is observed that the absorption is linear, subsequently gradual and finally reached a plateau. The increase in water uptake with fibre loading is due to the hydrophilic nature of isora fibre. This results in poor wettability and adhesion between untreated isora fibre towards polyester resin resulting in the higher amount of water uptake by the composite. SEM photograph of cross sectional view of isora fibre is given in the Figure 9.2.There are porous tubular structures present inside isora fibre through which water can easily penetrate. A large number of this type of cross sectional regions is present in the cut portions of the composite. Another possibility of water absorption in composites is through the interfacial region. Several researchers have reported the chances of thermal shrinkage in composites especially in thermosetting resin matrices during curing [22, 23]. As the temperature is raised to 50°C, the mole % uptake of water increased and it varied linearly with fibre loading. With increase of temperature, as a result of the expansion, the volume fraction of the composite accessible to water molecules is increased and enhanced the water uptake.

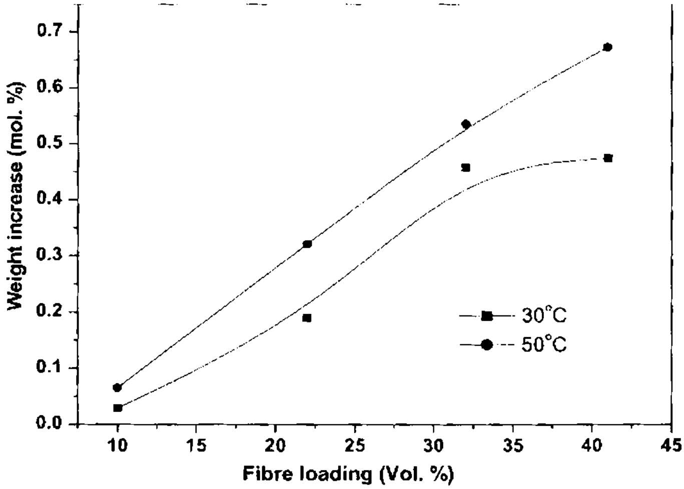


Figure 9.1. Sorption curves of untreated randomly oriented isora-polyester composites with fibre loading at two temperatures (immersion time-24 hours)

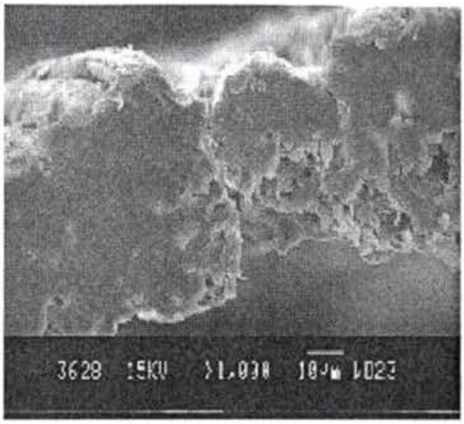


Figure 9.2. Scanning electron photograph of cross section of isora fibre.

9.2.1.2. Effect of alkali treatment on water uptake

The effect of duration of alkali treatment of isora fibre on the mole percent uptake of water of randomly oriented isora-polyester composites at 30°C is given in Figure 9.3. The behaviour is identical at lower and higher temperatures, the mole percent uptake of water by the composite decreased with increase in treatment time, reached minimum for 4-hour treatment, after which absorption of water increased for higher treatment time. The rate of increase at 30°C is small whereas at 50°C after a high initial rate of increase the effect levels off at higher treatment time.

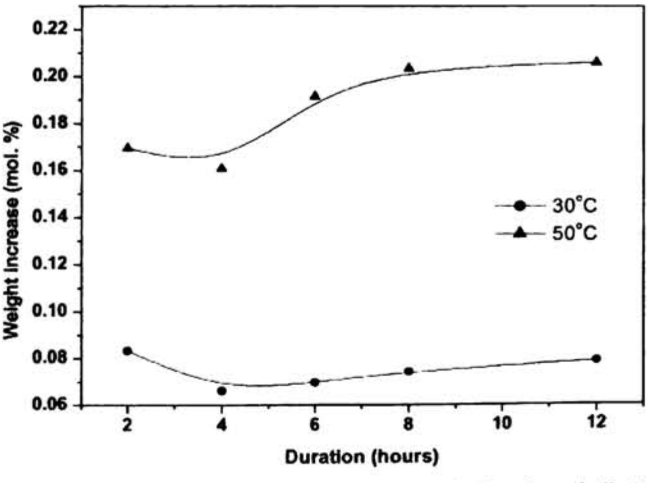


Figure 9.3. Variation of mol. % absorption of water with duration of alkali treatment of randomly oriented isora-polyester composites at two temperatures

The reduction in water uptake by the 4hour-treated fibre composite can be attributed to the enhanced interfacial bonding between the fibre and matrix supported by the mechanical properties of the alkali treated fibre composite discussed in Chapter 4. This prevents the transport of water to some extent through the interface. The fibre-matrix adhesion is relatively lower in other composites resulting in enhanced water absorption.

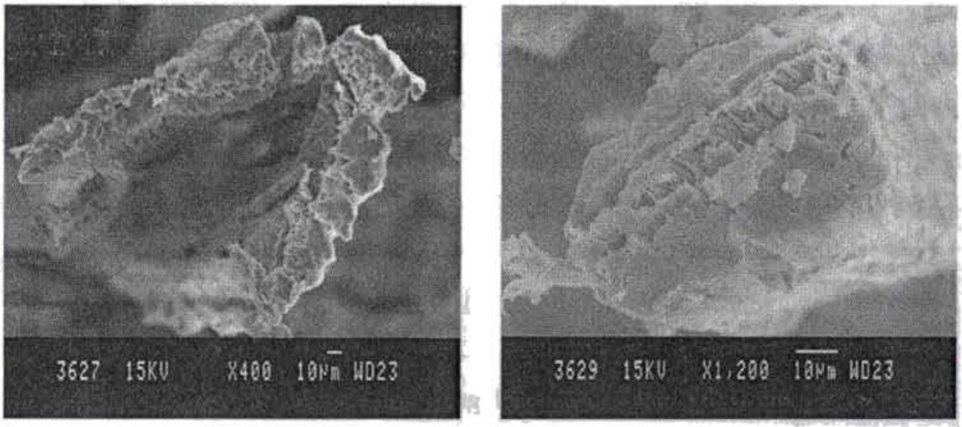


Figure 9.4. Scanning electron photographs of cross-section of alkali treated isora fibre.

On alkali treatment there is reduction in size of the central lacuna compared to the untreated fibre indicating cell wall thickening and shrinkage of fibres (Figure 9.4). Also the effect of alkali treatment on the fibre surface is evident from SEM studies explained in Chapter 4. The fibrillar nature as well as the porosity of the fibre is revealed in the fibre topography. Alkali treatment improves the fibre surface adhesive characteristics by removing natural and artificial impurities thereby producing a rough surface, which enhances the mechanical interlocking at the interface. Thus it is clear that water sorption can provide information regarding the efficiency of interfacial bonding.

9.2.1.3. Effect of chemical treatment on water uptake

The purpose of chemical treatment of fibre is to reduce its hydrophilic nature; thereby a strong interface is established between the treated fibre and the polymer matrix [28]. The effect of chemical treatment of isora fibre on the mole percent absorption of water of short isora-polyester composites at two temperatures is given in Figure 9.5. It is observed that chemical modification of the fibre reduced the water sorption property of the composites at both temperatures and the extent of decrease varies and depends on the chemical treatment (Figure 9.5). The improved moisture resistance caused by the application of the coupling agent can be explained by an improved fibre/matrix adhesion. The coupling agents build up chemical bonds and hydrogen bonds, which reduce the moisture-caused fibre/matrix debonding. It is found that all chemical modifications reduce the hydrophilic nature of isora fibre thereby favouring a strong interfacial adhesion between the fibre and the polyester resin. This in turn reduced the extent of water absorption. A strong adhesion at the interface is needed for an effective transfer of stress and load distribution throughout the interface. The lack of interfacial interaction leads to internal strains, porosity and environmental degradation [29, 30]. Among the chemically treated fibre composites, minimum water sorption is shown by benzoylated fibre composite and maximum by silane treated fibre composite. The mechanism of enhancement in interfacial adhesion has been discussed in Chapter 5.

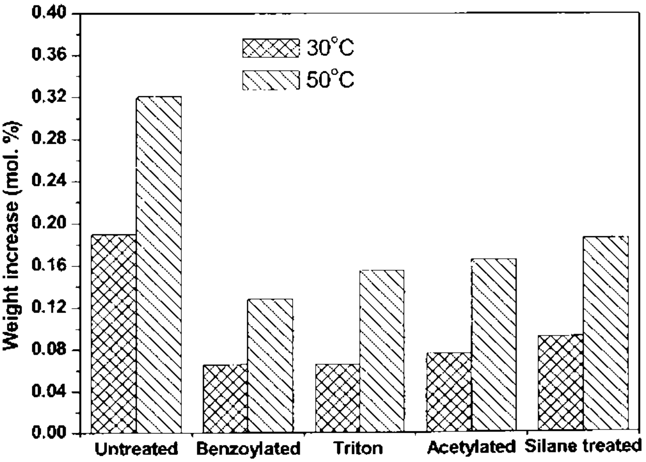


Figure 9.5. Effect of Chemical treatment on the mol. % water uptake of randomly oriented isora-polyester composites at two temperatures (fibre loading 24% v/v)

9.2.2. Oriented long isora-polyester composites

9.2.2.1. Effect of fibre loading on water sorption

Figure 9.6 shows the variation of water uptake by oriented long isora-polyester composites as a function of immersion time for different fibre loadings at 30°C. It is observed that the initial rate of water absorption and the equilibrium uptake of water by the composite increased with increasing fibre content. The increasing water absorption is caused, among other factors, by the higher hydrophilic nature of isora fibre compared to the polyester resin matrix and the greater interfacial area (capillary effect). The neat polyester resin shows very low water absorption due to its cross-linked network structure. The observed absorption of water in this case could have occurred through the micro cracks present inside the material.

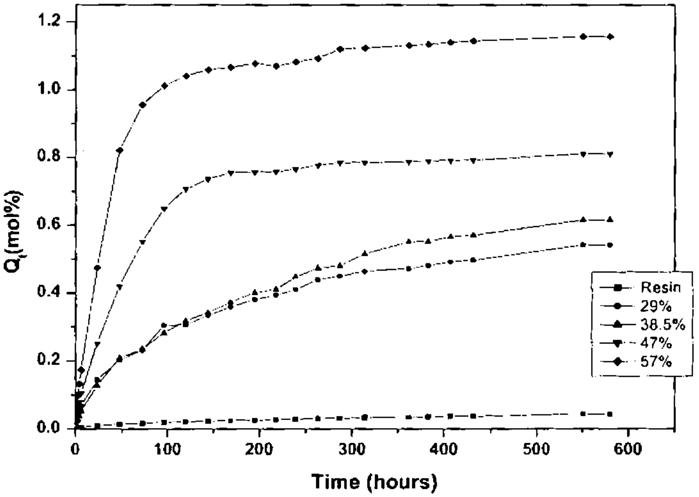


Figure 9.6. Effect of fibre loading on mol. % water uptake of untreated oriented long isora-polyester composites as a function of immersion time at 30° C

The equilibrium water uptake values of untreated oriented long isora-polyester composites at 30° C are plotted against fibre loading in the Figure 9.7. It is observed that Q_∞ values increased with increase in fibre content. As the volume fraction of the fibre increases the cellulose content also increases, which in turn results in the absorption of more water. The behaviour is almost linear.

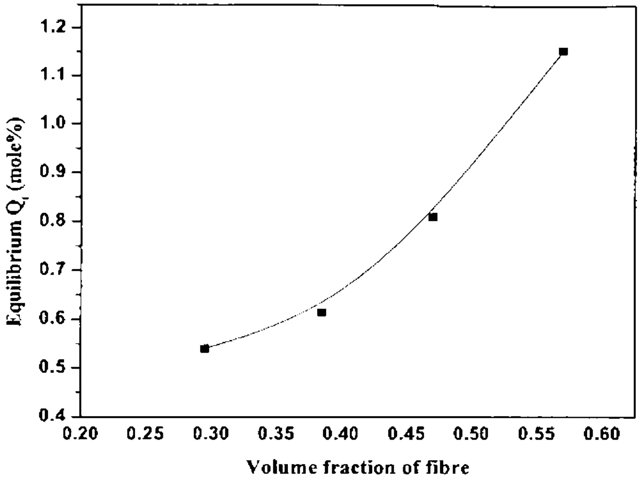


Figure 9.7. Effect of fibre loading on equilibrium mol. % water uptake of untreated oriented long isora-polyester composites at 30° C

9.2.2.2. Effect of fibre modifications on water sorption

Fibre modifications change the hydrophilicity of the fibre and change the extent of water sorption. Figure 9.8 shows the effect of fibre modification on water uptake of oriented long isora-polyester composites containing 57% fibre by volume.

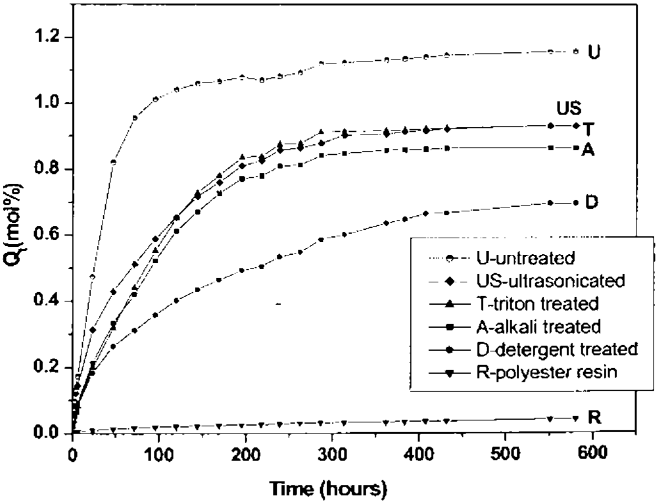


Figure 9.8. Effect of fibre treatments on mol. % water uptake of oriented long isora-polyester composites (V_f=57%) as a function of immersion time at 30° C

All fibre modifications reduced the water absorption by composites compared to untreated fibre composites. The initial water absorption rate is lowest for detergent treated fibre composite followed by alkali treated fibre composite. Initial water absorption rate followed the order: detergent treated < alkali treated= triton treated < ultrasonicated < untreated. At equilibrium also, the lowest water uptake is observed for detergent treated fibre composite and followed the order: detergent treated < alkali treated < triton treated= ultrasonicated < untreated. The reason for reduction in water uptake by the composite on fibre modification is the enhanced interaction between isora fibre and polyester resin in the composites, which has already been discussed in Chapter 6.

9.2.3. Oriented long isora-epoxy composites

9.2.3.1. Effect of fibre loading on water sorption

The variation of water sorption with fibre loading by oriented long isora-epoxy composites at 30°C, as a function of immersion time is shown in the Figure 9.9. It is observed that the initial rate of water absorption and the equilibrium uptake of water increased with increasing fibre content. The increasing water absorption is caused, among other factors, by the higher hydrophilic nature of isora fibre compared to the epoxy resin and the greater interfacial area (capillary effect). The neat epoxy resin shows very low water absorption due to its cross-linked network structure. The observed absorption of water in this case could have occurred through the micro cracks present inside the material.

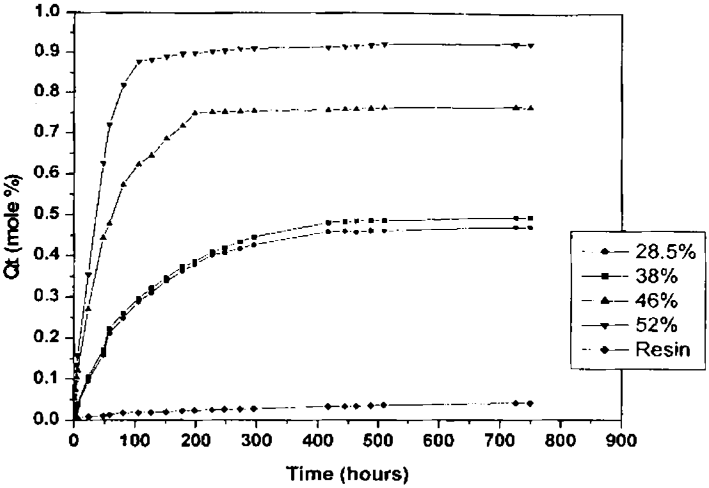


Figure 9.9. Effect of fibre loading on mol. % water uptake of untreated oriented long isora-epoxy composites as a function of immersion time at 30° C

The variation of equilibrium water uptake values of untreated oriented long isora-epoxy composites at 30^0 C, with fibre loading is given in Figure 9.10. It is observed that Q_∞ values increased with fibre content. As the volume fraction of the fibre increases the cellulose content increases, which in turn results in the absorption of more water. The behaviour is almost linear.

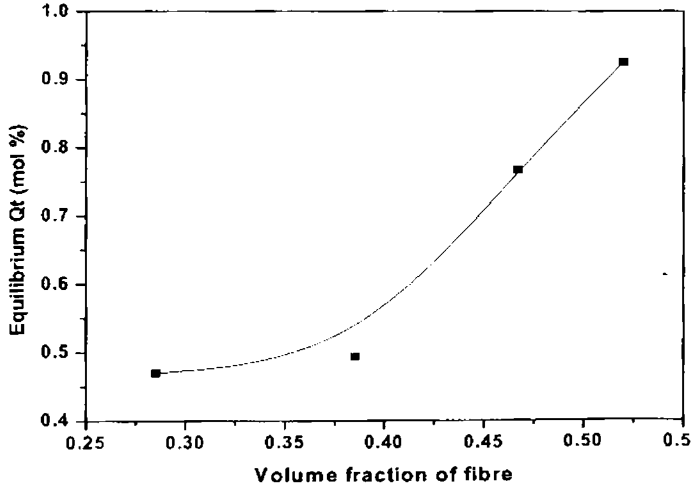


Figure 9.10. Effect of fibre loading on equilibrium mol. % water uptake of untreated oriented long isora-epoxy composites at 30° C

9.2.3.2. Effect of fibre modifications on water sorption

The effect of fibre modification on water uptake of oriented long isora-epoxy composites containing 52% fibre by volume is shown in Figure 9.11.

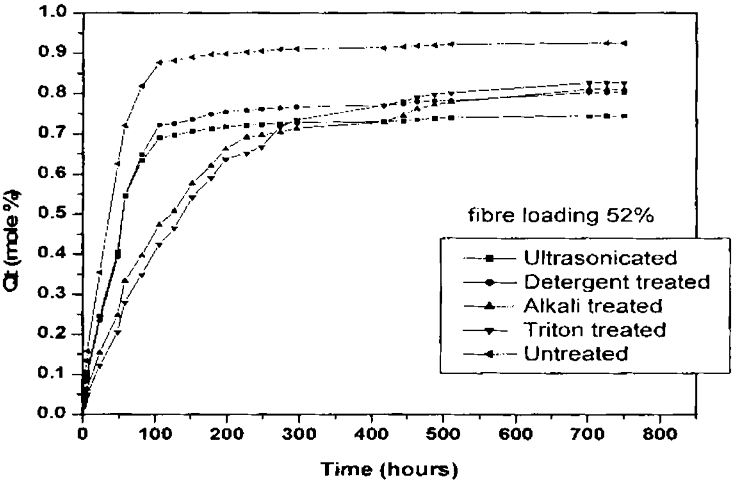


Figure 9.11. Effect of fibre treatments on mol. % water uptake of oriented long isora-epoxy composites as a function of immersion time at 30° C

All the fibre modifications reduced water absorption by the composites compared to untreated fibre composites. The initial water absorption rate is lowest for triton treated fibre composite and followed the order: triton treated < alkali treated < detergent treated = ultrasonicated < untreated. At equilibrium the lowest water uptake is observed for ultrasonicated fibre composite and followed the order: ultrasonicated < detergent treated = alkali treated< triton treated < untreated. As explained earlier (Section 9.2.2.2), the enhanced interaction between modified isora fibre and the epoxy resin in the composite is the cause of reduction in water uptake by the composite.

9.3. Kinetics of water sorption

Then kinetics of water absorption in permeable fibre/polymer composites is usually assumed to be a concentration independent Fickian diffusion process. In principle, the diffusion process of water in polymers and polymeric composites may depart from the idealizations inherent in the classical formulation of Fick. It is shown that non-Fickian aspects of the moisture absorption process have significant effects on the resulting hygro-thermal stresses in composite materials [31]. Loos and Springer [32] investigated the moisture absorption behaviour of many kinds of resin used for making polymer-matrix composites and showed that the materials obeyed the Fickian behaviour at low temperature and non-Fickian behaviour at higher temperatures. The characteristics of Fickian diffusion are: (1) the sorption curves are linear in the initial stages and (2) above the linear portion both absorption and desorption curves are concave to the abscissa.

To follow the mechanism of sorption, the moisture uptake data of isora-polyester and isora-epoxy composites were fitted to the equation [33],

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n\log t \qquad \text{.. } 9.1$$

where Q_t is the mole percent water uptake at time t, Q(is the mole percent water uptake at equilibrium. 'k' is a constant characteristic of the sample which indicates the interaction between the sample and water and 'n' indicates the mechanism of sorption.

For a Fickian mode of diffusion, the value of 'n' is equal to 0.5.This occurs when the segmental mobility of the polymer chains is faster than the rate of diffusion of permeant molecules. This happens in the case of diffusion into polymers, which are above their glass transition temperature up to about 50% of the equilibrium penetrant uptake. When 'n'=1, the diffusion process exhibits a case II behaviour. This occurs when the penetrant diffusion rates are much faster than polymer relaxation process, which is usual in rigid polymers with glass transition temperature well above the room temperature [34] When the 'n' value is in between 0.5 and 1, the diffusion is said to be anomalous. This is the case when permeant mobility and polymer segmental relaxation rates are almost equal. The values of 'n' and 'k' were determined by linear regression analysis. The values for isora-polyester composites are given in Table 9.1 and isora-epoxy composites in Table 9.2

It is observed that for both polyester and epoxy composites 'n' value lies in between 0.5 and 1. So the diffusion is termed anomalous. It is also observed that as the 'n' value increases, the value of 'k' decreases.

Table 9.1. Effect of fibre loading and chemical treatments on 'n' and 'k' values for oriented long isora-polyester composites at 30(C

Composite	**n**	**k×10^3**
29.5% composite (UT)	0.525	5.40
38.5% composite (UT)	0.666	1.66
47% composite (UT)	0.634	3.15
57% composite (UT)	0.673	3.04
Alkali treated	0.572	3.89
Ultrasonicated	0.501	8.41
Detergent treated	0.543	4.85
Triton treated	0.650	2.00

Table 9.2. Effect of fibre loading and chemical treatments on 'n' and 'k' values for oriented long isora-epoxy composites at 30°C

Composite	**n**	**k×10^3**
25.6% composite (UT)	0.733	1.04
38.5% composite (UT)	0.765	0.797
46.7% composite (UT)	0.625	3.91
52% composite (UT)	0.614	4.79
Alkali treated	0.681	1.35
Ultrasonicated	0.657	2.86
Detergent treated	0.658	2.52
Triton treated	0.680	1.08

9.4. Transport coefficients

The kinetic parameter, diffusion coefficient D can be calculated using equation [35]

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \qquad \text{.. 9.2}$$

where θ is the slope of the initial linear portion of the sorption curves of Q_t vs $t^{1/2}$, and h the initial sample thickness.

Table 9.3. Values of D, S and P for oriented long isora-polyester composites at 30°C

Composite	$D\times10^8$ (cm^2S^{-1})	S ($g\ g^{-1}$)	$P\times10^9$ (cm^2S^{-1})
29.5% composite (UT)	2.35	0.0972	2.29
38.5% composite (UT)	3.95	0.1106	4.37
47% composite (UT)	6.94	0.156	10.83
57% composite (UT)	11	0.208	22.9
Alkali treated	5.14	0.145	7.471
Ultrasonicated	4.11	0.154	6.349
Detergent treated	2.32	0.0962	2.233
Triton treated	6.66	0.153	10.18

Table 9.4. Values of D, S and P for oriented long isora-epoxy composites at 30°C

Composite	$D\times10^8$ (cm^2S^{-1})	S ($g\ g^{-1}$)	$P\times10^9$ (cm^2S^{-1})
25.6% composite (UT)	1.79	0.0889	1.59
38.5% composite (UT)	2.78	0.0847	2.35
46.5% composite (UT)	7.29	0.152	11.08
52% composite (UT)	14.9	0.166	24.9
Alkali treated	4.11	0.146	6.00
Ultrasonicated	7.23	0.134	9.68
Detergent treated	6.14	0.144	8.86
Triton treated	5.18	0.149	7.71

The values of diffusion coefficient *D*, of untreated isora-polyester and isora-epoxy composites at different fibre loadings and chemically treated isora-polyester and isora-epoxy composites are given in the Tables 9.3 and 9.4 respectively. According to Loos and Springer [32] the value of diffusion coefficient *D* for most of the polymers and their composites fall in the range of 10^{-11} to 10^{-12} m^2 S^{-1}. Several researchers [36, 37] have reported the value of diffusion coefficient in this range. It is observed that the *D* values increased with fibre loading at the given temperature. This is due to the inherent hydrophilic nature of the fibres. The diffusion coefficient characterises the ability of water molecule to diffuse through the polymer. Chemical treatments decreased the hydrophilicity of the fibre resulting in the lowering of *D* values of the composites.

The permeability of small molecule into a polymer is dependent on diffusivity as well as the sorption or solubility of a liquid in the polymer. Therefore sorption coefficient *S*, was calculated using the formula,

$$S = {}^{M_\infty}\!/_{M_p} \qquad \text{..} \; 9.3$$

where M_p is the mass of the initial polymer sample, M_∞ is the mass of the solvent taken up at equilibrium swelling. The values of sorption coefficient *S*, of untreated isora-polyester and isora-epoxy composites at different fibre loadings and chemically treated isora-polyester and isora-epoxy composites are given in Tables 9.3 and 9.4. The *S* values are found to increase with increase in isora fibre loading and surface treatments decreased the value of *S*.

The permeability coefficient *P*, which implies the net effect of sorption and diffusion, is given by the relation [35],

$$P = D \times S \qquad \text{..} \; 9.4$$

The values of permeability coefficient *P*, of untreated isora-polyester and isora-epoxy composites at different fibre loadings and chemically treated isora-polyester and isora-epoxy composites are given in Tables 9.3 and 9.4. The permeability coefficients of the composites varied in the same manner as *S*, ie. the *P* values increased with increase in fibre loading and surface treatments decreased the value of *P*.

9.5. Effect of thermal aging

9.5.1. Oriented long isora-polyester composites

9.5.1.1. Effect on Tensile properties

The effect of hot air oven aging on the tensile properties of oriented long untreated isora-polyester composites is given in Figure 9.12. It is observed that the tensile strength, Young's modulus and elongation at break values of the composite decreased with increase in treatment time. The decrease in tensile strength of the polyester may be due to the degradation of the polyester molecules on prolonged heating. In the case of composites, the decrease in tensile strength may be due to the loss of strength of isora fibre during prolonged exposure to elevated temperatures caused by the decomposition of volatile extractives present on the isora fibre surface. Although, the components of cellulose are supposed to be stable up to 160°C, the degradation reaction may initiate slowly on prolonged heating at 100°C [38]. The decomposition of the fibre will develop voids at the interface and this leads to poor fibre/matrix adhesion.

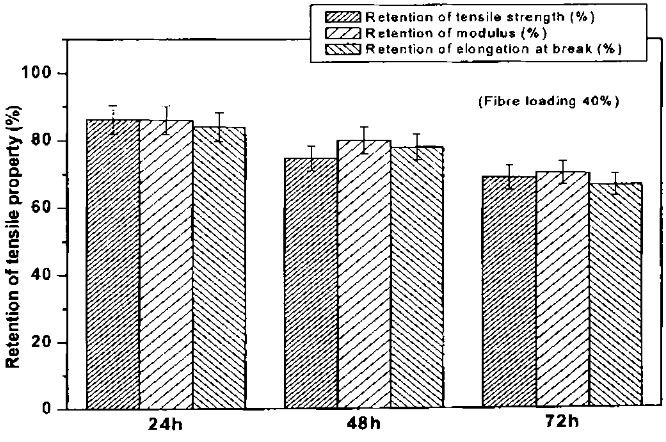


Figure 9.12. Effect of thermal aging on the tensile properties of untreated oriented long isora-polyester composites

The effect of alkali treatment of isora fibre on the retention of tensile properties of oriented long isora-polyester composites on hot air oven aging is given in Figure. 9.13. On alkali treatment of the fibre, retention of tensile properties generally enhanced compared to untreated fibre composite. This is due to the improvement in interfacial adhesion between treated fibre and polyester resin which is attributed to the reduction in the hydrophilicity of the fibre and improved thermodynamic compatibility between the treated fibre and polyester resin as discussed in Section 5.5.1. Retention of Young's modulus of the composites is higher for 48 and 72-hour aged samples compared to 24-hour aged sample. During thermal aging 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 aging. All these reactions greatly influence the performance of the composites.

When exposed to higher temperature (100°C) all composites showed a reduction in tensile properties but the relative extent of decrease is less pronounced in the case of treated fibre composites.

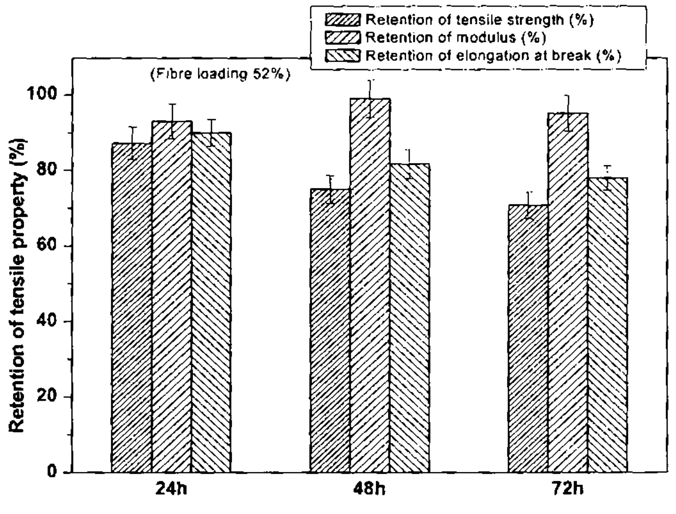


Figure 9.13. Effect of thermal aging on the tensile properties of alkali treated oriented long isora-polyester composites

It is also observed that the elongation and flexibility of the composites is decreased with aging. That is, oven aging makes the composites more brittle.

9.5.1.2. Effect on Flexural properties

The effect of hot air oven aging on the flexural properties of untreated oriented long isora-polyester composites is given in Figure 9.14.

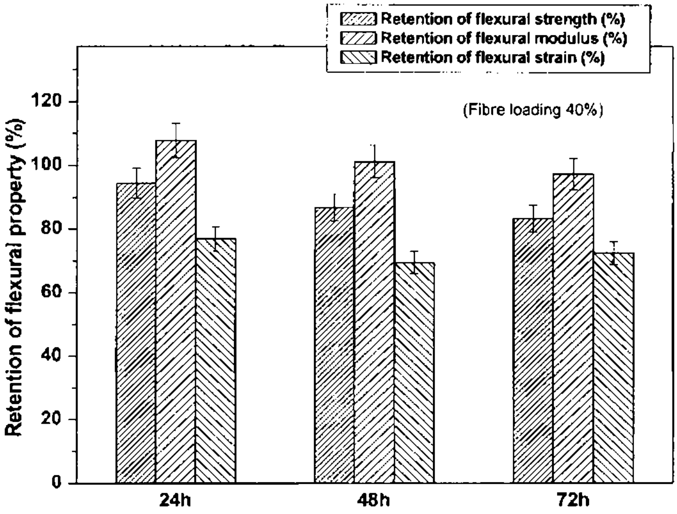


Figure 9.14. Effect of thermal aging on the flexural properties of untreated oriented long isora-polyester composites.

The flexural strength and flexural strain of the composites decreased on hot air oven aging whereas the flexural modulus increased up to 48-hour aging, compared to unaged sample.

The effect of hot air oven aging on the flexural properties of alkali treated oriented long isora-polyester composites are given in Figure 9.15.

It is observed that on alkali treatment of the fibre both flexural strength and flexural modulus of the composite are improved. This may be due to the additional cross-links formed in the composites. There is little change in flexural strain of the composites on thermal aging.

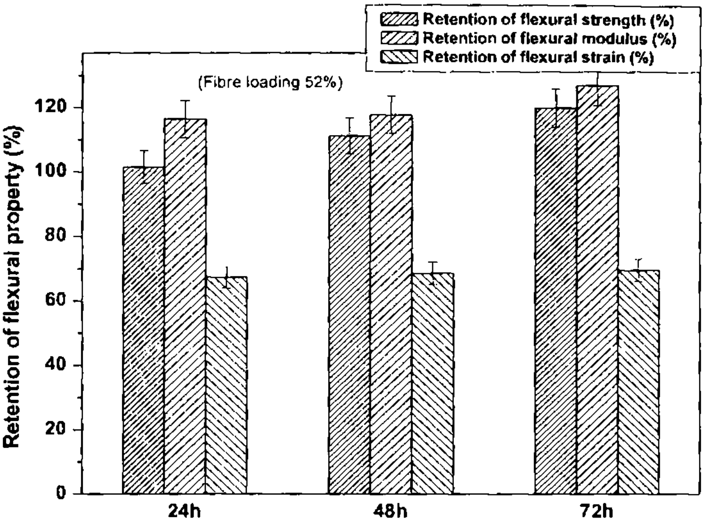


Figure 9.15. Effect of thermal aging on the flexural properties of alkali treated oriented long isora-polyester composites

9.5.2. Oriented long isora-epoxy composites

9.5.2.1. Effect on Tensile properties

The effect of hot air oven aging on the tensile properties of untreated oriented long isora-epoxy composites is given in Figure 9.16.

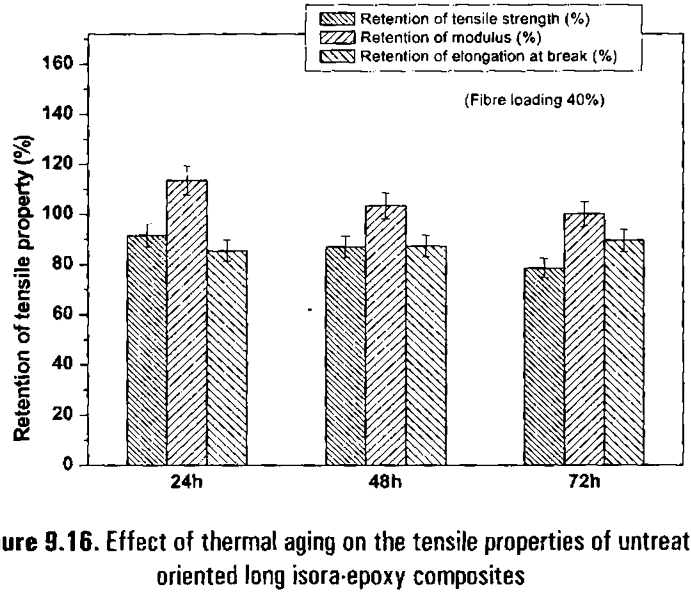


Figure 9.16. Effect of thermal aging on the tensile properties of untreated oriented long isora-epoxy composites

It is observed that the tensile strength and elongation at break values of the aged composites are lower than the unaged samples and also decrease with increase in exposure time as in the case of its polyester counterpart (Section 9.5.1.1). But the Young's modulus values of the composites showed improvement on thermal aging. This may be due to the additional cross-links formed in the composites.

9.5.2.2. Effect on Flexural properties

The effect of hot air oven aging on the flexural properties of untreated oriented long isora-epoxy composites is given in Figure 9.17. Unlike its polyester counterpart, the flexural strength and flexural modulus of the composite increased with increase in exposure time. This may be due to the additional cross-links formed in the composites. The flexural strain of the composite decreased on thermal aging.

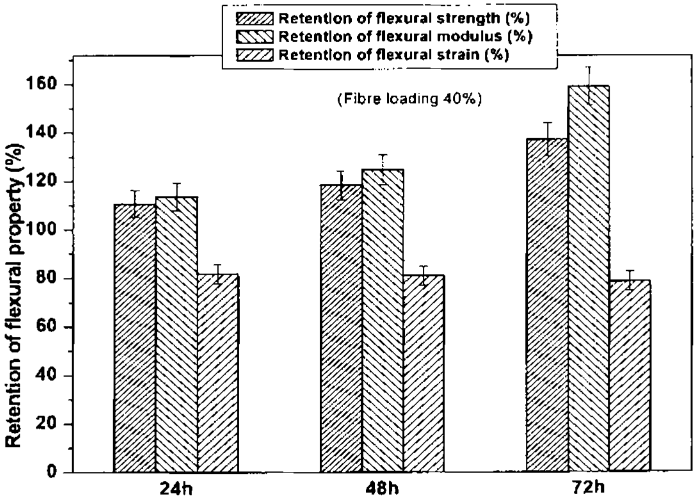


Figure 9.17. Effect of thermal aging on the flexural properties of untreated oriented long isora-epoxy composites

The elongation and flexibility of the composites decreased with aging. That is, oven aging makes the composites more brittle.

9.6. Conclusion

For randomly oriented isora-polyester composites, it is observed that the water absorption is linear initially, subsequently gradual and finally reached a plateau at 30°C. As the temperature is raised to 50°C, the mole % uptake of water increases and it varied linearly with fibre loading. Alkali treatment reduced the water uptake and it is minimum for 4 hour treated fibre composite, indicating enhanced interfacial bonding between the treated fibre and matrix.

The water absorption behaviour of oriented isora-polyester and isora-epoxy composites have been studied at 30°C, with reference to fibre loading and fibre surface modification and found to follow the same kinetics. The cross-linked polyester and epoxy resins showed minimum water absorption and as the amount of hydrophilic fibre increased, the water uptake also increased. Fibre modifications like ultrasonication, alkali, triton and detergent treatments decreased the water uptake in both composites. For both polyester and epoxy composites the 'n' value lies in between 0.5 and 1. So the diffusion is termed anomalous. Kinetic parameters such as diffusion coefficient, sorption and permeability coefficients were determined. The diffusion coefficient of the composites increased with fibre loading and decreased with fibre treatments. Sorption and permeability coefficients of the composites also varied in a similar manner.

The effect of hot air oven aging on the tensile properties of untreated oriented long isora-polyester composite showed that the tensile strength, Young's modulus and elongation at break values decreased with increase in treatment time. On alkali treatment, retention of tensile properties generally improved compared to untreated fibre composite, which is due to the improvement in interfacial adhesion between treated fibre and polyester resin. Retention of Young's modulus of the composites is higher for the 48 and 72 hour aged samples compared to the 24 hour aged sample. On alkali treatment of the fibre both flexural strength and flexural modulus of the composite improved. This may be due to the additional cross-links formed in the composites.

For oriented isora-epoxy composite, the tensile strength and elongation at break values of the thermal aged composites are lower than the unaged samples and also decrease with exposure time as in the case of its polyester matrix counterpart. But the Young's moduli values of the composites showed enhancement on thermal aging. This may be due to the additional cross-links formed in the composites. Unlike its polyester counterpart, the flexural strength and flexural modulus of the composite increased with exposure time. This may be due to the additional cross-links formed in the composites.

References

[1] Varelidis P.C., Kominos NP., Papaspyrides C.D., *Composites, Part A* (1998) **29A:** 1489–99.

[2] Apicella A., Nicolais L., Astarita G., Drioli E., *Polymer* (1981) **22:**1064-67.

[3] Marom G. In: Comyn J, editor. *Polymer permeability*, vol. 9. New York: Elsevier;1986. p. 341 [Chapter 9].

[4] Varelidis P.C., Papakostopoulos D.G., Pandazis C.I., Papaspyrides C.D., *Composites, Part A* (2000) **31:** 549–58.

[5] Mohd Ishak Z.A., Ariffin A., Senawi R., *Eur Polym J* (2001) **37:** 1635–47.

[6] Srivastava V.K., *Mater Sci Engg A* (1999) **263:** 56–63.

[7] Bastioli C., Casciola M., Romano G., In: Proceedings of the Third International Conference on Composite Interfaces, Cleveland; May 1990. p. 569–81.

[8] Lu X., Zhang MQ., Rong MZ., Yue DL., Yang GC., *Comp Sci Technol* (2004) **64:**1301–10.

[9] Gassan J., Bledzki AK., *Polym Compos* (1997) **18(2):**179–84.

[10] Joseph K, Thomas S, Pavithran C. *Comp Sci Technol* (1995) **53:** 99–110.

[11] Joseph P.V., Rabello M. S., Mattoso L.H.C., Joseph K., Thomas S., *Comp Sci Technol* (2002) **62:** 1357–72.

[12] Espert A, Vilaplana F, Karlsson S. *Composites Part A* (2004) **35:**1267–76.

[13] Lin Q, Zhou X, Dai G. *J Appl Polym Sci* (2002) **85(14):** 2824–32.

[14] Barsberg S., Thygesen LG., *J Colloid Interf Sci* (2001) **234:** 59–67.

[15] Pavlindo S., Paparpyrids C. D., *Comp Part A* (2003) **34:**1117-24.

[16] Rozman H. Z., Kumar R. N., Abusamah Addl M.R.M., Ishak Z. A. M., *J Wood Chem Technol* (1998) **18:** 471.

[17] Andreopulos A. G., Tarantil P. A., *J Appl Polym Sci* (1996) **70:** 747.

[18] Pothen L.A., Thomas S., Neelakantan R., *J Reinforced Plastics and Composites* (1997) **16(8):**744–65.

[19] Uma Devi, K. Joseph, K. C. Manikandan Nair, S. Thomas, *J Appl Polym Sci* (2004) **94:** 503-510.

[20] Siddaramaiah, S. V. Suresh, V. B. Atul, D. Srinivas, S. Girish *J Appl Polym Sci* (1999) **73:** 795-99.

[21] Nash B. N., Rana A. K., Mishra H. K., Nayak S. K., Tripathy S. S., *J Appl Polym Sci* (2000) **78:** 1671-79.

[22] Sreekala M. S., Kumaran M. G., Thomas S., *Comp Part A* (2002) **33:**763-77.

[23] Karmaker A. C., Hoffmann A., Hinrichsen G., *J Appl Polym Sci* (1994) **54:** 1803-1807.

[24] Bessadok A., Marais S., Gouanvé F., Colasse L., Zimmerlin I., Roudesli S., Métayer M., *Comp Sci Technol.,* (2007) **67: (3-4)** 685-697.

[25] de Albuquerque A. C., Joseph K., de Carvalho L. H., d' Almeida J. R. M. *Comp Sci Technol* (2000) **60:** 833-844.

[26] Rout J., Misra M., Tripathy S. S., Nayak S. K., Mohanty A. K., *Comp Sci Technol* (2001) **60:** 1303-1310.

[27] Hill C. A. S., Abdul Khalil H. P. S., *J Appl Polym Sci* (2000) **77:** 1322-1330.

[28] George J., Bhagavan S. S., Tomas S., *Composite interfaces* (1998) **5(3):**201-3.

[29] Felix J. M., Gatenholm P., *J Appl Polym Sci* (1991) **42:** 609.

[30] Bledzki AK., Reihmane S.,Gassan J., *J Appl Polym Sci* (1996) **59:** 1329-36.

[31] Cai L. W., Weitsman Y., *J. Comp. Mater.* (1992) **28(2):** 130-154.

[32] Loos A. C., Springer G. S., *Moisture absorption of Polyester to glass composites. In Environmental effects on composite materials,* ed. G. S. Springer, Technomic Publishing Co., Inc., Connecticut, p. 51, 1981.

[33] Adamson M. J., J. Mater. Sci., (1980) **15:** 1736.

[34] Mateo J. L., Bosch P., Serrano J., Calvo M., *Eur Polym J* (2000) **36:** 1903-10.

[35] Harogoppad S. B., Aminabhavi T. M., *J Appl Polym Sci* (1991) **42:** 2329-36.

[36] Ishak ZAM, Berry J. P., *J Appl Polym Sci* (1994) **51:** 2145.

[37] Ishak ZAM, Lim NC, *Polym. Eng. Sci.* (1994) **34:** 1645.

[38] Sapieha B.S., Pupo J.F., Schreiber H. P., *J Appl Polym Sci* (1989) **37:** 233.

Chapter 10

CONCLUSIONS AND FUTURE SCOPE OF WORK

Abstract

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

10.1. Summary and Conclusions

The summary and conclusions of the work carried out on the use of the natural fibre isora, as reinforcement in unsaturated polyester resin and epoxy resin are outlined in this chapter.

The science and technology of fibre reinforced polymer composites is advancing fast. 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 aerospace, automobile, marine industry etc. Compared to the various natural and synthetic fibres used as reinforcement for thermoset 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 the classification of composites, importance of fibre reinforced polymer composites, matrices and reinforcements used in composites, structure of natural fibres, advantages and disadvantages of natural fibres, factors influencing the performance of fibre reinforced composites, mechanism of fibre-matrix adhesion, fibre-matrix interface modifications, fabrication of composites, various models explaining the stress transfer in composites, characterization of isora fibre etc. are outlined in ***Chapter 1.***

The materials and various experimental techniques used in the investigation are briefly discussed in ***Chapter 2.***

Studies on the optimization of fibre length and fibre loading of randomly oriented isora-polyester composite are given in ***Chapter 3***. The fibre mats were prepared by hand lay up method and composites by compression moulding technique. The tensile properties of the composites have been analysed as a function of fibre length and fibre loading. The tensile strength, Young's modulus and elongation at break of the composites increase with fibre length and reached a maximum for 30mm length. There is an initial reduction in tensile strength of polyester at 10% fibre loading. After that the tensile strength increased with fibre loading and attained maximum value at 34% fibre loading. A decrease in tensile strength is observed for higher loadings. Various theoretical models were used to fit the tensile strength and Young's modulus of randomly oriented isora-polyester composites. The theoretical values were compared with experimental results. The models 'series' and 'Hirsch' were found the most useful in the systems investigated in this study. Flexural strength, modulus and strain of the composite were maximum for a fibre length of 40mm and for a fibre loading of 34% by volume. The impact strength of the composite increased linearly with fibre loading and is maximum at 48% fibre loading, after which the change is negligible.

The salient features of the alkali treatment of short isora fibre on the properties of randomly oriented isora-polyester composite are outlined in ***Chapter 4.*** The effect of alkali treatment on the surface morphology has been characterized by IR Spectroscopy and SEM studies. The tensile strength and modulus of the composite were found to be maximum for a fibre treatment time of 4 hours. The elongation at break of the composite decreased with treatment time. An alkali concentration of 1% yielded maximum tensile strength while a concentration of 4% yielded the maximum modulus for the composite. The improvement in tensile properties can be attributed to the improved wetting of alkali treated fibre with polyester. Alkali treatment makes the fibre surface rough, resulting in enhanced mechanical interlocking and stronger interfacial adhesion with the resin leading to better mechanical properties. Flexural properties also showed a similar dependence on alkali treatment time and alkali concentration. The impact strength of the composites decreased with alkali treatment time of fibre and attained a minimum value for 4 hour treatment. However, with prolonged treatment, impact strength increases.

The effect of surface modification of the hydrophilic isora fibre by different chemical treatments on the properties of randomly oriented isora-polyester composite is outlined in ***Chapter 5.*** The chemical treatments tried were acetylation, benzoylation, silane treatment and triton treatment. (Triton is iso octyl phenoxy poly ethoxy ethanol, a non ionic synthetic surfactant). Modified surfaces were characterized by IR Spectroscopy and SEM. All fibre modifications improved the tensile and flexural properties of the composite. The decrease in hydrophilicity and increase in thermodynamic compatibility of the treated fibre with the polymer matrix are responsible for the improvement in the mechanical properties. The maximum improvement in tensile properties was observed with triton treatment. SEM studies also suggest strong fibre-matrix adhesion in treated randomly oriented isora-polyester composites. In all cases except triton treatment, fibre modification decreases the impact strength of the composites.

The properties of oriented long isora fibre reinforced polyester composites are presented in ***Chapter 6.*** The effect of fibre loading and fibre surface modifications on the composite have been discussed. The fibre surface was modified by ultrasonication, alkali, triton and detergent treatments. The change in fibre morphology was characterized by SEM. The tensile strength and Young's modulus of the composite increased regularly with fibre loading and attained a maximum value at 43% loading after which a downward trend was observed. The elongation at break values of the composites decreased with fibre loading. The maximum flexural strength and modulus were observed for 56% loading. On alkali treatment of the fibre, the optimum loading for tensile properties increased from 43% to 66% and for flexural properties, from 56% to 66%, which is an indication of improved interfacial adhesion between the treated fibre and matrix. Of the various treatments, alkali treatment showed maximum improvement in tensile, flexural and impact properties. Impact strength of the composite increased with fibre loading, reached a maximum value for 57% by volume of fibre after which there was no significant increase in impact strength. The theoretical models 'ROM' (rule of mixture) and 'Hirsch' were found to be useful in fitting the tensile strength and Young's modulus of oriented isora-polyester composites.

The properties of oriented and randomly oriented isora fibre reinforced epoxy composites with special reference to the effect of fibre loading are reported in ***Chapter 7***. The effect of fibre surface modifications like alkali, triton and detergent treatments and ultrasonication, on the properties of the composite is also discussed. Randomly oriented isora-epoxy composites showed maximum properties at 45% fibre loading. Alkali treatment improved the tensile and flexural properties but decreased the impact strength. The tensile properties of oriented isora fibre reinforced epoxy composites were maximum at 49% fibre loading and the flexural properties at 45% fibre loading. All fibre treatments resulted in enhancement of properties. Triton treatment showed maximum improvement in tensile and flexural properties. The tensile fractographs of the composites were studied by SEM and it further showed improved fibre-matrix interaction for the samples which showed high strength and moduli. Impact strength of the composite was maximum at 55% fibre loading. Fibre treatments resulted in improved impact strength, which was maximum for triton treatment. Theoretical models 'Series' and 'Hirsch' were effective in fitting the properties of randomly oriented isora-epoxy composites and for oriented isora-epoxy composites 'ROM' and 'Hirsch' models were found useful.

The dynamic mechanical properties of the oriented and randomly oriented isora-polyester and isora-epoxy composites are presented in ***Chapter 8***. These properties were studied with special reference to the effect of fibre loading, orientation and chemical treatment as a function of temperature. The storage moduli of isora-polyester and isora-epoxy composites were found to increase with increase in fibre loading. All the composites showed decrease in modulus values with increase in temperature. The dynamic properties are strongly influenced by the fibre orientation. Oriented fibre composites showed higher values of storage modulus than randomly oriented fibre composites. Modified fibre composites showed higher storage modulus than that of untreated fibre composites and can be explained on the basis of better fibre-matrix adhesion.

The damping factor (tan δ) of the matrices decreased by the addition of the fibres and the area and height of the damping peak of the composites were lower and broader than that of the neat matrices. Fibre modification decreased the height and increases the width of the damping peak.

The storage modulus of the randomly oriented isora-polyester and isora-epoxy composites were calculated theoretically using the equation proposed by Einstein and compared with the experimental values. The experimental values of the composites are found to be much higher than the theoretical predictions. Higher modulus values of the composites indicate the enhanced reinforcing effect of the fibres with the matrices.

The damping factor (tan δ) of the randomly oriented isora-polyester and isora-epoxy composites were calculated theoretically using the equation proposed by Nielsen. The theoretical and experimental damping values of the composites showed that the damping behaviour of the composites does not follow the equation and that all values are lower than the predicted. But the agreement between the theoretical and experimental values is better for isora-epoxy composites compared to the isora-polyester composites.

In ***Chapter 9*** the water absorption kinetics of the oriented and randomly oriented isora-polyester composites and oriented isora-epoxy composites and the effect of hot air oven aging on the tensile and flexural properties of oriented isora-polyester and isora-epoxy composites are described.

For randomly oriented isora-polyester composites, it is observed that the water absorption is linear initially, subsequently gradual and finally reached a plateau at 30°C. As the temperature is raised to 50°C, the mole % uptake of water increases and it varied linearly with fibre loading. Alkali treatment reduced the water uptake and it is minimum for 4 hour treated fibre composite, indicating enhanced interfacial bonding between the treated fibre and matrix.

The water absorption behaviour of oriented isora-polyester and isora-epoxy composites have been studied at 30°C, with reference to fibre loading and fibre surface modification and found to follow the same kinetics. The cross-linked polyester and epoxy resins showed minimum water absorption and as the amount of hydrophilic fibre increased, the water uptake also increased. Fibre modifications like ultrasonication, alkali, triton and detergent treatments decreased the water uptake in both composites. For both polyester and epoxy composites the 'n' value lies in between 0.5 and 1. So the diffusion is termed anomalous. Kinetic parameters such as diffusion coefficient, sorption and permeability coefficients were determined. The diffusion coefficient of the composites increased with fibre loading and decreased with fibre treatments. Sorption and permeability coefficients of the composites also varied in a similar manner.

The effect of hot air oven aging on the tensile properties of untreated oriented long isora-polyester composite showed that the tensile strength, Young's modulus and elongation at break values decreased with increase in treatment time. On alkali treatment, retention of tensile properties generally improved compared to untreated fibre composite, which is due to the improvement in interfacial adhesion between treated fibre and polyester resin. Retention of Young's modulus of the composites is higher for the 48 and 72 hour aged samples compared to the 24 hour aged sample. On alkali treatment of the fibre both flexural strength and flexural modulus of the composite improved. This may be due to the additional cross-links formed in the composites.

For oriented isora-epoxy composite, the tensile strength and elongation at break values of the thermal aged composites are lower than the unaged samples and also decrease with exposure time as in the case of its polyester matrix counterpart. But the Young's moduli values of the composites showed enhancement on thermal aging. This may be due to the additional cross-links formed in the composites. Unlike its polyester counterpart, the flexural strength and flexural modulus of the composite increased with exposure time. This may be due to the additional cross-links formed in the composites.

Thus it can be concluded that, due to the low density and high specific properties of isora fibre, composites based on these fibres have good potential in structural or non- structural applications.

10.2. Future Outlook

i) Characterization of interface

The performance of composite is determined by the fibre/matrix interface. The interface could be characterized by various techniques like ESCA, microdebond test, single fibre pull out test etc.

ii) Preparation of isora micro fibril composites

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

iii) Reinforcement in thermoplastics

Isora, being identified as a very useful natural fibre reinforcement in natural rubber and thermosets, it can now be tried in thermoplastic matrices for developing value added engineering composites.

iv) Hybrid composites

Properties of isora fibre composites can be improved by hybridizing with synthetic fibres like glass, nylon etc. The effect of layering pattern on the properties of the hybrid composite can be explored.

v) Development of green composites

The possibility of using isora fibre as reinforcement in biodegradable matrices (like α-hydroxy lactic acid, β-hydroxy alkanoate etc.) to produce completely biodegradable green composite, can be investigated

ABBREVIATIONS AND SYMBOLS

A	Area of cross section
AE	Acoustic emission
ASTM	American standards and testing methods manual
AT	Alkali treatment
b	Width of specimen tested
BMC	Bulk moulding compounds
BP	Boiling point
BPA	Bisphenol A
cm	centimetre
CSM	Chopped strand mat
d	Depth of specimen
DGEBA	Diglycidyl ether of bisphenol A
DMA	Dynamic mechanical analysis
DMC	Dough moulding compounds
DSC	Differential scanning calorimetry
DT	Detergent treatment
E'	Storage modulus
E"	Loss modulus
EB	Elongation-at-break
FLD	Fibre length distribution
FOD	Fibre orientation distribution
FRC	Fibre reinforced composite
FRP	Fibre reinforced plastics
FTIR	Fourier Transform infrared
GP	General Purpose
GPa	Giga pascal
h	Hours

Hz	Hertz
IIR	Isobutylene-isoprene rubber (butyl rubber)
ILSS	Inter laminar shear strength
ISS	Interfacial shear strength
l_c	Critical fibre length
LCM	Liquid Composite Moulding
LDPE	Low density poly ethylene
L.R.	Laboratory reagent
m	metre
MA	Maleic anhydride
MEKP	Methyl ethyl ketone peroxide
min	Minutes
mm	millimetre
mol	Mole
MPa	Mega Pascal
n	Diffusional exponent
nm	Nanometre
NR	Natural rubber
OPEFB	Oil palm empty fruit bunch
P	Permeability coefficient
PAI	Poly (amide imide)
PAN	polyacrylonitrile
PAS	Poly aryl suphone
PE	Polyethylene
PEI	Poly eher imide
PEK	Poly (ether ketone)
PEEK	Poly (ether ether ketone)
PES	Poly ether sulphone

PET	Polyethylene terephthalate
PF	Phenol formaldehyde
PG	1, 2-Propylene glycol
phr	Parts by hundred parts by weight of resin
PMC	Polymer matrix composite
PMMA	poly methyl methacrylate
PP	poly propylene
PPDO	poly (p-dioxanone)
ppm	parts per million
PPS	Poly (phenylene suphide)
PSU	Polysulphone
Q_t	Mol. % uptake at equilibrium
Q_∞	Mol. % uptake at infinite time
rpm	Revolutions per minute
RRIM	Reinforced resin injection moulding
RTM	Resin transfer moulding
SBR	Styrene butadiene rubber
SEM	Scanning electron microscopy
SMC	Sheet moulding compounds
SRIM	Structural resin injection moulding
tan δ	Loss factor
T	Temperature
T_g	Glass transition temperature
TGA	Thermo gravimetric analysis
TT	Triton treatment
UT	Untreated
UD	Unidirectional
UHMWPE	Ultra high molecular weight polyethylene

UPR	Unsaturated polyester resin (GP grade)
US	Ultrasonication
UTM	Universal Testing Machine
UV	Ultra violet
VARI	Vacuum assisted resin injection
V_f	Volume fraction of fibre
V_m	Volume fraction of matrix
WAXRD	Wide angle X-ray diffractometer

PUBLICATIONS IN INTERNATIONAL JOURNALS

1. **M. K. Joshy**, Lovely Mathew and Rani Joseph, Studies on short isora fibre reinforced polyester composites, *Composite interfaces* **(2006) 13 (4-6): 377-390**
2. **M. K. Joshy,** Lovely Mathew and Rani Joseph, Effect of alkali treatment on the properties of Unidirectional isora fibre reinforced epoxy composites, *Plastics, Rubber and Composites* **(2007) 36 (6) : 259-266**
3. **M. K. Joshy,** Lovely Mathew and Rani Joseph, Studies on interfacial adhesion in Unidirectional isora fibre reinforced polyester composite, *Composite interfaces* **(2007) 14 (7-9): 631-646.**
4. **M. K. Joshy,** Lovely Mathew and Rani Joseph, Effect of alkali treatment on the mechanical properties of short randomly oriented isora fibre-polyester composites, *Progress in Rubber, Plastics and recycling Technology.* (accepted)
5. **M. K. Joshy,** Lovely Mathew and Rani Joseph, Influence of fibre surface modification on the mechanical performance of randomly oriented isora-polyester composites, *Polym. Comp.* (communicated)
6. **M. K. Joshy**, Lovely Mathew and Rani Joseph, Effect of interface modification on the properties of oriented isora fibre reinforced polyester composites, *J. of Applied Polym. Sci.* (communicated)
7. **M. K. Joshy,** Lovely Mathew and Rani Joseph, Studies on interfacial adhesion in oriented isora fibre reinforced epoxy composite, *Composite Part A* (communicated)
8. **M. K. Joshy** and Rani Joseph, Dynamic Mechanical Analysis of isora fibre reinforced polyester composites, *J. of Applied Polym. Sci.* (communicated)
9. **M. K. Joshy** and Rani Joseph, Viscoelastic properties of of isora fibre reinforced epoxy composites, *J. of Material Sciences* (communicated)
10. **M. K. Joshy** and Rani Joseph, Water sorption behaviour of isora fibre reinforced polyester composites, *Comp. Sci. Technol.* (communicated)
11. **M. K. Joshy** and Rani Joseph, Water sorption characteristics of isora fibre reinforced epoxy composites, *Composites.* (communicated)
12. **M. K. Joshy** and Rani Joseph, Effect of thermal aging on the properties of isora fibre reinforced polyester and epoxy composites, *J. of Applied Polym. Sci..* (communicated)

PAPERS PRESENTED IN INTERNATIONAL/NATIONAL SEMINARS/CONFERENCES

1. *"Studies on short isora fibre reinforced polyester composites":* **M. K. Joshy,** Lovely Mathew and Rani Joseph -Presented at the international conference organized by the School of Chemical Sciences, M.G University Kottayam on March 21-23, 2005
2. *"Studies on mechanical properties of unidirectional isora fibre reinforced polyester composites":* **M. K. Joshy,** Lovely Mathew and Rani Joseph-Presnted at the XVIII Kerala Science Congress, held at Trivandrum from January 29-31, 2006.
3. *"Studies on mechanical properties of unidirectional isora fibre reinforced epoxy resin composites":* **M. K. Joshy,** Lovely Mathew and Rani Joseph-Presented at the National conference organized by the Material Research Society of India held at CMS Conventional Centre, Lucknow, from February 13-15, 2006.
4. *"Mechanical properties of unidirectional isora fibre reinforced polyester and epoxy composites"* **M. K. Joshy,** Lovely Mathew and Rani Joseph-Presented at the 'Polymer 2006' National conference held at IACS, Kolkatta jointly organized by SPSI Kolkatta Chapter and IACS, from February 10-13, 2006.
5. *"Effect of chemical treatments on mechanical and thermal properties of short isora fibre reinforced polyester composites":* **M. K. Joshy,** Lovely Mathew and Rani Joseph-Presented at the National Seminar on 'Frontiers in Organic Chemistry' (FOCY 2007) organized by the Dept. of Chemistry, University of Calicut, from January 11-12, 2007.
6. *"Effect of surface modifications on the mechanical and thermal properties of unidirectional isora fibre reinforced polyester composites":* **M. K. Joshy,** and Rani Joseph- Presnted at the XIX Kerala Science Congress, held at Kannur from January 29-31, 2007.

CURRICULUM VITAE

Name	**JOSHY M. K.**
Official address	Selection Grade Lecturer, Department of Chemistry, S. N. M. College, Maliankara P. O., Ernakulam District, Kerala. PIN: 683516.
Permanent Address	Melekkattil House, VARADA, Fort Road, N. Paravur, Ernakulam District, Kerala. PIN: 683513.
Date of birth	30-04-1959
Qualification	M. Sc. (Pure Chemistry)
Teaching experience	25 Years
Topic of Research	Isora fibre reinforced polyester and epoxy composites
Research experience	Four years experience in the field of Natural fibre reinforced Polymer Composites
Research Publications	Published 3 Accepted 1 Communicated 8