

CHAPTER 10:

LIGNOCELLULOSIC FIBER REINFORCED RUBBER COMPOSITES

Maya JACOB JOHN¹

Rajesh D. ANANDJIWALA²

(1)CSIR Materials Science and Manufacturing, Fibres and Textiles Competence Area, P.O. Box 1124, Port Elizabeth 6000, South Africa, E-mail: mjohn@csir.co.za

(2) Department of Textile Science, Faculty of Science, Nelson Mandela Metropolitan University, P.O. Box 1600, Port Elizabeth 6000, South Africa, E-mail:Rajesh.Anandjiwala@nmmu.ac.za,

Sabu THOMAS

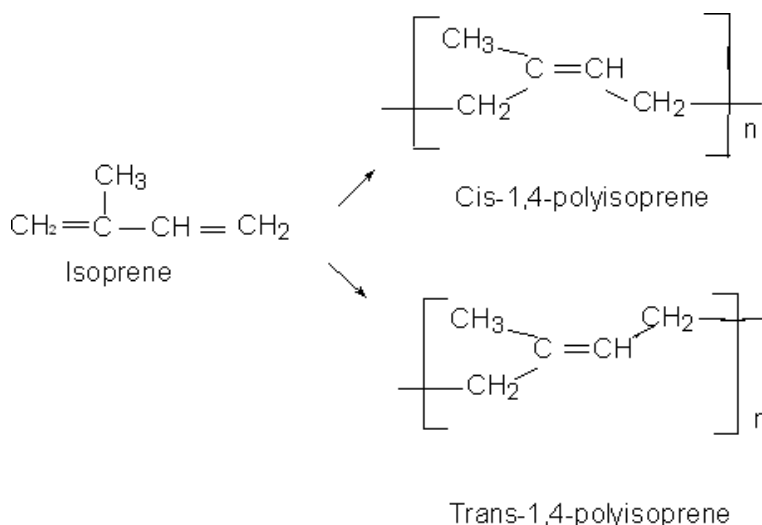
School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India,

1. INTRODUCTION

1.1 Natural Rubber [1]

NR is a naturally occurring elastomeric polymer of isoprene (2-methyl-1,3-butadiene). It can be extracted from latex of only one kind of tree, the *Hevea braziliensis*. Hevea rubber is produced in many tropical regions of Southeast Asia, Africa and Central and South America. There is practically only one other potential source of NR, that is the guayule shrub (*Parthenium argentatum*). Polyisoprene exists naturally in the form of two stereo-isomers, namely cis-1,4-polyisoprene and trans-1,4-polyisoprene.

Chemically NR is cis 1,4-polyisoprene –Figure 1-.A linear, long chain polymer with repeating isoprenic units (C_5H_8), it has a density of 0.93 at 20° C. Natural trans-1, 4-polyisoprene is a crystalline thermoplastic polymer, which is mainly used in golf ball covers, root canal fillings in dentistry, special adhesives and to a lesser extent in wire and cable coverings. It is obtained as gutta percha from *Palaquium oblongofolium* in South East Asia. It is much harder and less soluble than Hevea rubber. Certain trees like Chicle (*Achras sapota*) produce latex, which is a physical mixture of cis and trans polyisoprene. Cis-1, 4-polyisoprene can be produced synthetically by stereospecific polymerization reaction using Ziegler-Natta-heterogenous catalyst. The important components of NR are given in Table I.



Components	%
Rubber hydrocarbon	93.3
Acetone extract	2.9
Protein	2.8
Moisture	0.6
Ash	0.4

Figure 1. Structure of natural rubber

NR has a very uniform microstructure that provides the material with a some very unique and important characteristics, namely the ability to crystallize under strain, a phenomenon known as “strain – induced crystallisation”, and very low hysteresis. Stretching of vulcanizates of polyisoprene having at least 90 % cis content leads to crystallization, which in turn leads to strengthening of rubber.

Application of NR in rubber products gives the product very useful technical characteristics of very good tensile strength, high resilience, excellent flexibility and resistance to impact and tear, low heat-build-up, plus good “green” strength and building tack. However, NR is less resistant to oxidation, ozone, weathering and a wide range of chemicals and solvents, mainly due to its unsaturated chain structure and nonpolarity. These inherent drawbacks apparently cause limitations in the variety of NR usage, particularly for technical and engineering applications. Forms of NR modified through chemical manipulation of the polymer chain to achieve certain special properties have been attempted in the past, for instance by the Rubber-Stichting in the laboratories in Delft, albeit with very limited commercial success.

A relatively successful modification of NR was Epoxidised Natural Rubber (ENR), which has been produced in pilot-plant quantities in Malaysia. Prof Schuster from the German Institute of Rubber Technology is of the opinion that NR could provide an "ideal" EPDM rubber by means of hydrogenation and inserting polar groups which can lead to different types of rubbers that are more resistant to oil and heat. Also with the depletion of oil resources

NR would be used as a natural beneficial base to produce a variety of polymers. Schuster also added that NR availability in powdered form could be another innovation to pursue further, as it would allow continuous mixing of rubber with fillers and other ingredients in compounding. Operating at lower energy input and delivering higher mixing quality, continuous mixing of powder rubber could play a significant role in the future.

Chemical modification of NR can be categorised in three main categories [2]:

a. *Modification by bond rearrangement without introducing new atoms*

Examples of this type are carbon-carbon cross-linking, cyclisation, cis, trans-isomerisation, and depolymerisation. Cyclized NR, for example, is formed by treating NR with a proton donor such as sulphuric acid, sulphonic acid, stannic chloride or by heating NR. Cyclized NR is reported to be tough, hard and brittle but it still has some elastic behaviour. It is used in adhesives and in printing ink. It is also being blended with NR to give high modulus, high hardness and low specific gravity.

b. *Modification by attachment of new chemical groups (like chlorine and epoxy)*

The addition or substitution reactions at the olefinic double bonds results in the formation of chlorinated NR, hydrochlorinated NR and epoxidized NR (ENR). Chlorination and hydrochlorination of NR can be carried out in dry, solution or latex form. Chlorinated NR (CNR) is used as raw material for paint because of its resistance against acids and alkalis, and its wear resistance, ageing resistance and corrosion resistance in seawater.

c. *Grafting a second polymer onto the NR backbone*

Grafting is mostly carried out using vinyl monomers like methyl methacrylate (MMA) and styrene. The commercial available grafted copolymer of NR with poly (methyl methacrylate) (PMMA) is Heveaplus MG with two grades: 30% (MG 30) and 49% (MG49) of PMMA. The grafted products have degrees of grafting in the range of 60-80% and some free PMMA. Heveaplus MG has superior properties like hardness, modulus, abrasion, electrical resistance and light color. It is used to improve the impact properties of polystyrene, in blends with NR and also as reinforcing agent.

Some of the recent modifications of NR are deprotenized rubber (DPNR). This is very useful when low water absorption is wanted, vulcanizates with low creep are needed, or more than ordinary reproducibility is required. Normally NR has between 0.25 and 0.5% nitrogen as protein; deproteinized rubber has only about 0.07%. A drawback is that since protein matter in the rubber accelerates cure, deproteinized rubber requires more acceleration. DPNR is made by treating NR latex with a bioenzyme, which hydrolyzes the proteins to watersoluble forms. A protease such as *Bacillus subtilis* is used at about 0.3 phr. When the enzymolysis

is completed the latex is diluted to 3% total solids and coagulated by adding a mixture of phosphoric and sulfuric acid. The coagulated rubber is then pressed free of most of the water, crumbed, dried, and baled.

Another modification is oil-extended NR (OENR). There are three ways to make this kind of rubber: (1) coagulation of latex with oil emulsion, (2) Banbury mixing of oil and rubber, and (3) allowing the rubber to absorb the oil in pans until almost all is absorbed, then milling to incorporate the remaining oil. Recently rubber and oil have been mixed using an extruder. Another new modification is thermoplastic natural rubbers (TPNR). These are physical blends of natural rubber and polypropylene, mixed in different proportions to yield rubbers with different stiffness properties. They are suitable for injection molding into products for automotive applications such as flexible sight shields and bumper components.

In a recent study, a new rubber synthesis initiation site was found localized on the Hevea latex organelle membrane[3]. The membrane was fully equipped with enzyme system and the regulatory protein. Isolated protein fractions from the membrane were still active for the synthesis of rubber under proper optimum condition. Researchers think that it will be possible to utilize membrane proteins to form bioreactors for synthesis of functionalized natural rubber.

1.2 Grades and Grading [4]

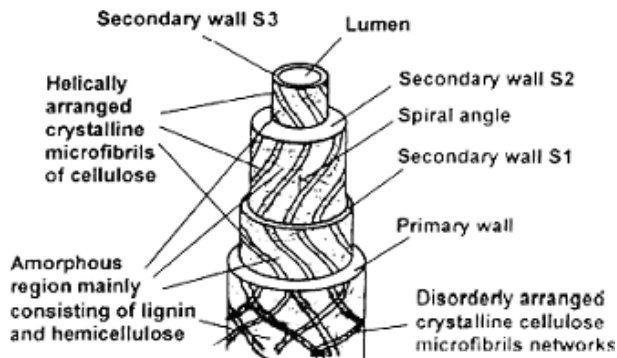
All types of NR that are not modified (such as oil extended NR) or technically specified rubbers (TSR's) are considered to be international grades. Grade designations usually use color or how the rubber was made; typical grade descriptions are pale crepe, rubber smoked sheet and thin brown crepe. The main disadvantage of this system is that grading is done on visual aspects. Almost exclusively, the darker the rubber, the lower the grade. Other grading criteria such as the presence or absence of rust, bubbles, mould and cut spots are subjective in nature. Perhaps the most valid assumption is that the darker the rubber the more dirt it contains. In the 1960's, Malaysia developed a grading scheme that was more sophisticated and useful to customers. The cornerstone of the new system was grading according to dirt content measured in hundredths of 1%. For eg: Standard Malaysian rubber (SMR) is a rubber whose dirt content does not exceed 0.5%. Dirt is considered to be the residue on a 45 μ m sieve after a rubber sample has been dissolved in an appropriate solvent, washed through the sieve and dried. The specification has other parameters including source material for the grade, ash and nitrogen content, volatile matter, plasticity retention index (PRI) and initial plasticity⁴. Acceptance of these standards is vigorous and other rubber producing countries followed suit. Letter abbreviations identify the rubber source SMR denotes rubber from Malaysia, SIR indicates Indonesian product, SSR indicates Singapore product and ISNR denotes Indian Standard Natural Rubber.

2. NATURAL FIBER

Natural fibres are subdivided based on their origins, coming from plants, animals or minerals. All plant fibres are composed of cellulose while animal fibres consist of proteins (hair, silk and wool). Plant fibres include bast (or stem or soft sclerenchyma) fibres, leaf or hard fibres, seed, fruit, wood, cereal straw and other grass fibres. Table I presents the list of biofibers. Over the last few years, a number

of researchers have been involved in investigating the exploitation of natural fibres as load bearing constituents in composite materials. The use of such materials in composites has increased due to their relative cheapness, their ability to recycle and for the fact that they can compete well in terms of strength per weight of material. Natural fibres can be considered as naturally occurring composites consisting mainly of cellulose fibrils embedded in lignin matrix. The cellulose fibrils are aligned along the length of the fibre, which render maximum tensile and flexural strengths, in addition to providing rigidity. The reinforcing efficiency of natural fibre is related to the nature of cellulose and its crystallinity. The main components of natural fibres are cellulose (α -cellulose), hemicellulose, lignin, pectins and waxes.

Biofibres can be considered to be composites of hollow cellulose fibrils held together by a lignin and hemicellulose matrix [5]. The cell wall in a fibre is not a homogenous membrane (Figure 2). Each fibril has a complex, layered structure consisting of a thin primary wall that is the first layer deposited during cell growth encircling a secondary wall. The secondary wall is made up of three layers and the thick middle layer determines the mechanical properties of the fibre. The middle layer consists of a series of helically wound cellular microfibrils formed from long chain cellulose molecules: the angle between the fibre axis and the microfibrils is called the microfibrillar angle. The characteristic value for this parameter varies from one fibre to another.



[Reference: Rong M.Z. et al., Comp. Sci. Tech., 61, 1437, 2001]

Figure 2. Structure of biofibre

Such microfibrils have typically a diameter of about 10-30 nm and are made up of 30 to 100 cellulose molecules in extended chain conformation and provide mechanical strength to the fibre. The amorphous matrix phase in a cell wall is very complex and consists of hemicellulose, lignin and in some cases pectin. The hemicellulose molecules are hydrogen bonded to cellulose and act as cementing matrix between the cellulose microfibrils, forming the cellulose-hemicellulose network, which is thought to be the main structural component of the fibre cell. The hydrophobic lignin network affects the properties of other network in a way that it acts as a coupling agent and increases the stiffness of the cellulose/hemicellulose composite.

The structure, microfibrillar angle, cell dimensions, defects and the chemical composition of fibres are the most important variables that determine the overall

properties of the fibres [6]. Generally, tensile strength and Young's modulus of fibres increases with increasing cellulose content. The microfibrillar angle determines the stiffness of the fibres. Plant fibres are more ductile if the microfibrils have a spiral orientation to the fibre axis. If the microfibrils are oriented parallel to the fibre axis, the fibres will be rigid, inflexible and have high tensile strength.

Fibre source	Species	Origin
Abaca	<i>Musa textilis</i>	Leaf
Bagasse	-	Grass
Bamboo	(>1250 species)	Grass
Banana	<i>Musa indica</i>	Leaf
Broom root	<i>Muhlenbergia macroura</i>	Root
Cantala	<i>Agave cantala</i>	Leaf
Caroa	<i>Neoglaziovia variegata</i>	Leaf
China jute	<i>Abutilon theophrasti</i>	Stem
Coir	<i>Cocos nucifera</i>	Fruit
Cotton	<i>Gossypium</i> sp.	Seed
Curaua	<i>Ananas erectifolius</i>	Leaf
Date palm	<i>Phoenix Dactylifera</i>	Leaf
Flax	<i>Linum usitatissimum</i>	Stem
Hemp	<i>Cannabis sativa</i>	Stem
Henequen	<i>Agave fourcroydes</i>	Leaf
Isora	<i>Helicteres isora</i>	Stem
Istle	<i>Samuela camerosana</i>	Leaf
Jute	<i>Corchorus capsularis</i>	Stem
Kapok	<i>Ceiba pentranda</i>	Fruit
Kenaf	<i>Hibiscus cannabinus</i>	Stem
Kudzu	<i>Pueraria thunbergiana</i>	Stem
Mauritius hemp	<i>Furcraea gigantea</i>	Leaf
Nettle	<i>Urtica dioica</i>	Stem
Oil palm	<i>Elaeis guineensis</i>	Fruit
Prassava	<i>Attalea funifera</i>	Leaf
Pineapple	<i>Ananas comosus</i>	Leaf
Phormium	<i>Phormium tenax</i>	Leaf
Roselle	<i>Hibiscus sabdariffa</i>	Stem
Ramie	<i>Boehmeria nivea</i>	Stem
Sansevieria (Bowstring hemp)	<i>Sansevieria</i>	Leaf
Sisal	<i>Agave sisilana</i>	Leaf
Sponge gourd	<i>Luffa cylindrica</i>	Fruit
Straw (Cereal)	-	Stalk
Sun hemp	<i>Crotalaria juncea</i>	Stem
Cadillo/Urena	<i>Urena lobata</i>	Stem
Wood	(>10,000 species)	Stem

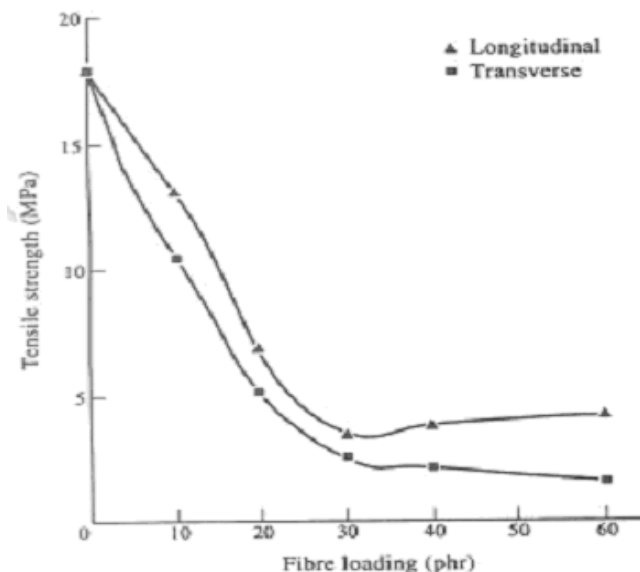
3. NATURAL FIBER REINFORCED RUBBER COMPOSITES

The primary effects of short fibre reinforcement on the mechanical properties of natural rubber composites include increased modulus, decreased elongation at failure, greatly improved creep resistance over particulate-filled rubber, increased hardness and a substantial improvement in cut, tear and puncture resistance. Hysteresis and fatigue strength are also improved. When fibres are aligned parallel to the stress direction, tensile strength develops a characteristic drop with increasing fibre volume content until a critical fibre level is reached. The critical concentration level at which the unreinforced matrix strength is recovered varies directly with the critical fibre aspect ratio. The stiffness and modulus of short fibre composite increase with fibre concentration though it may not be necessarily linear. Tear strength is highly dependent on fibre loading and is seen to increase with concentration.

The mechanical properties of lignocellulosic fibre reinforced natural rubber composites have been extensively studied. It has been reported by Dzyura¹¹⁹ that the minimum amount of fibres to restrain the matrix is smaller if the matrix strength is higher. Natural rubber is a very strong matrix because of its strain-induced crystallization. Generally it has been seen that the tensile strength initially drops down to a certain amount of fibre and then increases. The minimum volume of fibre is known as the critical volume above which the fibre reinforces the matrix. The critical volume varies with the nature of fibre and matrix, fibre aspect ratio and fibre / matrix interfacial adhesion.

At low fibre concentrations, the fibre acts as a flaw in the rubber matrix and the matrix is not restrained by enough fibres causing highly localized strains to occur in the matrix at low stress. This makes the bond between fibre and rubber to break leaving the matrix diluted by non-reinforcing debonded fibres. As the fibre concentration increases, the stress is more evenly distributed and the strength of composite increases. The incorporation of fibre into rubber matrix increases the hardness of the composite, which is related to strength and toughness. The close packing of fibres in the compounds increases the density while resilience decreases.

The reinforcement of coir fibre in natural rubber has been extensively studied [8]. Upon incorporation of coir fibre, it was seen that the tensile strength decreased sharply with increase in fibre loading up to 30 phr and then showed a slight increase for composites containing 40 and 60 phr fibre loading. This trend was observed in both longitudinal and transverse directions (Figure 3).



[Reference: Geethamma V.G. et al. J. Appl. Polym. Sci. 55 583 1995]

Figure 3. Variation in tensile strength with fiber loading.

The extent of coir fibre orientation from green strength measurements was also determined. It was observed that orientation was lowest when fibre loading was small and increased with loading. Maximum orientation was observed at 30 phr loading. The authors have gone on to report on the viscoelastic [9], water sorption [10], stress relaxation [11] and solvent sorption properties [12] of coir fiber reinforced rubber composites.

Researchers have also investigated the reinforcement effects of a leaf fibre - sisal fibre -in natural rubber [13]. They observed that the tensile strength decreased up to 17.5 % volume loading and then increased. The tear strength and modulus values showed a consistent increase with loading.

Attempts to incorporate oil palm fibre in rubber matrix have also been successful. The effect of fibre concentration on the mechanical properties of oil palm reinforced natural rubber composites was investigated by Ismail et al [14]. They observed the general trend of reduction in tensile and tear strength with increasing fibre concentration. The modulus and hardness of composites registered an increase with fibre loading. Another interesting study by the same group [15] reported on the fatigue and hysteresis behavior of oil palm wood flour filled natural rubber composites. It was observed that the composite with the highest loading was the most sensitive towards changes in strain energy and exhibited the highest hysteresis.

An interesting report on the reinforcement effect of grass fibre - bagasse - in natural rubber was presented by Nassar et al [16]. Aging experiments revealed tensile strength retention of 97 %. Scientists have also developed composites comprising of kenaf fibre and natural rubber [17]. An increase in rheometric and mechanical properties was observed. The kenaf fibre loaded composites also possessed good thermal stability and swelling resistance.

Pineapple [18] and jute fibre [19] have also found their way as a potential reinforcement in natural rubber. In a recent report, jute fabric was coated with natural rubber to develop double-texture rubberized waterproof fabric and fabric-reinforced rubber sheeting for hospitals. This product was found to be more superior than the existing market products [20].

Researchers have also designed novel rubber biocomposites by using a combination of leaf and fruit fibre in natural rubber [21,22]. The incorporation of sisal and coir fibre in NR was seen to increase the dielectric constant of the composites. These hybrid biocomposites were found to have enormous applications as antistatic agents. In another interesting study, the preparation of composites comprising of waste paper in natural rubber along with boron carbide and paraffin wax, for radiation shielding applications, was investigated [23].

Nashar et al [24]. investigated the effect of newsprint fibers with sodium silicate and magnesium chloride in natural rubber composite. It was observed that the addition of treated newsprint fiber waste at a concentration of 40 phr could lead to an end product characterized by good electrical and mechanical properties.

3.1 Biofibre - natural rubber adhesion

The compatibility of hydrophobic rubber matrix and hydrophilic cellulose fibre can be enhanced through the modification of polymer or fibre surface. The extent of adhesion is usually increased by the use of bonding agents and chemical

modification of fibres. The common bonding systems employed are: silica-phenol formaldehyde and resorcinol-hexamethylenetetramine-silica. Silica is believed to act as controller for resin formation and helps in developing adhesion between rubber and fibre. The importance of silica is still a matter of controversy.

Studies by Murty et al. [25] have indicated that silica is an essential component for enhancing the development of adhesion between fibre and rubber in the case of jute-NR composites. But studies by Varghese et al. [26] indicated that bonding between sisal and NR can be enhanced by use of resorcinol and hexamethylenetetramine in the ratio 5:3:2. It was found that adhesion imparted by this system was found to be better than that of normal HRH system.

Another interesting report [27] claimed that silica was not essential in producing good adhesion between coir fibre and NR. It was observed that the tensile strength of mixes that did not contain silica was significantly higher than that of the mixes containing silica. Thus, it is clear that nature of both rubber matrix and reinforcing fibre determines whether silica is needed or not as one of the components.

The adhesion of short oil palm fibre with natural rubber was investigated [28] using various bonding agents like phenol-formaldehyde; resorcinol-formaldehyde: silica; hexamethylenetetramine: resorcinol-formaldehyde: silica. It was observed that different bonding agents gave different cure characteristics and mechanical properties. Better mechanical properties were obtained for the bonding system RF: Sil : Hex (5:2:5) (See Table 3)

Table 3

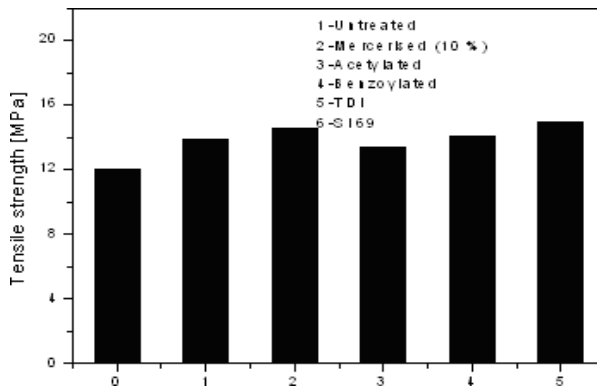
Cure characteristics	B (Gum)	H (U)	I (T)	J (U)	K (T)	L (U)	M (T)
Max. torque (Nm)	10	10.4	12.8	12.2	13.4	13.6	14.8
Min. torque (Nm)	0.4	0.6	0.7	0.6	0.7	0.8	0.9
Cure time t_{90} (min)	17.5	30.6	30.7	26.9	23.9	21.0	21.4
Scorch time t_2 (min)	6.1	5	4.4	10.1	9.3	5.5	5.3

Thomas and co-workers have also investigated the effect of chemical modification of banana fibre in natural rubber. It was found that modification of banana fibre resulted in superior mechanical properties [29]. The influence of alkali treatment on oil palm fiber reinforced natural rubber composites was investigated by the same group [30]. The authors observed superior mechanical properties after chemical modification due to better adhesion.

In an interesting study, researchers have used a novel fibre –isora fibre-in natural rubber [31]. Isora fibres are present in the bark of the *Helicteres isora* plant and are separated by retting process. Isora fibre resembles jute in appearance but surpasses it in strength, durability and lustre. The effects of different chemical treatments, including mercerisation, acetylation, benzoylation and treatment with toluene diisocyanate and silane coupling agents, on isora

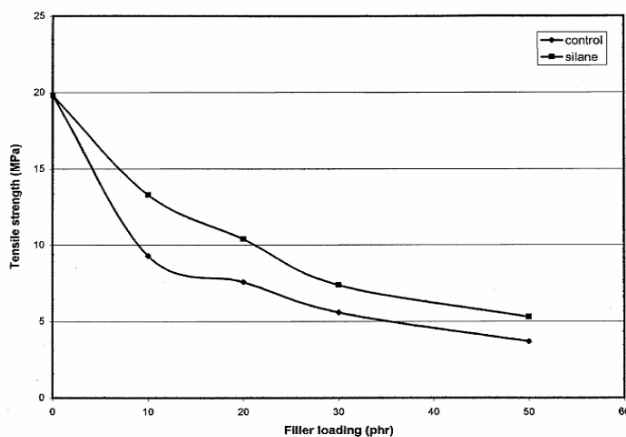
fibre properties and mechanical properties were analyzed. Isora fibre was seen to have immense potential as reinforcement in natural rubber. The variation of tensile strength with chemical modification is given in Figure 4.

The effect of fiber loading and bonding agents in bamboo fiber reinforced natural rubber composites was investigated by Ismail et al [32]. The authors observed that the presence of bonding agents gave shorter curing time and enhanced mechanical properties. The authors went on to study the effects of a silane coupling agent (Si 69) on curing characteristics and mechanical properties and observed that scorch time and cure time of the composites decreased with the presence of a silane coupling agent, Si69. The mechanical properties of composites were found to improve with the addition of Si69 [33] (Figure 5)



[Reference: Mathew et al., Prog. Rubb. Plast. Recycl. Tech., 20, 4, 337, 2004]

Figure 4. Variation of tensile strength with chemical modification

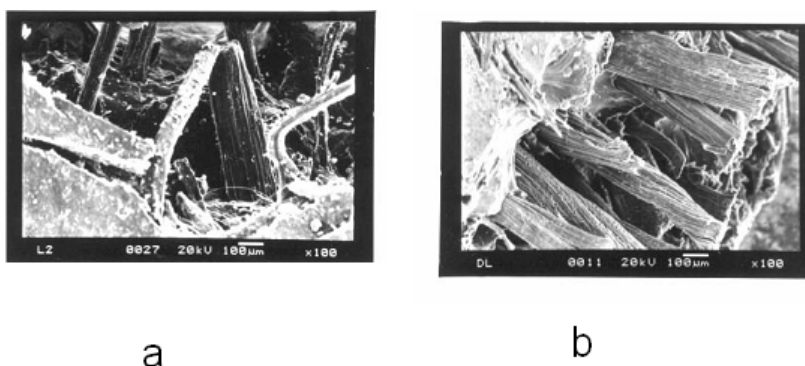


Reference : Ismail H et al. Eur. Pol. J. 38 39-47 2002

Figure 5. The effect of fiber loading on tensile strength of bamboo fiber reinforced natural rubber composites with and without a silane coupling agent.

The effect of plasma treatment on cellulose fibers in natural rubber composites was investigated by Gustav et al [34]. Chemiluminescence analysis was used to indicate the grafting on the surface of the cellulose fibres and also to estimate the effect of the plasma on the cellulose fibres. The results indicated the possibility of obtaining a surface layer on the fibres, which would lead to improving the mechanical properties of rubber composites

In an innovative study, a unique combination of sisal and oil palm fibres in natural rubber has been utilized to design hybrid biocomposites. It was seen that the incorporation of fibres resulted in increased modulus [35]. Chemical modification of both sisal and oil palm fibres was imperative for increased interfacial adhesion and resulted in enhanced properties [36]. Figures 6 a and b represents the untreated and alkali treated (4%) sisal-oil palm hybrid fiber reinforced natural rubber composites.



[Reference: Jacob M et al. Comp. Sci. & Technol. 64 955-965 2004]

Figure 6 a & b. SEM tensile fracture surface of untreated and 4 % NaOH treated sisal / oil palm reinforced natural rubber composites at 30 phr loading

The viscoelastic [37, 38], biodegradation [39], water sorption [40], dielectric [41] and stress relaxation [42] characteristics were also studied. Studies dealing with woven sisal fabric reinforced natural rubber composites [43] and its moisture uptake characteristics [44] were also reported.

The chemical modification of pineapple leaf fiber in natural rubber was investigated by Lopattananon et al [45]. Sodium hydroxide (NaOH) solutions (1, 3, 5, and 7% w/v) and benzoyl peroxide (BPO) (1, 3, and 5 wt % of fiber) were used to treat the surfaces of fiber. It was found that all surface modifications enhanced adhesion and tensile properties. The treatments with 5% NaOH and 1% BPO provided the best improvement of composite strength (28 and 57% respectively) when compared with that of untreated fiber composites. The SEM micrographs SEM photomicrographs of fracture surfaces of PALF-natural rubber composites containing (a) untreated, (b) 1%, (c) 3%, and (d) 5% (by weight of fiber) BPO-treated pineapple fibers illustrating the interface of the treated fiber composites are given in Figure 7. For all treated samples, the rubber matrices are more bonded

with the fibers when compared with untreated fiber, suggesting an enhanced adhesion over that of untreated fiber composites.

De et al [46] improved adhesion between grass fiber [*Cyperus Tegetum Rox b*] and natural rubber matrix by alkali treatment. The cure characteristics and mechanical properties of grass-fiber-filled natural rubber composites with different mesh sizes were studied with various fiber loadings. Increasing the amount of fibers resulted in the composites having reduced tensile strength but increased modulus. Figure 8 shows the variation of tensile strength with grass fibre loading. As the vulcanizates became more

and more stiff with increases in fiber loading and mesh size, tensile strength gradually decreased. The better mechanical properties of the 400-mesh grass-fiber-filled natural rubber composite showed that the rubber/fiber interface was improved by the addition of resorcinol formaldehyde latex (RFL) as bonding agent for this particular formulation.

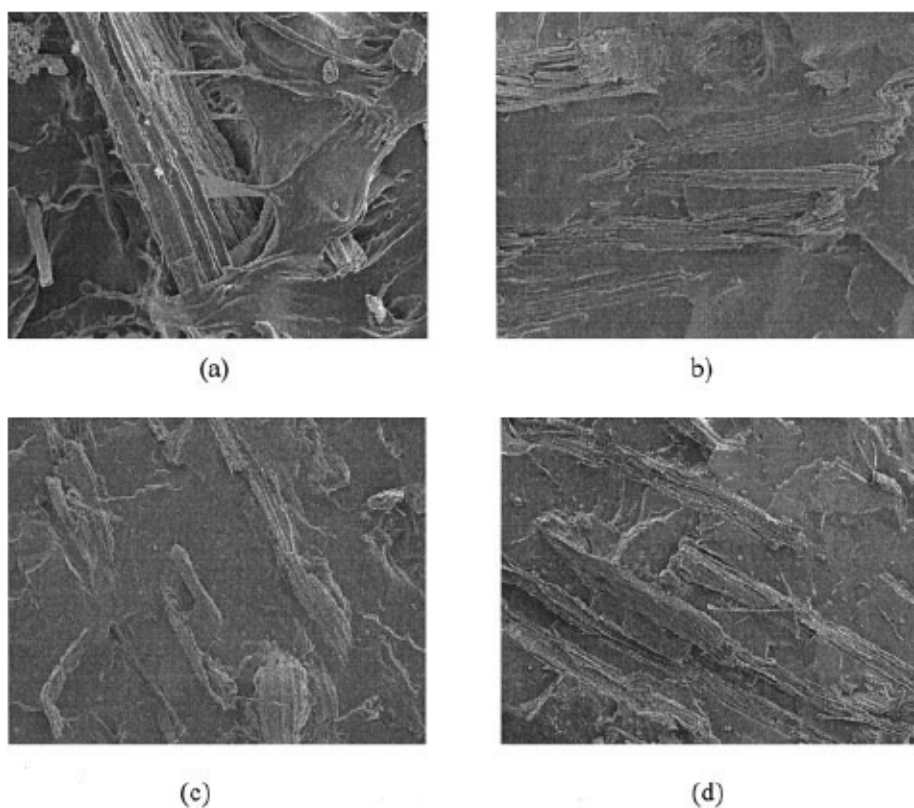


Figure 7. SEM photomicrographs of fracture surfaces of PALF-natural rubber composites containing (a) untreated, (b) 1%, (c) 3%, and (d) 5% (by weight of fiber) BPO-treated pineapple fibers illustrating the interface of the treated fiber composites

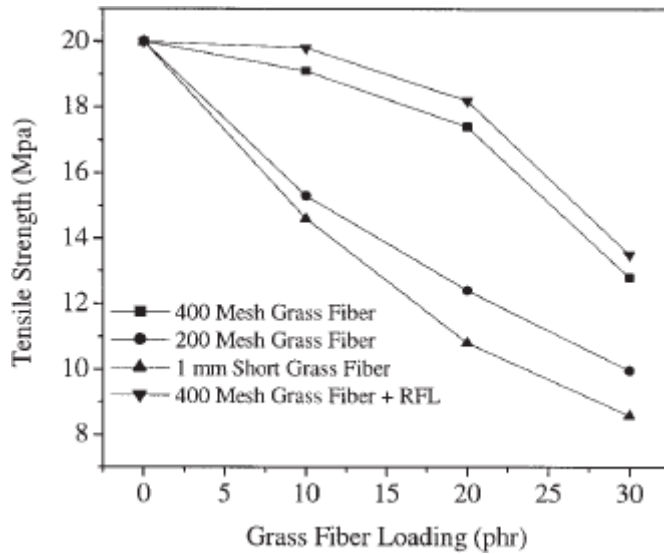
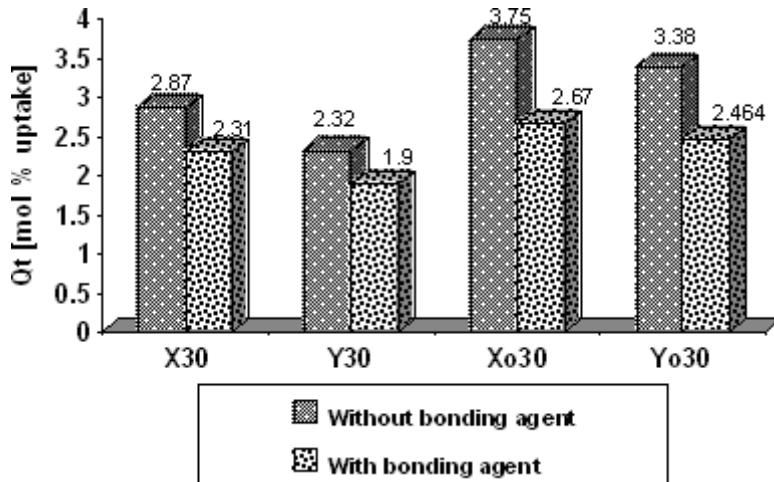


Figure 8. Variation of tensile strength with grass fibre loading

Equilibrium swelling technique was used by Mathew et al. [47] to study the interfacial adhesion in isora fibre reinforced natural rubber composites. The authors observed that the presence of bonding agent increased the interfacial adhesion between the fibre and matrix. The composites containing bonding agents were less prone to solvent sorption (Figure 9).



[Reference: Mathew L. et al. In Proceedings from ICBC 2005, March 21-23, 61, 2005]

Figure 9. Variation of Q_t with chemical modification

As an extension of their study [48], the solvent swelling characteristics of natural rubber composites containing both untreated and alkali treated isora fibres were investigated in aromatic and aliphatic solvents like toluene, and n-hexane. The diffusion experiments were conducted by the sorption gravimetric method. The restrictions on elastomer swelling exerted by isora fibre as well as the anisotropy of swelling of the composite were confirmed by this study. Composite cured at 100°C shows the lowest percentage swelling. The uptake of aromatic solvent is higher than that of aliphatic solvent for the composites cured at all temperatures. The effect of fibre loading on the swelling behaviour of the composite was also investigated in oils like petrol, diesel, lubricating oil etc. The % swelling index and swelling coefficient of the composite were found to decrease with increase in fibre loading. This is due to the increased hindrance exerted by the fibres at higher fibre loadings and also due to the good fibre-rubber interactions. Maximum uptake of solvent was observed with petrol followed by diesel and then lubricating oil. The presence of bonding agent in the composites restricted the swelling considerably due to the strong interfacial adhesion. At a fixed fibre loading, the alkali treated fibre composites showed lower percentage swelling compared to the untreated one.

Another interesting study, using the swelling technique to estimate interfacial adhesion was reported in the case of sisal / coir fibre reinforced natural rubber composites [49]. The bonding agent added mixes showed enhanced restriction to swelling and it was seen that the ratio of change in volume fraction of rubber before and after swelling to the volume fraction of rubber before swelling ($V_o - V_r/V_o$) was lower for bonding agent added composites, when compared to an unbonded one.

4. SYNTHETIC RUBBER COMPOSITES

Styrene butadiene rubbers (SBR) are the most commonly used synthetic rubbers today. They are produced by copolymerization of butadiene and styrene. Prasanthakumar et al. [50] showed the effect of fiber surface modifications, NaOH treatment, acetylation, and benzylation on the interfacial adhesion of sisal fiber and SBR matrix. The authors also analyzed the dynamic mechanical behavior of sisal fiber-reinforced styrene butadiene rubber. They found that the storage modulus of the composites increases with increasing fiber volume fraction, fiber surface modifications, and bonding agent. The stress relaxation behavior of short jute fiber-reinforced nitrile rubber composites was studied in detail by Bhagawan et al [51]. Flink and Stenberg [52] studied the stress relaxation behavior of short cellulose fiber-reinforced natural rubber composites. They reported that the stress relaxation measurements give an idea about the level of adhesion in fibre-rubber composites. An account of lignocellulosic fibre reinforced synthetic rubber composites has been documented by Joseph et al [53]. The influence of cellulose as filler in vulcanised rubber composites was investigated by Nunes and Mano [54]. Cellulose filler was used in the range of 0 to 30 phr. The best results were shown by the natural rubber-regenerated cellulose systems. The different behavior of the systems was explained by experimental evidence. The reinforcement mechanism for NR compositions, which involved an induced crystallizing rubber (NR), seemed to be different from the mechanism for SBR and NBR

The influence of sisal fibre in waster tire composites was investigated by Martins and Mattosso [55]. Treatment of fibers was found to improve composite performance.

5. APPLICATIONS

In automotive and truck tires they find application in better abrasion resistance for the chafer strip and in improved cut resistance to treads, especially for trucks and OTR vehicles.⁵² As short fibers have higher green strength and cut, tear, and puncture resistance, they can be used for sheeting. The fibers

also provide higher green strength and cut, tear, and puncture resistance. Some applications for such reinforced sheeting are in roofing membranes. Short fibers can be utilized as the sole reinforcement for a moderate-performance hose or as an auxiliary reinforcement with cord constructions. They can provide stiffening to soft inner tubes for the application of metal braids and can extend hose life by bridging the stresses across weakened filaments. Other uses are as belts, diaphragms, and gaskets. Some other applications are roofing, hose, dock and ship fenders, and general uses such as belts, tires, and other industrial articles.

REFERENCES

- [1] <http://www.rubber-stichting.info/index.html>
- [2] A.S. Hashim, S.K. Ong, R.S. Jesyy (2002) <http://www.rubber-stichting.info/index>
- [3] D. Wititsuwaannakul, A. Rattanapittayaporn, T. Koyama , R. Wititsuwaannakul. (2004) Involvement of Hevea Latex Organelle Membrane Proteins in the Rubber Biosynthesis Activity and Regulatory Function *Macromol. Biosci.*, 4, 314–323
- [4] Rubber Compounding, Principles, Materials and Techniques. (1993) F. W. Barlow. 2nd edition
- [5] K. Jayaraman. (2003) Manufacturing sisal–polypropylene composites with minimum fibre degradation. *Comp. Sci. Tech.*, 63, 367-374
- [6] K.G. Satyanarayana, K.K. Ravikumar , K. Sukumaran , P.S. Mukherjee , S.G.K. Pillai , & A.K. Kulkarni (1986), Structure and properties of some vegetable fibres, *J. Mater. Sci.*, 2, 57-63
- [7] Dzyura E.A., *Int. J. Polym. Mater.*, 8 165 1980
- [8] V.G. Geethamma, R. Joseph, S. Thomas. (1995) Short coir fiber-reinforced natural rubber composites: Effects of fiber length, orientation, and alkali treatment *J. Appl. Polym. Sci.*, 55, 583-594
- [9] V.G., Geethamma, G. Kalaprasad , G. Groeninckx , S. Thomas. (2005) Dynamic mechanical behavior of short coir fiber reinforced natural rubber composites, *Composites Part A*, 36, 11, 1499-1506
- [10] V.G. Geethamma, S. Thomas.(2005) Diffusion of water and artificial seawater through coir fiber reinforced natural rubber composites, *Polymer Composites*, 26, 2 136-143
- [11] V.G. Geethamma., L.A.Pothen , B.Rao , N.R. Neelakantan , S. Thomas., (2004) Tensile stress relaxation of short-coir-fiber-reinforced natural rubber composites *Journal of Applied Polymer Science*, 94, 96-104

- [12] V.G. Geethamma , S. Thomas , (2004).Transport of organic solvents through coir-fiber-reinforced natural rubber composites: a method for evaluating interfacial interaction, *Journal of Adhesion Science and Technology*, 18, 951-966
- [13] S. Varghese , B. Kuriakose , S. Thomas , A.T. Koshy , (1994).Mechanical and viscoelastic properties of short fiber reinforced natural rubber composites: effects of interfacial adhesion, fiber loading, and orientation ,*J. Adhesion Sci. Technol.*, 8, 235-248
- [14] H. Ismail , N. Rosnah , U.S. Ishiaku , (1997). Oil Palm Fibre-reinforced Rubber Composite: Effects of Concentration and Modification of Fibre Surface, *Polym. Inter.*, 43, 223-230
- [15] H. Ismail , R.M. Jaffri , H.D. Rozman, (2000). Oil palm wood flour filled natural rubber composites: fatigue and hysteresis behaviour, *Polym. Inter.* 49, 618-622
- [16] M.M. Nassar , E.A. Ashour , S.S. Washid , (1996). Thermal characteristics of bagasse, *J. Appl. Polym. Sci.*, 61, 885-890
- [17] El Sabbagh S.H., El Hariri D.M., Abd. El Ghaffar M.A., Proceedings from the 3rd International Symposium on Natural Polymers & Composites. ISNa Pol / May 14-17th, pp. 469 2000
- [18] T.B. Bhattacharya, A.K. Biswas, J. Chatterjee, D. Pramnck (1986). Short pineapple leaf fibre reinforced rubber composites, *Plast. Rubber Process Appl.*, 6, 119-125
- [19] N. Arumugam , K. Tamareselvy , K. Venkata Rao , P. Rajalingam (1989). Coconut-fiber-reinforced rubber composites, *J. Appl. Polym. Sci.* 37 2645-2659
- [20] D. Das , M Datta , R.B Chavan , S.K Datta , (2005). Coating of jute with natural rubber *Journal of Applied Polymer Science*, 98 , 5 484-489
- [21] P. Haseena , G. Unnikrishnan , Proceedings from International Conference on Advances in Polymer Blends and Composites (ICBC 2005) March 21-23 ,51, 2005
- [22] P. Haseena, G. Unnikrishnan, (2005) Mechanical properties of sisal/coir hybrid fibre reinforced natural rubber, *Progress in Rubber, Plastics and Recycling Technology*, 21,155-181
- [23] M. Madani, A.H. Basta, A. E-S. Abdo, H. El-Saied, (2004).Utilization of waste paper in the manufacture of natural rubber composite for radiation shielding, *Prog. Rubb., Plast. Recyc.Tech.*, 20, 287-310
- [24] Nashar, D.E.El. ,Abd-El-Messieh, S.L.,Basta, A.H., (2004) Newsprint paper waste as a fiber reinforcement in rubber composites, *Journal of Applied Polymer Science*, 91, 3410-3420
- [25] V.M. Murty , S.K. De , (1982) Effect of particulate fillers on short jute fiber-reinforced natural rubber composites, *J. Appl. Polym. Sci.*, 27, 4611
- [26] S. Varghese, B. Kuriakose , S. Thomas , A.T. Koshy (1991).Studies on natural rubber-short sisal fiber composites, *Indian J. Nat. Rubb. Res.*, 4, 55
- [27] V.G. Geethamma, K. Thomas Mathew , R. Lakshminarayanan , S.Thomas (1998). Composite of short coir fibres and natural rubber: effect of chemical modification, loading and orientation of fibre, *Polymer*, 39, 1483-149
- [28] H. Ismail , N. Rosnah , H.D. Rozman (1997). Curing characteristics and mechanical properties of short oil palm fibre reinforced rubber composites, *Polymer*, 38, 4059-4064

- [29] A. Jacob, M. Jacob , S. Thomas (Influence of chemical modification on mechanical and swelling characteristics of banana fiber reinforced natural rubber composites J. Appl. Polym. Sci. (Communicated)
- [30] S. Joseph , K. Joseph , S. Thomas (2006). Green composites from natural rubber and oil palm fiber: Physical and mechanical properties, *Int. J. Pol. Mat.*, *55*, 925 - 945
- [31] Mathew L; Joseph K U; Joseph R., (2004) Isora fibres and their composites with natural rubber, *Progress in Rubber, Plastics and Recycling Technology* *20*, *4*, 337-349
- [32] H. Ismail, M.R. Edyham , B. Wirjosentono (2002). Bamboo fibre filled natural rubber composites: the effects of filler loading and bonding agent, *Polymer Testing*, *21*, 139-144
- [33] H. Ismail , S. Shuhelmy , M.R. Edyham , (2002). The effects of a silane coupling agent on curing characteristics and mechanical properties of bamboo fibre filled natural rubber composites, *Eur. Pol. J.*, *38*, 39-47
- [34] G. Ahlblad , A. Kron , B. Stenberg (1994). Effects of plasma treatment on mechanical properties of rubber/cellulose fibre composites, *Polymer International*, *33*, 103-109
- [35] M. Jacob , K.T. Varughese , S. Thomas (2004). Natural rubber composites reinforced with sisal / oil palm hybrid fiber: Tensile and Cure characteristics, *J. of Applied Polymer Science*, *93*, 2305-2312
- [36] M. Jacob, K.T. Varughese, S. Thomas (2004).Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites, *Composites Science & Technology*, *64*, 955-965
- [37] M. Jacob, B. Francis , K.T. Varughese , S. Thomas (2006). Dynamical mechanical analysis of sisal/oil palm hybrid fiber-reinforced natural rubber composites, *Polymer Composites*, *27*, 671-680
- [38] M. Jacob , B. Francis , K.T. Varughese , S. Thomas (2006). The effect of silane coupling agents on the viscoelastic properties of biofibre reinforced natural rubber composites, *Macromolecular Materials and Engineering*, *291*, 1119-1126
- [39] Maya Jacob, K.T. Varughese and Sabu Thomas "Durability and ageing characteristics of hybrid bio-fiber reinforced natural rubber biocomposites." *Journal of Biobased Materials and Bioenergy* *1*, 118-126, 2007
- M. Jacob, K.T. Varughese ,S. Thomas, (in press), Durability and ageing characteristics of hybrid bio-fiber reinforced natural rubber biocomposites, *International Journal of Biomaterials and Bioenergy*
- [40] M. Jacob , K.T. Varughese , S. Thomas (2005). Water sorption studies of hybrid biofiber-reinforced natural rubber biocomposites, *Biomacromolecules*, *6*, 2969-2979
- [41] M. Jacob, K.T. Varughese , S. Thomas (2006). Dielectric characteristics of sisal-oil palm hybrid biofibre reinforced natural rubber biocomposites *J. Mat. Sci.*, *41*, 5538-5547
- [42] M. Jacob , K.T. Varughese , S. Thomas (2006) Stress relaxation and thermal analysis of hybrid biofiber reinforced rubber biocomposites. *Journal of Reinforced Plastics and Composites*, *25*, 1903-1917
- [43] M. Jacob, K.T. Varughese , S. Thomas (2006). Novel woven sisal fabric reinforced natural rubber composites: Tensile and swelling characteristics, *J. Comp. Mat.*, *40*, 1471 – 1485

- [44] M. Jacob , K.T. Varughese , S. Thomas (2006). A study on the moisture sorption characteristics in woven sisal fabric reinforced natural rubber biocomposites, *J. Appl. Polym. Sci.*, 102, 416-423
- [45] N. Lopattananon , K. Panawarangkul , K. Sahakaro , B. Ellis , (2006) Performance of pineapple leaf fiber-natural rubber composites: The effect of fiber surface treatments, *J. of Appl. Polym. Sci.*, 102, 1074-1084
- [46] D. De, D. De, B. Adhikari , (2006). Curing characteristics and mechanical properties of alkali-treated grass-fiber-filled natural rubber composites and effects of bonding agent, *J. Appl. Polym. Sci.*, 101, 3151-3160
- [47] L.Mathew, K.U. Joseph, R. Joseph, Proceedings from International Conference on Advances in Polymer Blends and Composites (ICBC 2005) March 21-23 ,61, 2005
- [48] L. Mathew, K.U. Joseph, R. Joseph (2006).Swelling behaviour of isora/natural rubber composites in oils used in automobiles *Bulletin of Materials Science*, 29, 91-99
- [49] A.P. Haseena , K.P. Dasan , R. Namitha , G.Unnikrishnan, S. Thomas, (2004).Investigation on interfacial adhesion of short sisal/coir hybrid fibre reinforced natural rubber composites by restricted equilibrium swelling technique, *Comp. Interf.*, 11, 489
- [50] R.Prasanthakumar, Ph.D. thesis, Mahatma Gandhi University, Kottayam, Kerala, India, 1992.
- [51] S.S. Bhagawan, D.K. Tripathy, and S.K. De, (1987). Stress relaxation in short jute fiber-reinforced nitrile rubber composites, *J. Appl. Polym. Sci.*, 33, 1623
- [52] P. Flink and B. Stenberg (1990), An indirect method which ranks the adhesion in natural rubber filled with different types of cellulose fibres by plots of $E(t)/E[t=0]$ versus $\log t$, *Br. Polym. J.*, 22, 193
- [53] S. Joseph, M. Jacob and S. Thomas (2004) , "Natural Fibers, Biopolymers and their Biocomposites" Chapter title: "Natural Fiber/Rubber Composites And Their Applications" Edited by A.K. Mohanty, Manjusri Misra, Lawrence T. Drzal , CRC Press.
- [54] R. C. R. Nunes, E. B. Mano (1995) Influence of cellulose as a filler in vulcanized rubber composites, *Polymer Composites*,16, 421
- [55] M. A. Martins, L. H. C. Mattoso (2004) Short Sisal Fiber-Reinforced Tire Rubber Composites: Dynamic and Mechanical Properties, *J. Appl. Polym. Sci.*, 91, 670