Mechanical Properties of Short-Isora-Fiber-Reinforced Natural Rubber Composites: Effects of Fiber Length, Orientation, and Loading; Alkali Treatment; and Bonding Agent

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ABSTRACT: A series of short-isora-fiber-reinforced natural rubber composites were prepared by the incorporation of fibers of different lengths (6, 10, and 14 mm) at 15 phr loading and at different concentrations (10, 20, 30, and 40 phr) with a 10 mm fiber length. Mixes were also prepared with 10 mm long fibers treated with a 5% NaOH solution. The vulcanization parameters, processability, and stress–strain properties of these composites were analyzed. Properties such as tensile strength, tear strength, and tensile modulus were found to be at maximum for composites containing longitudinally oriented fibers 10 mm in length. Mixes containing fiber loadings of 30 phr with bonding agent (resorcinol-formaldehyde [RF] resin) showed mechanical properties superior to all other composites. Scanning electron microscopy (SEM) studies were carried out to investigate the fiber surface morphology, fiber pullout, and fiber–rubber interface. SEM studies showed that the bonding between the fiber and rubber was improved with treated fibers and with the use of bonding agent. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1640–1650, 2007

Key words: compounding; composites; fibers; reinforcement; rubber

INTRODUCTION

Short-fiber-reinforced rubber composites are a rapidly growing class of materials because of their improved physical and mechanical properties, easy processability, and economic advantages. These materials bridge the gap between elastomers and fibers by combining the strength and stiffness of short fibers with the elasticity of rubber.[1] Complexly shaped engineering components may be developed with short-fiber-reinforced elastomers. The most important parameters that affect the short-fiber-reinforcement are fiber aspect ratio, fiber dispersion and orientation, fiber loading, fiber length, and adhesion between the fiber and the matrix.[2] A considerable amount of research work has been done in the field of short-fiber-reinforced elastomer composites. Many researchers have studied the effect of different fibers in natural and synthetic rubbers.[3–9] Recently, we reported the possibilities of isora fiber as a potential reinforcement in rubber and polyesters.[10,11] A detailed investigation on the characterization and properties of isora fiber

was done.[12] Isora fiber imparts mechanical properties comparable to those of other natural fibers. Isora shrub, which grows as undergrowth in forests, is seen in many parts of South India. The fiber is present in the bark of the Helicteres Isora plant and is separated by a retting process. Isora is a very strong fiber that resembles jute in appearance but has better strength, durability, and luster.[13] Ropes and cordages made of isora fiber are better and smoother than coir products.[14] The use of a biodegradable matrix and natural fibers as reinforcement has opened new potential applications to these composites as they are ecofriendly materials. Nowadays, natural fibers are getting more attention from researchers. Natural cellulosic fibers, when used as reinforcement, impart mechanical properties comparable to those of synthetic fibers such as glass. Composites fabricated with these natural fibers have the potential to be an attractive alternative to synthetic fiber composites and are currently being explored in sectors such as the automobile and building industries. In addition, these fibers offer an excellent opportunity for use and are an abundant source of such materials. Natural fibers have advantages over synthetic fibers because of their renewable nature, low cost, easy availability, biodegradability, and ease of chemical modification. These fibers, however,

exhibit a large variation in quality and are sensitive to moisture. The main problems that are usually encountered when natural fibers are used as reinforcement are that the incorporation of a hydrophilic fiber into a hydrophobic polymer leads to a heterogeneous system, with the result that they exhibit properties inferior to those of the unfilled system because of poor adhesion at the fiber–matrix interface. The surface characteristics of the reinforcing fibers are, therefore, important in the transfer of stresses from the matrix to the fiber.

In the past, many attempts have been made to modify the surface properties of natural fibers to enhance adhesion with polymers. Various methods, such as corona treatment, plasma treatment, mercerization, heat treatment, graft copolymerization, and silane treatment,[15–21] have been reported to enhance the compatibility in natural fiber composites. This article reports the cure characteristics and mechanical properties of short-isora-fiber-reinforced natural rubber (NR) composites, with special reference given to the effect of fiber length, fiber orientation, fiber treatment, fiber loading, and the use of a bonding agent.

EXPERIMENTAL

Materials

Isora fiber, lingocellulosic in nature, was isolated from the bark of the Helicteres Isora plant by a retting process. It was reported to contain 74.8% cellulose, 23% lignin, 1.1% fat and wax, 0.9% ash, and 0.3% nitrogen.[22] The physical properties of isora fiber are given in Table I. The NR used in the study was Indian Standard Natural Rubber grade 5 obtained from RRII (Kottayam, Kerala, India). The bonding agents, RF resin (ρ [density] = 2.3), was supplied by (M/S West Coast Polymers Pvt., Ltd. (Kannur, Kerala, India), and precipitated silica (ρ = 2.03) with an average size of 40 nm supplied by Minar Chemicals (Alwaye, Kerala, India) and was commercial grade. Hexamethylene tetramine (ρ = 1.33) was supplied by E. Merck (A. G., Germany) was chemically pure grade. All other ingredients were commercial grade.

TABLE I
Properties of Isora Fiber

Physical property		Chemical constituent	%
Diameter (μ)	10.1	Cellulose	74.8
Density (gm/cm^3)	1.35	Lignin	23.0
Tensile strength (MPa)	500–600	Fat	1.09
Elongation at break (%)	5–6	Ash	0.954
Microfibrillar angle (°)	20–26	Nitrogen	0.26
Length/diameter ratio	99		
Young's modulus (GPa)	18–20		

TABLE II
Mixes with Various Fiber Lengths

Ingredient[a]	Gum	L_1	L_2	L_3
NR	100	100	100	100
Zinc oxide	5.0	5.0	5.0	5.0
Stearic acid	2.0	2.0	2.0	2.0
TDQ[b]	1.0	1.0	1.0	1.0
CBS[c]	0.6	0.6	0.6	0.6
TMTD[d]	0.1	0.1	0.1	0.1
S	2.5	2.5	2.5	2.5
Untreated isora fiber	0	15	15	15
Fiber length (mm)	0	6	10	14

[a] Ingredient, parts per hundred rubber (phr).
[b] TDQ, 2,2,4 trimethyl 1,2 dihydro quinoline polymerized.
[c] CBS, N-cyclohexyl benz thiazyl sulphenamide.
[d] TMTD, Tetramethyl thiuram disulphide.

Fiber preparation and alkali treatment

Theh fiber, separated from the bark of Helicteres Isora plant by a retting process, was chopped almost accurately to different lengths of 6, 10, and 14 mm with a fiber chopper, on which the length of fiber cuttings could be adjusted, and was washed with water to remove undesirable impurities and dried. Treated fiber was prepared from raw fiber by immersion in 5% aqueous NaOH for 4 h. Washing with water was done several times followed by drying in an air oven at 70°C for 14 h.

Composite preparation

The composites were prepared by the incorporation of short isora fibers of different lengths (6, 10, and 14 mm; 15 phr) and different loadings (10, 20, 30, and 40 phr; 10 mm fiber length) for both treated and untreated fibers into the NR matrix as per the formulation given in Tables II and III. Mixes were prepared in a laboratory (150 × 300 mm) two-roll mixing mill as per ASTM standard D 3184-80 at a nip gap of 1.3 mm. The samples were milled for a time sufficient to disperse the fibers in the matrix. The final sheeting was done by the passing of the compound through a tight nip gap of 0.8 mm. The bonding agents (resorcinol, hexa, and silica) were incorporated along with the other ingredients. The fiber was incorporated at the end of mixing process, with care taken to maintain the direction of compound flow so that majority of fibers followed the direction of flow. To study the extent of fiber breakage, which occurred during the milling operations, the fibers were extracted from the green compound by dissolution in toluene, and their length and diameter were measured with a traveling microscope. The cure characteristics were studied by an oscillating disk rheometer (Goettfert elastograph, Goettfert, Germany). The samples were vulcanized at 150°C in a hydraulic press up to their respective optimum cure times (t_{90}'s) as measured on a Goettfert elastograph.

TABLE III
Mixes[a] with Various Fiber Loadings and Bonding Agents

Mix	Gum	X_{10}	X_{20}	X_{30}	X_{40}	Y_{10}	Y_{20}	Y_{30}	Y_{40}
Untreated fiber	0	10	20	30	40	—	—	—	—
Treated fiber	0	—	—	—	—	10	20	30	40

Mix	—	X_{10b}	X_{20b}	X_{30b}	X_{40b}	Y_{10b}	Y_{20b}	Y_{30b}	Y_{40b}
Resorcinol	0	2.5	5.0	7.5	10	2.5	5.0	7.5	10
Hexa	0	1.6	3.2	4.8	6.4	1.6	3.2	4.8	6.4
Silica	0	1	2	3	4	1	2	3	4
Untreated fiber	0	10	20	30	40	—	—	—	—
Treated fiber	0	—	—	—	—	10	20	30	40

[a] Basic recipe: NR = 100 phr, ZnO = 5 phr, stearic acid = 2 phr, TDQ = 1 phr, CBS = 0.6 phr, TMTD = 0.1 phr, and S = 2.5 phr.

Characterization of treated fibers and testing of the composites

The scanning electron microscopy (SEM) photographs of the fibers and the fractured surfaces were taken with a Jeol JSM 35 C model scanning electron microscope (Philips, The Netherlands). The fiber and the fracture surfaces were sputter-coated with gold within 24 h of testing with a fine coat JFC-1100 instrument. Dumbbell- and crescent-shaped tensile and tear specimens with longitudinal and transverse fiber orientations were punched from the vulcanized sheets. Stress–strain measurements were carried out at a crosshead speed of 500 mm/min on a Shimadzu model AG1 universal testing machine (Schimadzu, Japan). Tensile and tear strengths were measured according to ASTM D 412-68 and D 624-54, respectively. The compression set of the specimens was measured in accordance with ASTM D 395-86 (method B). The abrasion resistance of the samples was tested with DIN 53516. The hardness was measured with a Shore A type durometer (Zwick, Germany) according to ASTM 2240-81.

RESULTS AND DISCUSSION

Evaluation of fiber breakage

Mixes L_1, L_2, and L_3 were the NR mixes containing fibers 6, 10, and 14 mm in length, respectively (Table II). Control of the fiber length and aspect ratio of the fibers in the rubber matrix was difficult because of fiber breakage during processing. The severity of fiber breakage depended mainly on the type of fiber, the initial aspect ratio, and the magnitude of stress and strain experienced by the fibers during processing.[23] Shear force during mixing oriented most of the fibers along the mill-grain direction. It may have also caused breakage of fibers. The average diameter (10 µ) of the fiber remained unchanged after mixing. The results of the fiber breakage analysis are given in Table IV. The data show that compound L_2 contained a total of 52.3% of the

fiber in the range 2–6 mm in length and 63.3% of fiber in the range 4–8 mm in length after mixing, and the aspect ratio remained higher than 200, which is generally required for effective stress transfer in short-fiber elastomer composites.[24] From Table V, it is clear that the reinforcement was high for compound L_2, which contained fibers with an original length of 10 mm before mixing, as evident from the high tensile strength, modulus, and tear strength compared to L_1. The tensile strength and modulus of compound L_3 were comparable to those of L_2, even though it contained almost the same level of fibers (48.9%) having lengths in the range 2–6 mm as that of compound L_1 (48.3%). This was likely because of the presence of 39.7% of fibers that had final lengths in the range 6–10 mm in L_3, which was almost comparable to that present in L_2 (38.7%). These observations indicated that an original fiber length of 10 mm was the critical fiber length, which was essential for getting better reinforcement in short-isora-fiber NR composites.

Cure characteristics

Tables VI and VII show the variation in the cure characteristics of composites with various fiber lengths and loadings, respectively. The maximum torque is a measure of crosslink density and stiffness in the rub-

TABLE IV
Distribution of Fiber Lengths After Mixing

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

Mixes L_1, L_2, and L_3 contained fibers 6, 10, and 14 mm in length before mixing.

TABLE V
Mechanical Properties of Vulcanizates with Various Fiber Lengths

Property	Orientation	Gum	L_1	L_2	L_3
Tensile modulus (300% E; MPa)	L	2.3 (0.28)	2.71 (1.18)	2.95 (0.55)	2.80 (1.05)
	T	2.3 (0.22)	2.30 (0.95)	2.40 (0.73)	2.30 (0.91)
Tensile strength (MPa)	L	25.9 (0.48)	14.0 (1.02)	16.2 (0.87)	15.9 (0.90)
	T	25.0 (0.39)	12.1 (0.98)	13.8 (0.97)	14.0 (0.95)
Elongation break (%)	L	1050 (0.29)	700 (1.15)	625 (0.45)	695 (0.77)
	T	1045 (0.31)	725 (1.06)	650 (0.88)	715 (1.11)
Tear strength (kN/m)	L	35.1 (0.42)	37.5 (0.92)	42.0 (0.65)	42.5 (0.61)

L = longitudinal; T = transverse. Mixes L_1, L_2, and L_3 contained fibers 6, 10, and 14 mm in length before mixing. The numbers given in the parentheses are the standard deviations.

ber. In general, for all of the mixes, the torque initially decreased, then increased, and finally leveled off. The initial decrease in torque to a minimum value was due to the softening of the rubber matrix, whereas the increase in torque was due to the crosslinking of rubber. The leveling off was an indication of the completion of curing. The addition of fibers into the mix generally increased the torque values. Also, the torque increased with increasing fiber length and reached a maximum at a fiber length of 10 mm. This increase was due to the presence of longer fibers, which imparted more restriction to deformation. However, the maximum torque was slightly higher for 10 mm than 14 mm. This may have been because longer fibers underwent fiber entanglement and breakage during mixing. The maximum torque also increased with increasing fiber loading. This was because of the increase in the stiffness and hardness of the composite.[25] These torque values were also increased by alkali treatment, as the treated fiber may have provided a better surface for reinforcement. t_{90} was not very much affected by the modification of fiber surface. The optimum t_{90} increased with the addition of bonding agent. According to Chakraborty and Setu,[25] the longer t_{90} was due to the better bonding between the fiber and the matrix when the bonding agent was used. Maximum and minimum torque values also increased in the presence of bonding agent. This was due to the strong bonding at the fiber–rubber interface, and consequently, the composite become stronger harder and stiffer.

Extent of fiber orientation from green strength (S) measurements

S of short-fiber-reinforced composites depends on the degree of fiber orientation. The extent of fiber orientation can be calculated with the following equation:

$$\text{Orientation (\%)} = (S_L/S_{G,L})/(S_L/S_{G,L} + S_T/S_{G,T})$$

where S is the green strength and the subscripts G, L, and T denote gum, longitudinal, and transverse,

respectively. The effect of fiber loading on the percentage orientation is shown in Figure 1. At low fiber loadings, the percentage orientation was the lowest, as the fibers could randomly move around, which led to increased chaocity and decreased levels of orientation. As fiber loading increased, percentage orientation increased, with the maximum value for composite containing 30 phr fiber. At 40 phr fiber loading, the percentage orientation decreased, which indicated that the fibers could not orient themselves because of the entanglement caused by the increased content of fibers.

Mechanical properties

Effect of fiber length

The effect of fiber length and orientation on the properties of the composites is given in Table V. The properties increased with increasing fiber length. The increase in the strength with increasing fiber length was attributed to the fact that the extent of load transmittance is a function of fiber length and the magnitude of fiber matrix interfacial bond.[26] In fiber-reinforced composites, there exists a critical fiber length at which the load transmittance from the matrix to the fiber is at maximum. The critical fiber length is that length that is required by the fiber to develop its fully stressed condition in the matrix. Longer fibers impart more restriction to deformation, whereas shorter fibers create friction and heat generation due to the increased number of fiber ends. The tensile and tear strengths showed a maximum value

TABLE VI
Vulcanization Parameters for Mixes with Various Fiber Lengths

	Mix			
	Gum	L_1	L_2	L_3
Minimum torque (Nm)	0.01	0.03	0.02	0.02
Maximum torque (Nm)	0.21	0.24	0.30	0.28
Scorch time (min)	2.36	1.8	1.76	1.76
t_{90} (min)	4.32	4.62	5.42	5.46

TABLE VII
Vulcanization Parameters for Mixes with Various Fiber Loadings and Bonding Agents

Mix	Gum	X_{10}	X_{20}	X_{30}	X_{40}	Y_{10}	Y_{20}	Y_{30}	Y_{40}
t_{90} (min)	4.32	5.4	5.5	5.7	5.85	4.61	4.91	5.22	5.64
Maximum torque (Nm)	0.22	0.29	0.32	0.35	0.40	0.32	0.34	0.40	0.51
Mix		X_{10b}	X_{20b}	X_{30b}	X_{40b}	Y_{10b}	Y_{20b}	Y_{30b}	Y_{40b}
t_{90} (min)	4.32	7.24	7.76	8.12	8.36	6.9	7.0	7.32	7.68
Maximum torque (Nm)	0.22	0.33	0.35	0.52	0.64	0.35	0.47	0.58	0.69

for the composites with fibers having an original length of 10 mm before mixing. The interaction between the fiber and the matrix reached its maximum at this fiber length, and the effect of fiber length decreased with longer fibers because of fiber entanglement and breakage. At higher fiber lengths, the dispersion of fibers in the rubber matrix was difficult. Hence, a further increase in fiber length beyond 10 mm decreased the mechanical properties such as tensile strength and tear strength. These observations indicated that an original fiber length of 10 mm was the critical fiber length that was essential for the production of better reinforcement in short-isora-fiber NR composites.

Effect of fiber orientation

Fiber orientation affected the composites properties. During the milling of rubber composites, the majority of the fibers tend to orient along the flow direction, which causes the mechanical properties to vary in different directions.[27] In the case of short-fiber-reinforced composites, longitudinal and transverse orientations are possible. In the longitudinal orientation, the fibers are aligned along the mill-grain direction, and in the transverse one, the fibers are aligned across the grain direction. Properties such as the tensile modulus, tensile strength, and tear strength of the composites with longitudinal orientation were always higher than the composites with transverse fiber orientation (Table V). The extent of fiber orientation could also be understood qualitatively from the examination of the SEM photographs. Figure 2(a,b) shows the tensile fracture surfaces of the longitudinally and transversely oriented composite (X_{30}). The broken fiber ends protruding from the fracture surface [Fig. 2(a)] indicated that the fibers were well aligned longitudinally in the direction of applied force. Although in the transverse orientation, the fibers were aligned across the direction of applied force [Fig. 2(b)]. The tensile strength of the composites depended on the fibers, which obstructed the progress of the fracture front. In the longitudinal orientation, the crack progresses in the direction perpendicular to the fiber alignment caused greater

obstruction by the fibers, and hence, the tensile strength increased. Breakage and pulling out of the fibers took place when the fibers were oriented longitudinally, whereas in the transverse orientation, crack progressed in the direction of fiber alignment, and a lower resistance by the fibers was observed. The increase in tear strength in the longitudinal orientation was due to the obstruction caused to the tear path by the short fibers.

Effect of chemical treatment and fiber loading

Good interfacial strength between the fiber and rubber is an essential factor for achieving good fiber reinforcement. The interfacial strength depends on the surface topology of the fiber. In cellulose fibers, even though they possess hydroxyl groups on their surface, the lignin and other waxy contents make them a less effective reinforcement. Hence, to improve adhesion between isora fiber and rubber, they should be subjected to some chemical treatment to remove the lignin and other waxy impurities, so the mixes Y_{10}, Y_{20}, Y_{30}, and Y_{40} were prepared with
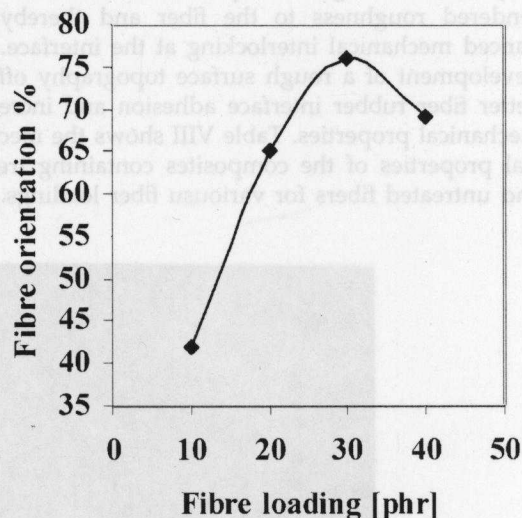
Figure 1 Effect of fiber loading on the percentage fiber orientation of the composites.
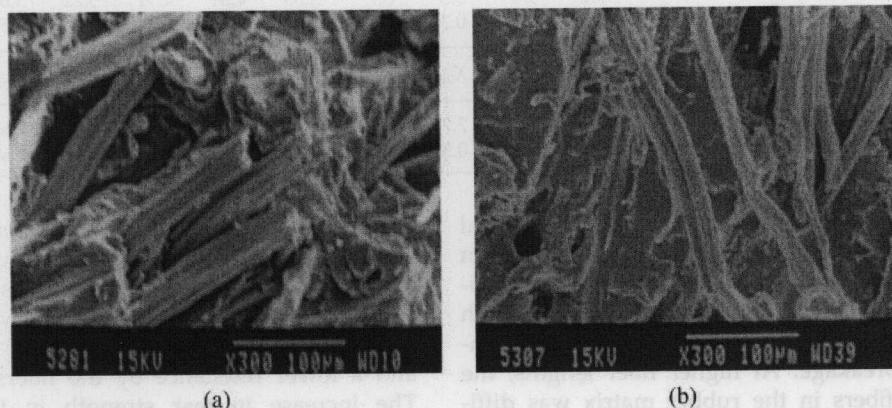
(a)

(b)

Figure 2 SEM photographs showing the (a) longitudinal and (b) transverse orientation of fibers in composite X_{30}.

alkali-treated fibers. The surface topology of isora fiber was studied by SEM, as shown in Figure 3(a,b). In Figure 3(a), the multicellular nature of the raw fiber is shown. The fibrillar nature and porosity of the fiber was revealed from the fiber topography. The porous surface morphology was useful for better mechanical interlocking with the matrix for composite fabrication. SEM of the alkali-treated fibers [Fig. 3(b)] provided strong evidence for the physical microcellular structural changes occurring in the fiber surface on mercerization. Here, pores became clearer, and fibers became thinner; also, fibers underwent fibrillation as shown in the figure. This may have been due to the dissolution and leaching out of fatty acids and lignin components of the fiber. This rendered roughness to the fiber and thereby enhanced mechanical interlocking at the interface. The development of a rough surface topography offered better fiber rubber interface adhesion and increased mechanical properties. Table VIII shows the mechanical properties of the composites containing treated and untreated fibers for variousu fiber loadings. The

tensile properties (e.g., tensile modulus, tensile strength, tear strength) of the composites filled with treated fibers were higher than those filled with untreated fibers at similar loadings. To obtain good fiber reinforcement in the rubber composites, the adhesion between the rubber and the fiber was very important. From these results, it was clear that the aqueous alkali treatment of isora fiber improved the fiber adhesion to rubber matrix. The surface of fibers could be modified by aqueous alkali treatment at elevated temperatures, and this improved the adhesion properties significantly.[28] According to Flodin and Zadorecki,[29] fiber treatment can be used to prevent debonding at the fiber interface because covalent bonds can be formed between the rubber matrix and fiber. Strong adhesion between the treated fiber and rubber led to higher shear strength at the fiber–rubber interface. A stronger force had to be used to overcome the shear strength, which resulted in a higher tensile strength. The elongation at break for the composites with treated fibers was lower than composites with untreated fibers at similar loading.
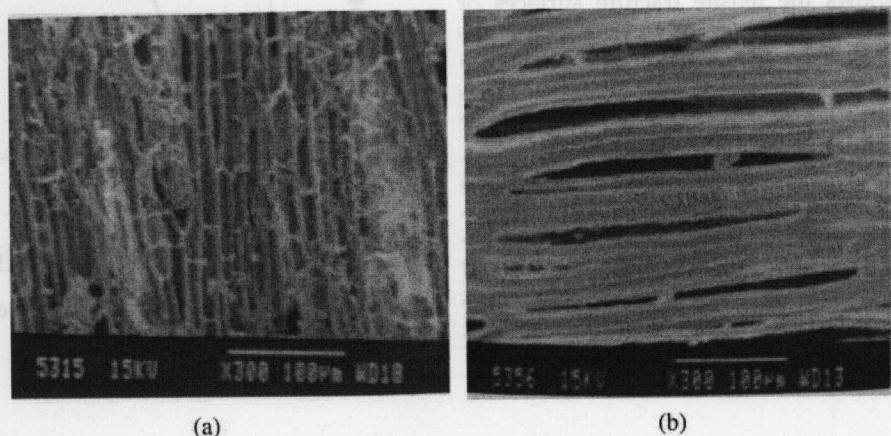

(a)

(b)

Figure 3 SEM photographs of (a) raw and (b) alkali-treated fibers.

TABLE VIII
Mechanical Properties of Vulcanizates with Various Fiber Loadings

Property	Orientation	Gum	X_{10}	X_{20}	X_{30}	X_{40}	Y_{10}	Y_{20}	Y_{30}	Y_{40}
Modulus (300% elongation; MPa)	L	2.3 (0.32)	2.8 (0.19)	2.9 (0.41)	3.2 (0.92)	3.0 (0.65)	3.1 (1.12)	3.3 (0.84)	3.8 (0.64)	3.5 (1.05)
	T	2.3 (0.30)	2.0 (0.89)	2.1 (0.16)	2.2 (1.25)	2.4 (2.18)	2.5 (0.14)	2.6 (0.78)	2.8 (0.55)	2.9 (1.12)
Tensile strength (MPa)	L	25.9 (0.96)	20.9 (0.88)	14.0 (1.01)	9.8 (1.28)	9.0 (0.77)	21.1 (0.32)	15.2 (0.28)	10.7 (1.31)	9.8 (0.68)
	T	25.0 (0.93)	13.2 (0.82)	10.1 (1.44)	6.8 (1.05)	6.2 (0.79)	15.2 (0.59)	11.5 (1.34)	8.2 (1.28)	7.8 (0.37)
Elongation at break (%)	L	1050 (0.88)	860 (0.96)	615 (0.16)	437 (0.83)	380 (0.75)	790 (2.04)	605 (1.16)	400 (0.81)	310 (0.95)
	T	1045 (0.86)	900 (1.08)	690 (0.28)	480 (0.84)	425 (1.17)	612 (0.93)	625 (0.48)	412 (2.03)	395 (0.19)
Tear strength (kN/m)	L	35.1 (0.68)	36.5 (0.96)	42.8 (0.77)	46.8 (0.18)	40.9 (0.99)	38.1 (0.83)	44.6 (1.52)	47.9 (1.17)	43.1 (0.31)
	T	34.5 (0.74)	35.5 (1.11)	40.1 (1.41)	43.9 (0.32)	39.5 (0.53)	37.5 (1.00)	41.9 (0.86)	44.2 (0.56)	40.8 (0.57)
Hardness (Shore A)	—	45	50	63	69	72	55	65	73	76

L = longitudinal; T = transverse. The numbers given in parentheses are the standard deviations.

This was due to the better strength and stiffness achieved from strong adhesion between the fiber and rubber. Consequently, the toughness of the composites was reduced, which resulted in a lower elongation at break. A higher toughness was obtained from weak interfacial adhesion, as shown by the higher elongation at break for composites filled with untreated fibers. Figure 4(a,b) shows the SEM of the tensile fracture surfaces of composites with untreated and treated fibers (X_{30} and Y_{30}). In the case of untreated fiber composites, because of the weak interfacial adhesion between the fiber and rubber, fiber pullout may have taken place, which left holes on the surface when stress was applied [Fig. 4(a)]. Although Figure 4(b) shows the presence of broken fibers on the fracture surface, which was due to the
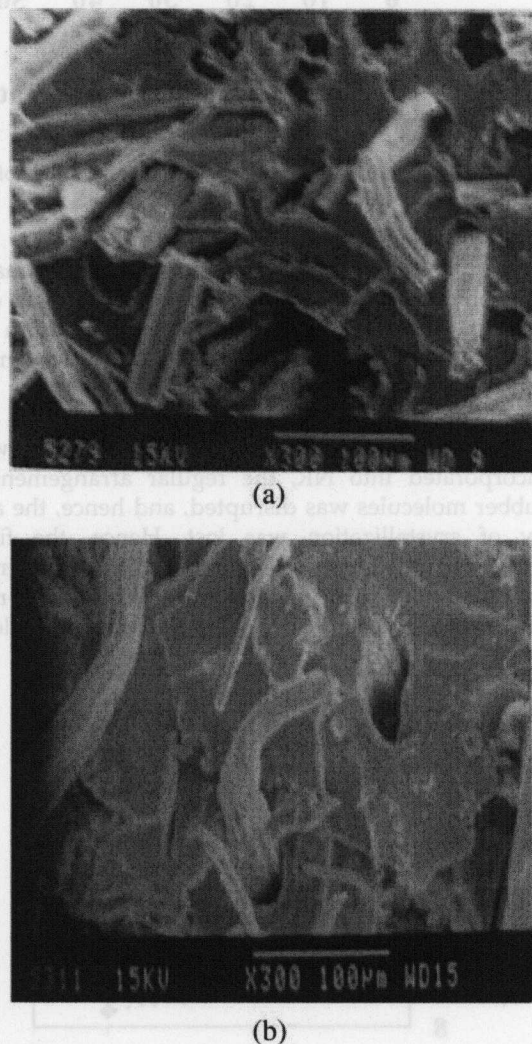

(a)

(b)

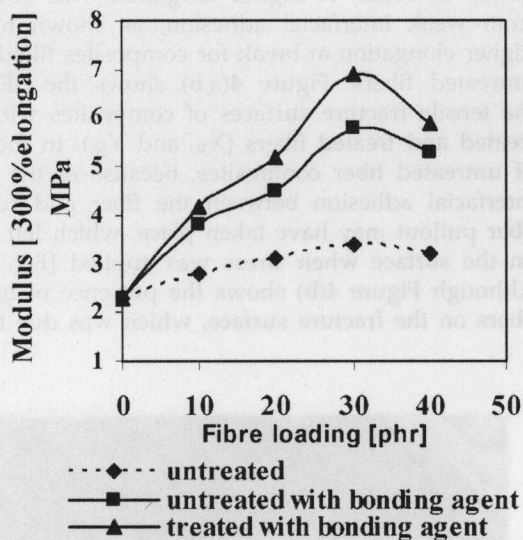**Figure 4** SEM of the fractured surface containing (a) untreated and (b) alkali-treated fibers of composites X_{30} and Y_{30}.

Figure 5 Effect of fiber loading on the modulus of the composites.

Figure 7 Effect of fiber loading on the tear strength of the composites.

strong adhesion between the fiber and rubber matrix for composites with treated fibers, composites containing treated fibers showed enhancement in the modulus compared to the untreated ones for similar fiber loadings.

NR inherently possesses high tensile strength due to strain-induced crystallization. When fibers were incorporated into NR, the regular arrangement of rubber molecules was disrupted, and hence, the ability of crystallization was lost. Hence, the fiber-reinforced NR composites possessed a lower tensile strength than gum compounds. When fiber-reinforced rubber composites were subjected to a load,
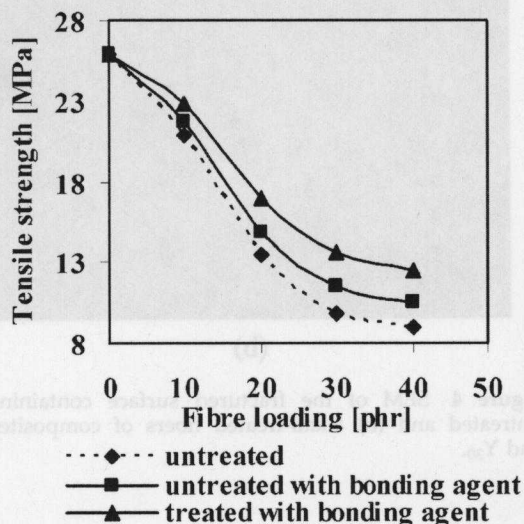
the fibers acted as carriers of load, and stress was transferred from the matrix along the fibers, which resulted in composites with good mechanical properties. The uniform distribution of stress was dependent on the population and orientation of the fibers. At low levels of fiber loading, the orientation of fibers was poor, the fibers were not capable of transferring load to one another, and stress accumulated at certain points of the composite, which led to a low modulus. As shown in Table VIII, modulus showed a clear continuous increase up to 30 phr fiber loading in the case of longitudinal orientation. At higher levels of fiber loading, the increased popu-
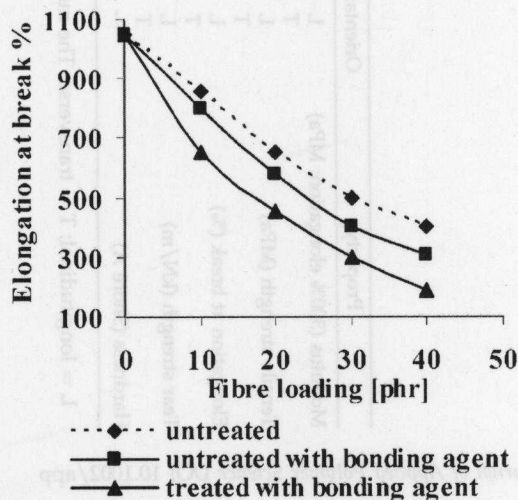

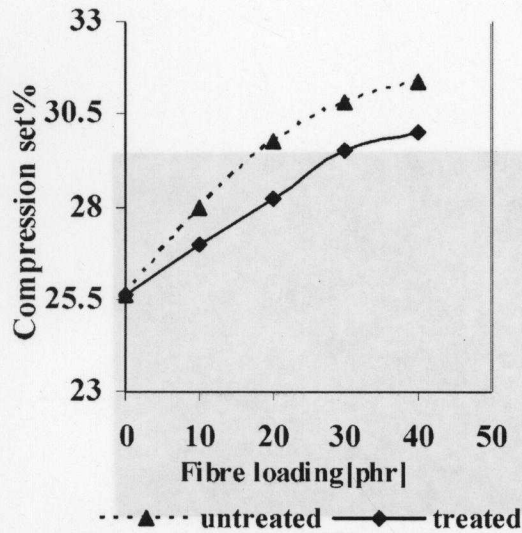**Figure 6** Effect of fiber loading on the tensile strength of the composites.

Figure 8 Effect of fiber loading on the elongation at break of the composites.

Figure 9 Variation of compression set with fiber loading for the composites with bonding agent.

phr fiber loading. When the fiber loading increased further, tear strength again decreased as the increased strain in the matrix between closely packed fibers increased tearing and reduced the tear strength. Maya and Thomas[30] also observed similar results. There was a reduction in elongation at break with increasing fiber loading. Increased fiber loading in the rubber matrix resulted in the composites becoming stiffer and harder. This reduced the composite's resilience and led to lower elongation at break. Flink[31] and Akhtar and De[32] reported similar observations. The elongation at break for composites with treated fibers was lower than for composites with untreated fiber at similar loading. This was due to the better strength and stiffness achieved from strong adhesion between fiber and rubber. Consequently, the toughness of the composites decreased, which resulted in a still lower elongation at break. Higher toughness was obtained from weak interfacial adhesion, as shown by the higher elongation at break for composites filled with untreated fibers.

lation of fibers led to agglomeration, and stress transfer was partially blocked. On transverse orientation, the modulus increased gradually but at a lower value than longitudinal orientation. Also, with increasing fiber loading, the tensile strength of the composites showed an abrupt decrease up to a loading of 30 phr, and thereafter, a gradual decrease both in longitudinal and transverse orientations was observed. At intermediate levels of loading (30 phr), the population of fibers was just sufficient for maximum orientation, and fibers actively participated in stress transfer. As fiber loading increased, tear strength gradually increased and reached a maximum at 30
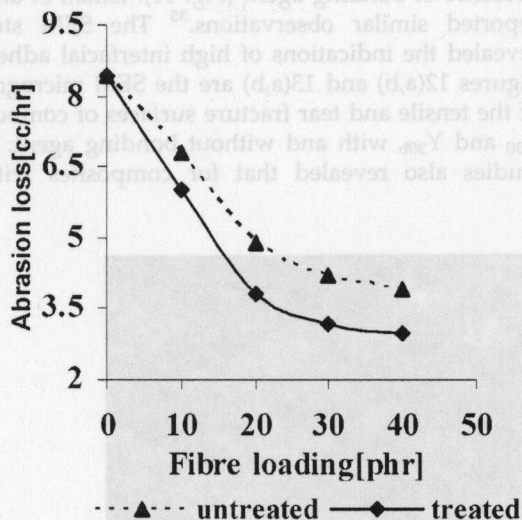
Effect of bonding agent

A further increase in the properties was seen with the incorporation of a bonding agent in the system. It has already been established that a tricomponent system consisting of hexamethylene tetramine, resorcinol, and fine particle of silica can be used as a bonding agent for most rubber and fiber combinations.[33] The presence of bonding agent in the mixes improved the mechanical properties, such as modulus, tensile strength, and tear strength. Alkali treatment of fibers further enhanced the effect of the bonding agent, as shown by the higher modulus,
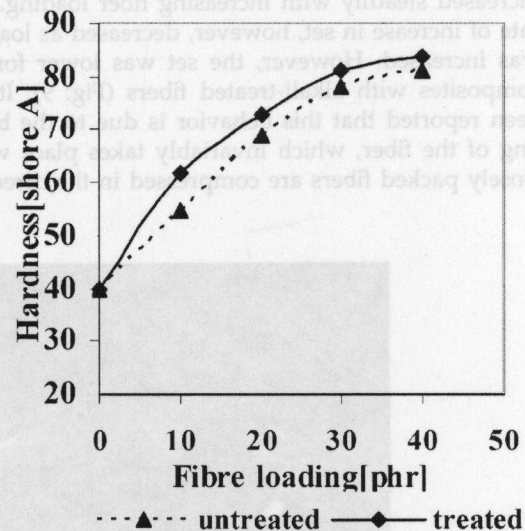
hardness of the composites also increased in the presence of bonding agent (Fig. 11). Ismail et al. also reported similar observations.[34] The studies revealed the indications of high interfacial adhesion. Figures 12(a,b) and 13(a,b) are the SEM micrographs of the tensile and tear fracture surfaces of composites X_{30} and Y_{30}, with and without bonding agent. SEM studies also revealed that for composites without

agent are given in Figures 9–11. Compression set increased steadily with increasing fiber loading. The rate of increase in set, however, decreased as loading was increased. However, the set was lower for the composites with alkali-treated fibers (Fig. 9). It has been reported that this behavior is due to the buckling of the fiber, which invariably takes place when closely packed fibers are constrained in the direction

Figure 10 Variation of abrasion loss with fiber loading for the composites with bonding agent.

Figure 11 Variation of hardness with fiber loading for the composites with bonding agent.
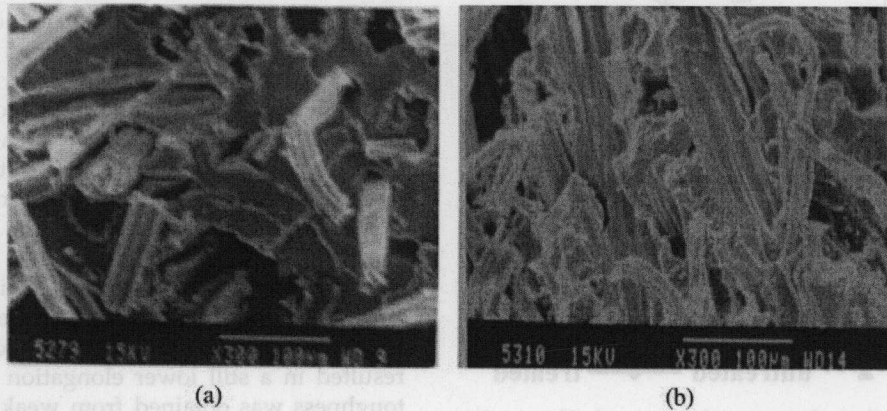
Figure 12 SEM micrographs of the tensile fractured surfaces containing (a) untreated fiber without bonding agent and (b) treated fiber with bonding agent of composites X_{30} and Y_{30b}.

tensile strength, and tear strength in Figures 5–7. The treated fiber provided a better surface for strong adhesion between the fiber and matrix, and the stress transfer became more efficient, and consequently, there was a better enhancement in the properties. The elongation at break for composites with the bonding agent had a lower value than for composites without bonding agent. Again, treated fibers showed a lower elongation at break than untreated fibers (Fig. 8). The variation of compression set, abrasion loss, and hardness with fiber loading for the treated and untreated fiber composites with bonding agent are given in Figures 9–11. Compression set increased steadily with increasing fiber loading. The rate of increase in set, however, decreased as loading was increased. However, the set was lower for the composites with alkali-treated fibers (Fig. 9). It has been reported that this behavior is due to the buckling of the fiber, which invariably takes place when closely packed fibers are compressed in the direction

of their alignment.[34] Because of the strong adhesion between the treated fibers and rubber, the extent of buckling was reduced in treated fiber composites, which resulted in a low value for the set. Abrasion loss decreased with increasing fiber concentration in the composite (Fig. 10). Here, also the treated fiber composites showed better resistance to abrasion compared to the untreated fiber composites. The better abrasion resistance of the treated fiber composites may have resulted from the combination of higher tear strength, tensile strength, and modulus achieved through better bonding with the rubber matrix. The hardness of the composites also increased in the presence of bonding agent (Fig. 11). Ismail et al. also reported similar observations.[35] The SEM studies revealed the indications of high interfacial adhesion. Figures 12(a,b) and 13(a,b) are the SEM micrographs of the tensile and tear fracture surfaces of composites X_{30} and Y_{30b} with and without bonding agent. SEM studies also revealed that for composites without
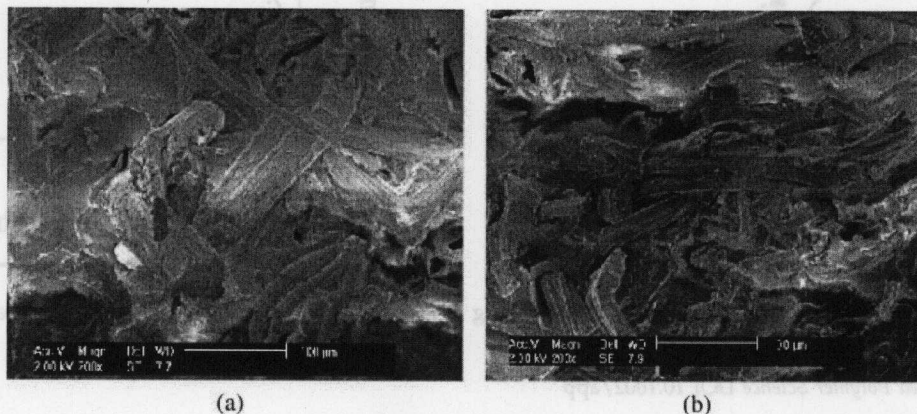

Figure 13 SEM micrographs of the tear fractured surfaces containing (a) untreated fiber without bonding agent and (b) treated fiber with bonding agent of composites X_{30} and Y_{30b}.

bonding agent, failure occurred at the weak fiber–rubber interface, whereas for composites containing treated fiber and bonding agent, failure occurred at the fiber due to strong adhesion between the fibers and matrix.

CONCLUSIONS

The mechanical properties of short-isora-fiber-reinforced NR composites were enhanced by chemical treatment on the fiber surface and by the use of bonding agent. Longitudinally oriented fiber composites had superior properties to transversely oriented ones. The optimum length and loading of isora fiber in the NR composites were be 10 mm and 30 phr, respectively, for the achievement of good reinforcement. The surface morphology of isora fiber was modified by alkali treatment. SEM analysis revealed that better adhesion was observed between alkali-treated isora fiber and NR in the composites. The presence of bonding agents in the composites prolonged t_{90}. SEM studies also revealed that for the control compound (untreated fiber without bonding agent), failure occurred at the weak fiber–rubber interface, whereas for composites containing treated fiber and bonding agent, failure occurred in the fiber because of strong adhesion at the fiber–rubber interface.

References

1. Ismail, H.; Rosnah, N.; Rozman, H. D. Polymer 1997, 38, 4059.
2. Geethamma, V. J.; Thomas, S.; Kuriakose, B. J Appl Polym Sci 1995, 55, 583.
3. Varghese, S.; Thomas, S.; Kuriakose, B. Indian J Nat Rubber Res 1991, 4, 55.
4. Maya, J.; Thomas, S. Compos Sci Technol 2004, 64, 955.
5. Setua, D. K.; De, S. K. Rubber Chem Technol 1983, 56, 808.
6. Arumugham, N.; Tamaraselvy, K. J Appl Polym Sci 1989, 37, 2645.
7. Ismail, H.; Edyham, M. R. Polym Test 2002, 21, 139.
8. Ismail, H.; Rozman, H. D.; Ishiaku, U. S. Polym Int 1997, 43, 223.
9. Prasanth Kumar, K.; Thomas, S. Bull Mater Sci 1995, 18, 1021.
10. Lovely, M.; Joseph, K. U.; Rani, J. Prog Rubber Plast Recyl Technol 2004, 20, 337.
11. Joshy, M. K.; Lovely, M.; Rani, J. Proceedings of International Conference in Blends and Composites, Kerala, India, 2005; p 113.
12. Lovely, M.; Joseph, K. U.; Rani, J. Advances in Eco Materials; Stallion: Singapore, 2005; Vol. 2, p 44.
13. Krishnamurthy, T. Minor Forest Products of India 1993; Oxford and IBH: New Delhi, 1993; p 338.
14. Punnose. Ind Textile J 1952, 63, 388.
15. Belgacem, M. N.; Btaille, P. J Appl Polym Sci 1994, 53, 379.
16. Felix, J. M.; Carlson, C. M. G. J Adhes Sci Tech 1994, 8, 163.
17. Geethamma, V. J.; Thomas, S. Polymer 1998, 39, 1483.
18. Sapieha, S.; Pupo, J. F. J Appl Polym Sci 1989, 37, 233.
19. Felix, J. M.; Gatenholm, P. J Appl Polym Sci 1991, 42, 609.
20. Bisanda, B. T. N.; Ansell, M. P. Compos Sci Technol 1991, 41, 167.
21. Ismail, H.; Edyham, M. R.; Shuhelmy, S. Eur Polym J 2002, 38, 39.
22. Betrabet. J Sci Ind Res B 1956, 15, 671.
23. Pramanik, P. K.; Khastgiri, D. K. Plast Rubber Compos Process Appl 1991, 15, 189.
24. Goetller, L. A.; Shen, K. S. Rubber Chem Technol 1983, 56, 619.
25. Chakraborty, S. K.; Setu, D. K. Rubber Chem Technol 1982, 55, 1286.
26. Prasanthakumar, K.; Thomas, S. Bull Mater Sci 1995, 18, 1021.
27. Prasanthakumar, K.; Thomas, S. J Appl Polym Sci 1995, 58, 597.
28. Czvikovszky, T.; Kovacs, I. J Appl Polym Sci 1985, 30, 1827.
29. Flodi, P.; Zadorecki, Z. J Appl Polym Sci 1985, 30, 3971.
30. Maya, J.; Thomas, S. Compos Sci Technol 2004, 64, 955.
31. Flink, P. J Appl Polym Sci 1988, 35, 2155.
32. Akhtar, S.; De, S. K. J Appl Polym Sci 1986, 32, 5123.
33. Varghese, S.; Kuriakose, B.; Thomas, S. J Adhes Sci Technol 1994, 8, 235.
34. Murthy, V. M.; De, S. K. Rubber Chem Technol 1982, 55, 287.
35. Ismail, H.; Rosnah, N. Polym Int 1997, 43, 223.