Curing Characteristics and Mechanical Properties of Alkali-Treated Grass-Fiber-Filled Natural Rubber Composites and Effects of Bonding Agent

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ABSTRACT: To improve adhesion between fiber and matrix, natural rubber was reinforced with a special type of alkali-treated grass fiber (*Cyperus Tegetum Rox b*). 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. 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. The optimum cure time decreased with increases in fiber loading, but there was no appreciable change in scorch time. Although the optimum cure time of vulcanizates having RFL-treated fibers was higher than that of the other vulcanizates, it decreased with fiber loading in the presence of RFL as the bonding agent. But this value was lower than that of the rubber composite without RFL. Investigation of equilibrium swelling in a hydrocarbon solvent was also carried out. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3151–3160, 2006

Key words: RFL; fibers; composites; mechanical properties; natural rubber

INTRODUCTION

Short-fiber-reinforced rubber composites have attracted much attention because of easy processability, improved physical and mechanical properties, and economic advantage. Short-fiber-reinforced rubber has been successfully used in the production of V-belts, hoses, tire treads, seals, and complex-shaped mechanical goods. The ultimate properties of the composite depend on fiber concentration, fiber dispersion, fiber–rubber adhesion, fiber orientation, and fiber aspect ratio. Synthetic fibers like glass, rayon, nylon, aramid, and asbestos have been used by a number of scientists in natural and various synthetic rubbers.[1–6] Sreeja and Kutty[7] studied the cure characteristics and mechanical properties of short-nylon-fiber-based natural rubber composites. It was found that incorporation of short nylon fibers into a natural rubber matrix marginally reduced the flowability. Both the scorch time and the cure time were found to decrease from the gum compound by loading 20 phr short fibers. Tear strength, heat buildup, and compression set were improved, whereas resilience and abrasion loss were lessened with increased fiber loading compared to those of gum vulcanizate. A short-polyester-fiber-reinforced natural rubber composite was studied by Senapati et al.[8] Natural fibers offer an excellent opportunity to utilize an abundant natural source of such materials. Arumugam et al.[9] studied the effects of fiber content and bonding agent on the physical properties and aging characteristics of coconut-fiber-reinforced natural rubber composites. It was observed that coconut fibers acted as a reinforcing agent only above 10 phr loading and that the adhesion between coconut fibers and the rubber matrix was enhanced by a bonding agent. The composites had a superior antiaging property for fiber loading of 30 phr in the presence of bonding agents. De et al.[10–12] reported their studies on short-jute-fiber-reinforced natural rubber and carboxylated nitrile rubber composites. Natural rubber reinforced with short silk fibers was reported by Setua and De.[13] It has been reported that the introduction of silk fibers into natural rubber vulcanizates increases hardness, heat buildup, compression set, and tear resistance and decreases resilience and elongation at break. Owolabi et al.[14] used coir fiber as the reinforcing filler for plastics. The tensile strength, flexural strength, and water absorption of coir–polyester composites were

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improved by the addition of glass fibers.[15] Thomas et al.[16] reported the effects of fiber length, orientation, and alkali treatment of coir fiber on the properties of short-coir-fiber-reinforced natural rubber composites. It was found that the mechanical properties of the composites in the longitudinal direction were superior to those in the transverse direction and that the optimum fiber length was 10 mm. Bhattacharya et al.[17] investigated the effect of short-pineapple-leaf-fiber-reinforced natural rubber composites. Varghese et al.[18] reported the curing characteristics and mechanical properties of short-sisal-fiber-filled natural rubber composites. The effects of filler loading and a silane coupling agent (Si-69) of bamboo-fiber-filled natural rubber composites were studied by Ismail et al.[19] It was found that Si-69 improved adhesion between fiber and rubber. They also studied oil-palm-wood-flour-filled natural rubber composites.[20] For composites with the same filler loading, they observed shorter scorch time and optimum cure time for semi-EV composites compare to those of CV composites. The semi-EV composites showed maximum rheometric torque and superior mechanical properties with higher fiber loading. Adhikari et al.[21] reported the effect of fiber loading, mesh size, and silane coupling agent on grass-fiber-filled natural rubber composites.

In the present investigation grass fiber (*Cyperus Tegetum Rox b)* was used as filler for natural rubber. To improve fiber–rubber adhesion, the grass fiber was treated with dilute alkali. The effects of filler loading at different mesh sizes on the curing characteristics and mechanical properties of grass-powder-filled natural rubber composites are reported. Because the 400-mesh grass-fiber-filled natural rubber composite showed superior mechanical properties, the effect of resorcinol formaldehyde latex (RFL) as the bonding agent in this composite was investigated. The effect of the RFL bonding system was compared between water-leached and alkali-treated grass-fiber-filled natural rubber composites. Scanning electron microscopy (SEM) was done to see the filler dispersion in the composite. The aging characteristics of grass-fiber-filled natural rubber composites also were studied. Equilibrium swelling in a hydrocarbon solvent was investigated in order to see the combined effects of crosslink density and the rubber–fiber interaction. The reinforcing property of the alkali-treated grass fibers was also compared with that of water-leached (WL) fibers.

EXPERIMENTAL

Materials

Grass (*Cyperus Tegetum Rox b*), an agricultural product of India, was used after water leaching and alkali treatment. The major constituents of grass are lignin (40%), cellulose (15%), hemicellulose (21%), water-soluble matter (22%), and ash (2%). Natural rubber (RSS 1), zinc oxide (S. D. Fine Chem., India), stearic acid (Loba Chemie, India), sulfur (S. D. Fine Chem., India), N-cyclohexyl-2-benzothiazyl sulfenamide (CBS; ICI, India), sodium hydroxide (S. D. Fine Chem, India), RFL (Birla Tires Ltd.), and toluene (S. D. Fine Chem., India) were used as received.

Fiber preparation

Small pieces of grass fiber were collected and immersed in water for 24 h. Water-soluble matters were removed from the grass, which finally was washed thoroughly with distilled water. Then the fibers were dried and directly transferred to the grinder, where they were ground for 15 min. From this ground mass, 400-mesh-size particles were separated with the help of a sieve shaker. The pH of the water-leached grass powder in the water slurry was found to be 5.6.

Alkali treatment of grass fiber was carried out by immersion in 5% aqueous sodium hydroxide for 15 min, followed by a thorough washing with distilled water until all alkali was removed and then drying. Then grinding of alkali-treated grass fiber was carried out and the different mesh sizes of the grass powders were separated by sieving with a sieve shaker. Thus, 200- and 400-mesh-sized grass powders and 1-mm short fiber were obtained for the preparation of grass rubber composites. The pH of the alkali-treated grass powder in water slurry was found to be 8.1.

For coating with a bonding agent, both the water-leached and alkali-treated grass powders were soaked with 5 parts RFL (by weight of rubber) followed by drying in ambient temperature (28°C).

Preparation of rubber composite

The formulations of the rubber compounds are shown in Table I. The rubber compounds were prepared in a laboratory-size two-roll mixing mill whose roll size was 6 × 13 in at a friction ratio of 1.2 as per ASTM D 15-54T (1954). The natural rubber was first masticated for 2 min to form a band, followed by the sequential addition of the additives in the order ZnO, stearic acid, CBS (accelerator), sulfur, and grass powder. The total mixing time was kept fixed in all cases. The RFL-treated grass powder was dispersed at the end of the mixing process in order to maintain the direction of compound flow, so that the majority of fibers followed the direction of flow. The rubber compounds were cured in a hot hydraulic press (Carver Model 2518) at 150°C in order to obtain composite sheets as per the respective optimum cure times obtained from the oscillating disk rheometer.

TABLE I
Mix Formulation of Water-Leached and Alkali-Treated Grass–Rubber Compounds

	Formulation code												
Ingredients (phr)	1	2 (2a)	3 (3a)	4 (4a)	5	6	7	8	9	10	11 (11a)	12 (12a)	13 (13a)
Natural rubber (NR)	100	100	100	100	100	100	100	100	100	100	100	100	100
GP (AT-400 mesh)	—	10	20	30	—	—	—	—	—	—	10	20	30
[GP (WL-400 mesh)]	—	(10)	(20)	(30)	—	—	—	—	—	—	(10)	(20)	(30)
GP (AT-200 mesh)	—	—	—	—	10	20	30	—	—	—	—	—	—
GP (AT-1mm SF)	—	—	—	—	—	—	—	10	20	30	—	—	—
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2
CBS	1	1	1	1	1	1	1	1	1	1	1	1	1
Sulfur	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75	1.75
RFL	—	—	—	—	—	—	—	—	—	—	5	5	5

GP, grass powder; WL, water leached; AT, alkali treated; SF, short fiber.

Evaluation of properties

The cure characteristics of the rubber compounds were measured with the help of a Monsanto Oscillating Disc Rheometer, R-100, at 150°C.

Stress–strain properties were measured following ASTM D 412-51T (1957) on a tensile testing machine (Hounsfield, Model H10KS) at room temperature (25°C ± 2°C) with a uniform speed of separation of 500 mm/min. The aging characteristics of the vulcanizates were determined in a forced-air-circulated aging oven at 70°C ± 2°C for 72 h. Hardness (Shore A) of the vulcanized samples was measured by a Hiroshima hardness tester as per ASTM D 1415-56T.

The tensile fracture surface of the composites was studied by a Jeol JSM 5000 scanning electron microscope. The fracture ends of the tensile specimens were mounted on aluminum stubs and sputter-coated with a thin layer of gold in order to avoid electrical charging during the examination.

The equilibrium swelling experiments of the vulcanizates were performed in toluene at room temperature. The samples were allowed to swell for 72 h in toluene. Crosslinking of the composites was measured using the equation[22]

$$\frac{1}{Q} = \frac{W_S - W_D}{\left(\dfrac{W_0 \times 100}{W_F}\right)} \tag{1}$$

where Q is the swelling value; $1/Q$ is the crosslinking value; and W_S, W_D, W_0, and W_F are the swollen weight, dried weight, weight of the original sample, and formula weight, respectively. The formula weight (W_F) is the total weight of rubber plus the compounding ingredients based on 100 parts of rubber.

The extent of interaction between rubber and fiber could be assessed using the Kraus[23,24] and Cunneen–Russell and Lorentz–Park[25] equations. The Kraus equation is

$$\frac{V_{r0}}{V_{rf}} = 1 - m\left[\frac{f}{1-f}\right] \tag{2}$$

where V_{r0} is the volume fraction of the rubber gum vulcanizates, f is the volume fraction of the fiber obtained from the ratio of volume of filler/total volume of the recipe, and m is the polymer–fiber interaction parameter. V_{rf} is the volume fraction of a rubber network in the swollen phase and is given in eq. (3), the equation of Ellis and Welding:[26]

$$V_2 = \frac{\left(\dfrac{W_2}{d_2}\right)}{\left(\dfrac{W_1}{d_1}\right) + \left(\dfrac{W_2}{d_2}\right)} \tag{3}$$

where W_1 is the weight fraction of the solvent, d_1 is the density of the solvent, W_2 is the weight fraction of the polymer in the swollen specimen, and d_2 is the density of the polymer.

The Cunneen–Russell equation is

$$\frac{V_{r0}}{V_{rf}} = ae^{-z} + b \tag{4}$$

where V_{r0} and V_{rf} are the same as defined earlier, z is the weight fraction of the fiber, and a and b are constants.

The Lorentz–Park equation for rubber filler interaction is

$$\frac{Q_f}{Q_g} = ae^{-z} + b \tag{5}$$

TABLE II
Curing Characteristics of Water-Leached and Alkali-Treated Grass Fiber–Rubber Composites

	Formula code												
Cure characteristics	1	2 (2a)	3 (3a)	4 (4a)	5	6	7	8	9	10	11 (11a)	12 (12a)	13 (13a)
Optimum cure time (t_{90}, min)^{AT}	11	7.8	7.3	6.8	7.0	6.5	6.5	6.8	6.5	6.0	8.0	7.8	7.0
Optimum cure time (t_{90}, min)^{WL}	—	(9.5)	(10.0)	(10.5)	—	—	—	—	—	—	(10)	(10.5)	(11)
Scorch time (t_{s2}, min)^{AT}	5	2.5	2.5	3.0	2.5	2.5	2.5	2.5	2.5	2.5	1	1	1.5
Scorch time (t_{s2}, min)^{WL}	—	(4.0)	(3.5)	(3.5)							(2.5)	(2.0)	(2.0)
Extent of cure (dNm)^{AT}	46	49	52	54	48	53	56	52	55	56	54	57	60
Extent of cure (dNm)^{WL}	—	(47)	(47.3)	(49)							(48)	(49)	(51)
Cure rate index (min^{-1})^{AT}	17	21	24	21	22	25	25	24	25	29	14.3	14.8	18.2
Cure rate index (min^{-1})^{WL}	—	(18.2)	(15.4)	(14.3)							(13.3)	(11.7)	(11.1)

where Q is the swelling value and the subscripts f and g refer to filled and gum vulcanizates, respectively.

RESULTS AND DISCUSSION

Curing characteristics of rubber composites

The compound formulations of grass powder and short fibers with natural rubber and various additives are shown in Table I. The curing characteristics of the grass fiber–rubber composites are shown in Table II. Figure 1 shows that the maximum rheometer torque (extent of cure) increased with an increase in fiber loading of the alkali-treated grass fiber–rubber composite samples. The extent of cure increased because of the increased stiffness from higher loading of the grass filler. But in the presence of RFL, the extent of cure of the composites increased for both the alkali-treated (AT) and the water-leached (WL) grass-fiber-based composites. This was because of strong bonding at the fiber/matrix interface, which consequently made the composite stronger, harder, and stiffer. It can be seen that compounds with RFL-treated fibers showed higher torque than did composites with untreated fiber (both for WL and AT) because of better adhesion between the fibers and the rubber matrix. But alkali-treated RFL fibers were cured to a greater extent than were water-leached RFL-modified fibers. From this observation it can be concluded that the interaction between the RFL- and alkali-treated grass fibers was better than that with the water-leached grass fibers. This is because of the generation of additional functionality on the fiber surface after alkali treatment, which can bond with RFL. The result was that alkali-treated grass-fiber-based composite sample showed a greater extent of cure than did that of the water-leached grass-fiber-based composite sample. Other researchers[27,28] made similar observations. From Figure 1 it can be observed that the optimum cure time decreased with increased fiber loading for alkali-treated grass-fiber-based composite samples, whereas for WL grass-fiber-based composite samples, the optimum cure time increased with an increase in fiber loading. This decrease in the optimum cure time of the alkali-treated grass-fiber-filled compounds compared to that of the control compounds can be attributed mostly to the influence of pH (8.1) on the grass fillers. It is known that a vulcanization reaction becomes faster in an alkaline pH,[29,30] but the presence of RFL in the vulcanizate prolonged the cure time. Chakraborty et al.[27] observed longer curing times because of better bonding between jute fibers and the matrix when different bonding agents were used. The scorch time of the vulcanizates was not much affected by increased fiber loading. The scorch time also not influenced much for the water-leached and alkali-

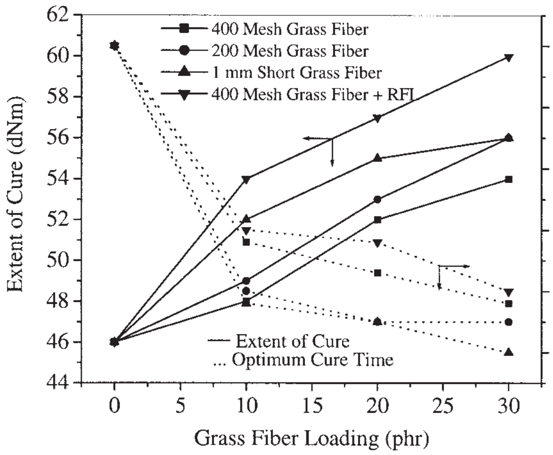


Figure 1 Effect of grass fiber loading on optimum cure time (t_{90}) and extent of cure (dNm) of the grass fiber–rubber composite.

TABLE III
Mechanical Properties of Water-Leached and Alkali-Treated Grass Fiber–Rubber Composites

Mechanical properties	1	2 (2a)	3 (3a)	4 (4a)	5	6	7	8	9	10	11 (11a)	12 (12a)	13 (13a)
200% Mod^{AT}, MPa	1.04	1.26	1.60	1.86	1.11	1.44	1.62	1.06	1.41	1.55	1.80	2.31	2.54
200% Mod^{WL}, MPa	—	(1.09)	(1.71)	(2.03)							(1.75)	(2.27)	(2.32)
300% Mod^{AT}, MPa	1.21	1.75	2.13	2.42	1.41	1.79	2.0	1.37	1.71	1.85	2.42	2.99	3.21
300% Mod^{WL}, MPa	—	(1.51)	(2.32)	(2.61)							(2.31)	(2.75)	(2.92)
TS^{AT}, MPa	20.0	19.1	17.4	12.8	15.3	12.4	9.96	14.6	10.8	8.59	19.8	18.2	13.5
TS^{WL}, MPa	—	(20.5)	(15.8)	(10.6)							(20.8)	(16.5)	(11.2)
% EB^{AT}	1578	1525	1386	1199	1479	1312	1212	1452	1303	1180	1370	1264	1047
% EB^{WL}	—	(1534)	(1255)	(999)							(1548)	(1315)	(1036)
Hardness^{AT}, Shore A	37.3	42.8	48.3	51.3	44.3	51.5	57	47.2	53.7	60.3	45	50	54
Hardness^{WL}, Shore A	—	(38.7)	(43.7)	(48.7)							(50)	(51)	(55)
Swelling value^{AT}, Q	4.29	4.51	4.4	4.29	4.87	4.74	4.64	4.63	4.81	4.96	4.32	4.15	4.08
Swelling value^{WL}, Q	—	(4.54)	(4.19)	(4.27)							(4.48)	(4.08)	(4.0)

treated grass-fiber-loaded vulcanizate in the presence of a bonding agent.

Mechanical properties of grass fiber–rubber composites

The tensile properties, hardness, and swelling values of rubber compounds containing various proportions of water-leached and alkali-treated grass fibers are shown in Table III. Figure 2 shows the effects of grass fiber loading and the bonding agent on modulus at 200% and 300% elongations. From Figure 2 it is evident that 200% modulus continuously increased with increases in fiber loading and decreases in particle size. Because the highest 200% modulus was obtained for 400-mesh grass-fiber-filled natural rubber composite, the effect of the bonding agent was studied for this particular formulation. The presence of RFL further increased the value of the 200% modulus. The same trend was observed for increases in the 300% modulus with increases in fiber loading. This was because with the increase in fiber loading, the extent of bonding between the fiber and the matrix increased, and the vulcanizates became stiff. The presence of RFL further strengthened fiber–rubber bonding, as shown in Scheme 1. RFL interacted with the primary hydroxyl group of cellulose to form an ether linkage, as shown in Scheme 1(a). Identical condensation reaction occurred between methylol groups of phenols during phenolic resin synthesis in the presence of an acid or

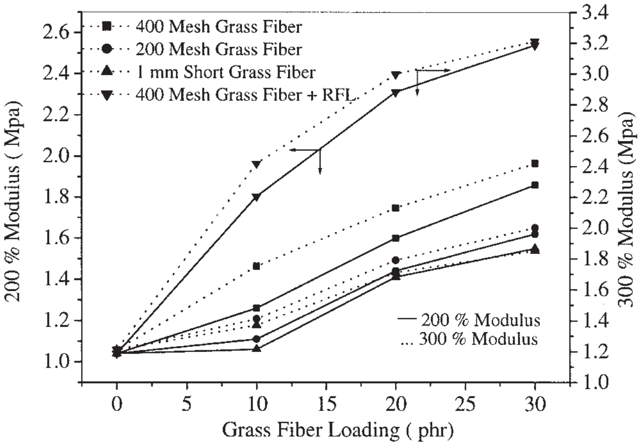
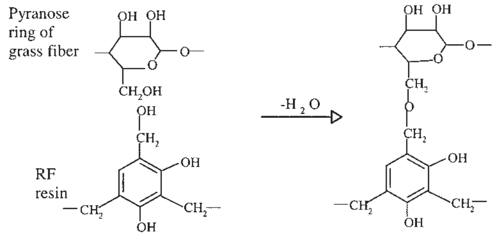
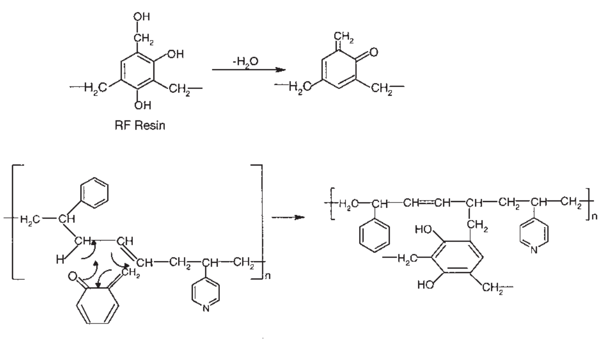


Figure 2 Effect of grass fiber loading on 200% and 300% moduli of the grass fiber–rubber composite.



a) Possible reaction between RF resin and rayon cord



b) Reaction of RF resin with butadiene unit of RFL

Scheme 1

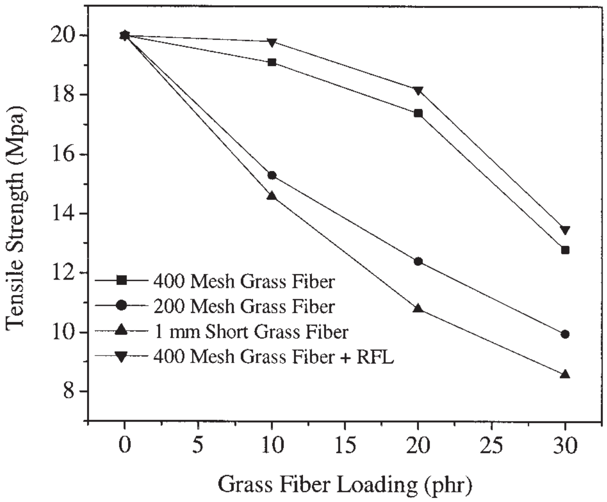


Figure 3 Effect of grass fiber loading on tensile strength of the grass fiber–rubber composite.

an alkali catalyst. Regarding interaction/bonding of RFL with the matrix rubber hydrocarbon, the allylic hydrogen of the butadiene unit in the terpolymer of RFL (VP, styrene, and butadiene units) may react with the resorcinol formaldehyde resins, as shown in Scheme 1(b).[31]

The effect of fiber loading on the tensile strength of alkali-treated grass-fiber-filled natural rubber composites both in the presence and the absence of RFL is shown in Figure 3. As the vulcanizates became more and more stiff with increases in fiber loading and mesh size, tensile strength gradually decreased. Because of the increase in fiber concentration, stress transmission from matrix to fiber was very difficult. Therefore, the continuity of the matrix phase was disturbed by the increasing fiber content, which was corroborated by the SEM micrograph. Because the presence of RFL leads to stronger adhesion at the fiber/matrix interface, RFL-treated fibers showed higher tensile strength in rubber vulcanizates at all levels of fiber loading. Stress transfer becomes more efficient and consequently enhances tensile strength. Miwa et al.[32] reported that strong adhesion between fiber and matrix resulted in higher shear strength at the interface and that strong force was required to overcome shear strength at the interface, which resulted in higher tensile strength.

Figure 4 shows that elongation at break was lower in vulcanizates with a bonding agent than in the control compound. Elongation at break decreased with an increase in fiber loading because of the introduction of more and more grass fibers into the rubber matrix. The vulcanizate became stiff and chain mobility decreased. Again, vulcanizates with alkali-treated RFL-modified fibers showed lower elongation at break than did those with untreated fibers.

The presence of a bonding agent also enhanced composite hardness, as shown in Figure 4. With an increase in the proportion of grass fiber loading for a particular mesh size, the vulcanizate became stiff and hardness increased. Similarly, for a definite proportion of loading, say, 10, 20, or 30 phr, hardness increased when mesh size increased. As the fineness of 400-mesh grass is more than that of 200-mesh powder, the 400 mesh containing vulcanizate was soft compared to the 200-mesh or 1-mm fiber-loaded vulcanizate.

Aging performance of grass fiber–rubber composites

As the aging performance of rubber compounds containing grass fiber needs attention, accelerated aging tests also were performed in a forced-air-circulated aging oven with the vulcanized rubber compounds as formulated in Table I. The results of aging tests with formulations 2–10 containing various proportions and different mesh sizes of alkali-treated grass fiber were with those of a control, formulation 1 (without grass fiber). Figure 5 shows the effect of alkali-treated grass fiber loading on percent retention of 200% modulus of grass fiber–rubber composites after 72 h of aging. The results indicate that more than 100% retention of 200% modulus occurred after 72 h of aging. Because as aging progresses, residual curing occurs beyond curing for optimum curing time, which is the time required for 90% of the maximum curing, the vulcanizate became stiffer.

The percent retention of the tensile strength of the alkali-treated grass-fiber-loaded natural rubber composites after 72 h of aging is shown in Figure 6. It was found that grass fiber–rubber composites showed retention of tensile strength that was superior to that of the control formulation. This indicates there is some

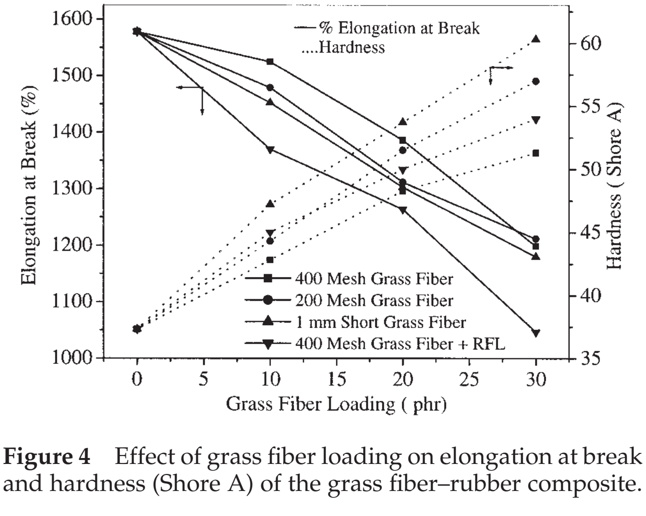


Figure 4 Effect of grass fiber loading on elongation at break and hardness (Shore A) of the grass fiber–rubber composite.

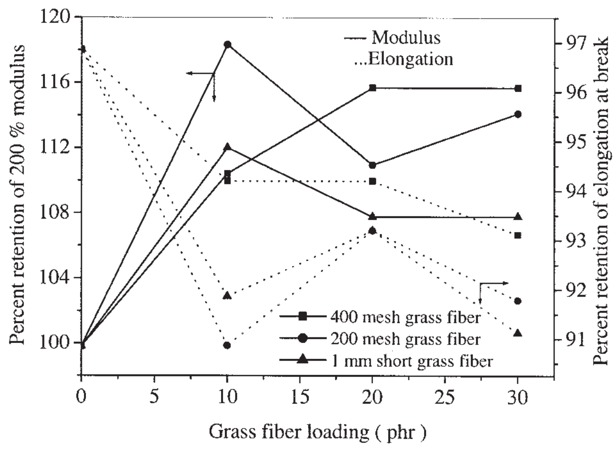


Figure 5 Percent retention of 200% modulus and elongation at break after 72 h of aging.

antiaging property of rubber vulcanizate in the presence of grass fiber. Because of the presence of a phenolic—OH group in the grass fiber, the material showed an antioxidant property; therefore, no foreign antioxidant is required in a grass-fiber-filled natural rubber composite. Such characteristics of grass–rubber composites indicate their better prospect in the future.

The percent retention of elongation at break of alkali-treated grass-fiber-loaded fiber–rubber composites after 72 h of aging is shown in Figure 5. Although after aging elongation at break decreased for all composites studied, the drop was more pronounced in the 200-mesh and 1-mm fiber-filled composites, which was a result of the increase in stiffness of the finished material.

Rubber–fiber interaction

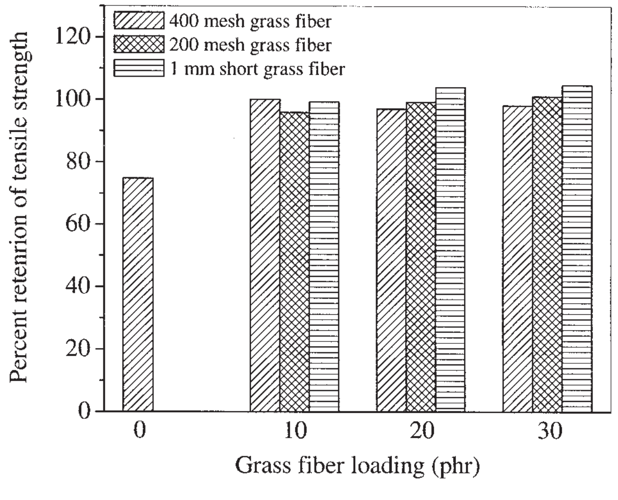


Figure 6 Percent retention of tensile strength after 72 h of aging.

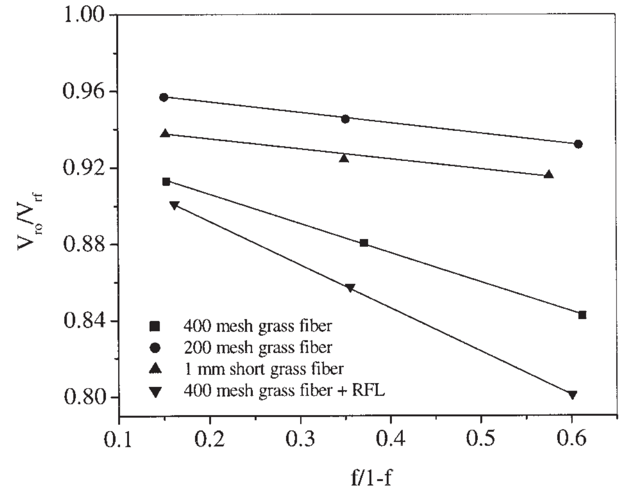


Figure 7 Variation of V_{ro}/V_{rf} with $f/1 - f$ (Kraus plot).

Because the Kraus equation is in the form of a straight line, a plot of V_{r0}/V_{rf} versus $f/1 - f$ should give a straight line whose slope (m) will be a direct measure of the reinforcement of the fiber. The ratio of V_{r0}/V_{rf} represents the degree of restriction of the swelling of the rubber matrix because of the presence of fiber. According to the Kraus theory, reinforcing fillers will have a negative higher slope. The Kraus plot, V_{r0}/V_{rf} against $f/1 - f$, is shown in Figure 7. In the present study it was found that as fiber loading increased, the solvent uptake of the sample decreased, causing an increase in V_{rf} values, which decreased the ratio of V_{r0}/V_{rf} because V_{r0} is constant. It can be seen from the graph that V_{r0}/V_{rf} decreased with fiber loading. Such a characteristic leads to a negative slope, indicating the fibers have a reinforcing effect. It is evident that the lowest V_{r0}/V_{rf} was obtained for the 30 phr 400-mesh alkali-treated grass-fiber-filled natural rubber composite. Again, in the presence of RFL, the value of V_{r0}/V_{rf} decreased further compared to that of the composite without RFL. This can be associated with enhanced fiber–rubber adhesion in the composite. Because there is better bonding between fiber and matrix because of a strong interface, it restricts the entry of solvent.

From the Cunneen–Russell equation, V_{r0}/V_{rf} is plotted against e^{-z}, which gives a straight line with a positive slope, as shown in Figure 8. This shows that as fiber loading increased, the extent of reinforcement also increased.

According to the Lorentz–Park equation, a plot of Q_f/Q_g versus e^{-z} produced a straight line with a positive slope, in good agreement with the above findings. The values of Q_f/Q_g with variable fiber loading and different mesh sizes of grass fibers are listed in Figure 9, which shows that the higher the Q_f/Q_g was, the lower was the extent of interaction between the fiber and the matrix. It can be seen from Figure 9 that as fiber loading increased, Q_f/Q_g decreased, indicating

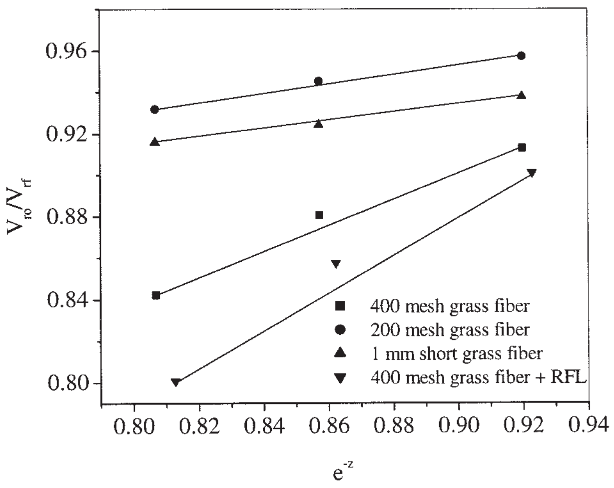


Figure 8 Variation of V_{ro}/V_{rf} with e^{-z} (Cunneen–Russell plot).

greater interaction between the grass fibers and the rubber matrix. The ratio of Q_f/Q_g was lowest for alkali-treated 400-mesh 30 phr grass-fiber-loaded vulcanizate in the presence of a bonding agent. This conclusively proves that the maximum interaction between grass fibers and rubber matrix occurs in the presence of RFL as the bonding agent.

Figure 10 shows the swelling value, which gives an indirect measure of crosslink density, of the grass-fiber-filled rubber vulcanizate plotted against different fiber loading values. It was found that for a particular mesh size, the grass-fiber-loading swelling value continuously decreased with an increase in fiber loading, that is, crosslink density increased as fiber loading increased. The swelling value of water-leached fiber-filled composite was higher than that of the alkali-treated fiber-filled composite, which confirmed the better adhesion between the alkali-treated fibers and the rubber matrix. The presence of a bonding agent further decreased the swelling of the composite, that is, crosslink density increased in the presence of a bonding agent. In addition to sulfur crosslink bonds in the matrix rubber phase, components of the RFL formed bonds with cellulosic units of grass and butadiene units of the RFL bonding agent. Also, the butadiene unit of RFL may form bonds with the rubber, both physically (secondary valence interaction) and chemically through sulfur. Hence, the inclusion of RFL-modified grass fiber in the rubber was able to increase the crosslink density.

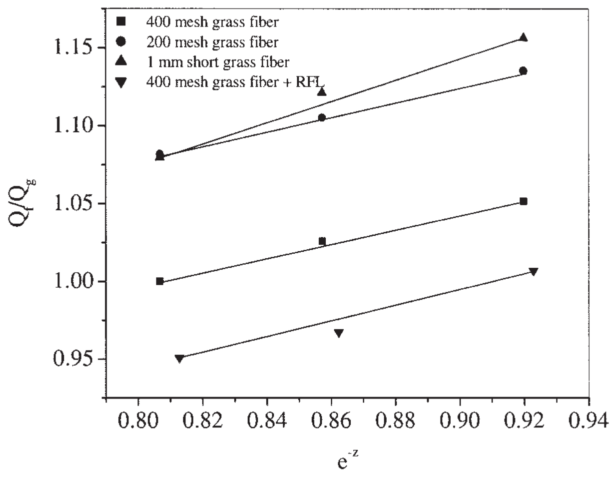


Figure 9 Variation of Q_f/Q_g with e^{-z} (Lorentz–Park plot).

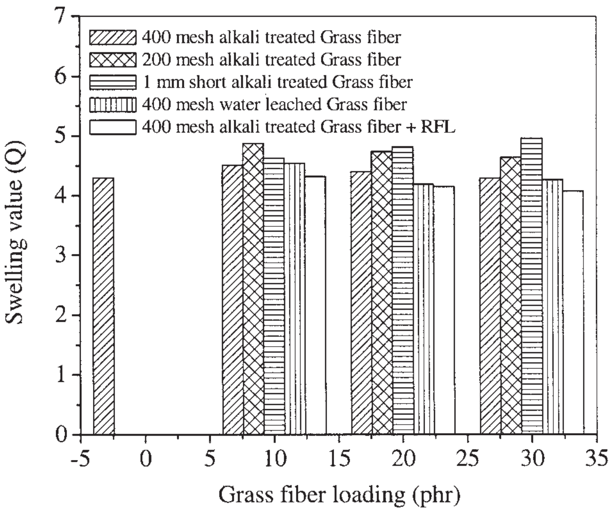


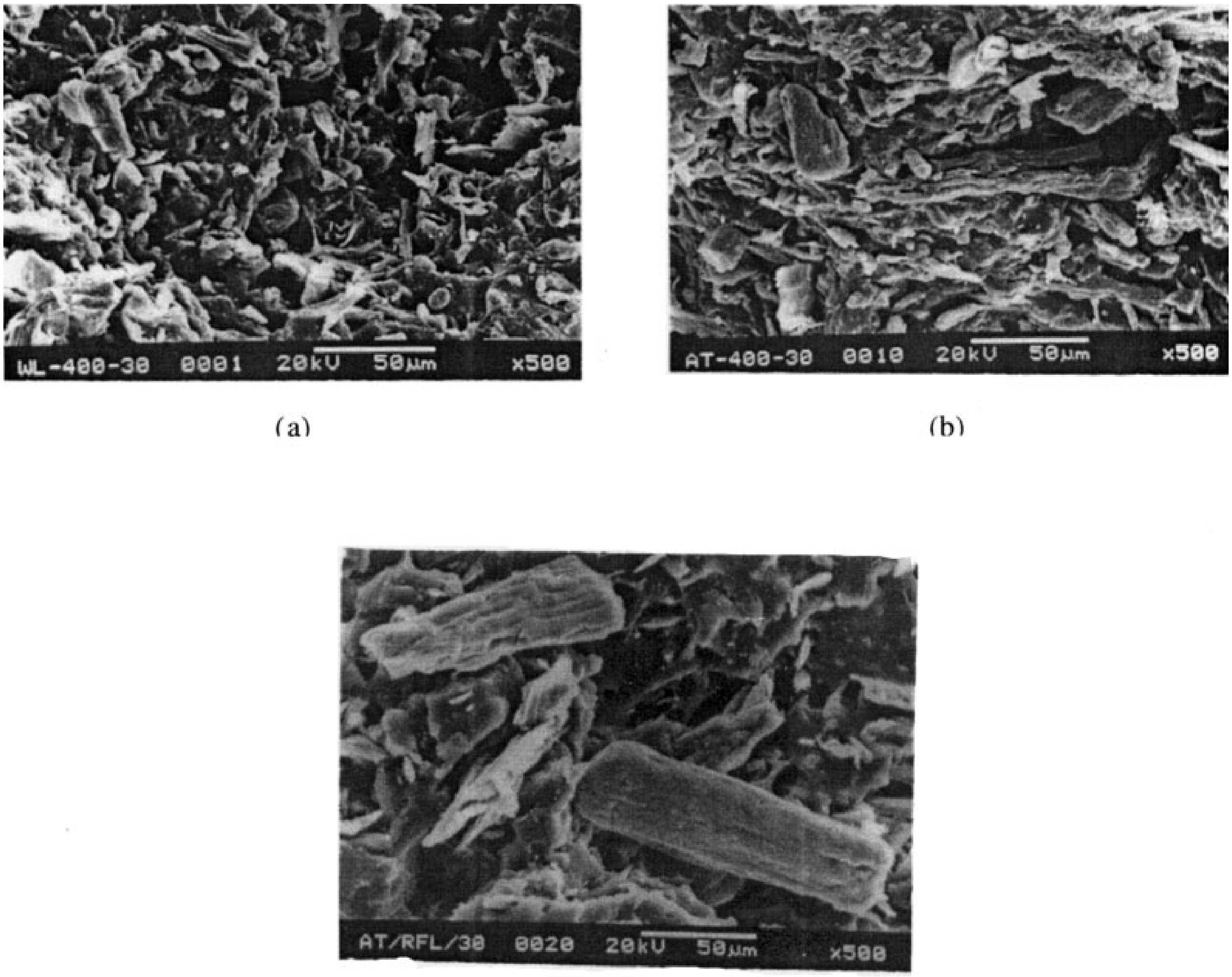
Figure 10 Variation of swelling value with different levels of fiber loading.

Scanning electron microscopy of grass-fiber-filled rubber composite

The SEMs of tensile-fractured surface of alkali-treated grass fiber–rubber composites, both in the presence and the absence of RFL, are shown in Figure 11(a–c). Figure 11(a) shows a water-leached fiber-filled NR composite, in which an increase in holes occurred because the fibers were pulled out from the rubber matrix. Figure 11(b,c) depicts the alkali-treated fiber-filled NR composite in the absence and the presence of the RFL bonding agent, which showed better adhesion occurring between the fibers and the rubber matrix. The fibers were well wetted by the rubber matrix, and there was fiber breakage because of strong adhesion.

CONCLUSIONS

- Maximum rheometric torque increased with increased fiber loading, which further increased in the presence of RFL as the bonding agent. This



(a)

(b)

(c)

Figure 11 SEM photographs of grass-fiber-filled natural rubber compounds: (a) WL-400-30 phr at 500×; (b) AT-400-30 phr at 500×; (c) AT-400-30 phr + RFL at 500×.

indicates better adhesion between the grass fiber and the rubber matrix.

- The optimum cure time decreased with an increase in alkali-treated grass fiber loading, but in the presence of RFL, this value was higher than that of the composite without RFL.
- RFL treatment of grass fiber increased the modulus, hardness, and crosslink density of the vulcanizate but also increased the tensile strength and elongation at break of the composite.
- The grass-fiber-filled composite showed a antiaging property superior to that of the control formulation.
- The SEM micrograph of the water-leached grass-fiber-filled composite shows that the fiber pulled out from the composite, whereas in the alkali-treated grass fiber composite with RFL as the bonding agent, the fibers were well wetted by the rubber matrix, and there were fiber breakage because of strong adhesion.

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