Preparation of Rubber Composites from Ground Tire Rubber Reinforced with Waste-Tire Fiber Through Mechanical Milling

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ABSTRACT: Composites made from ground tire rubber (GTR) and waste fiber produced in tire reclamation were prepared by mechanical milling. The effects of the fiber content, pan milling, and fiber orientation on the mechanical properties of the composites were investigated. The results showed that the stress-induced mechanochemical devulcanization of waste rubber and the reinforcement of devulcanized waste rubber with waste-tire fibers could be achieved through comilling. For a comilled system, the tensile strength and elongation at break of revulcanized GTR/fiber composites reached maximum values of 9.6 MPa and 215.9%, respectively, with 5 wt % fiber. Compared with those of a composite prepared in a conventional mixing manner, the mechanical properties were greatly improved by comilling. Oxygen-containing groups on the surface of GTR particles, which were produced during pan milling, increased interfacial interactions between GTR and waste fibers. The fiber-filled composites showed anisotropy in the stress–strain properties because of preferential orientation of the short fibers along the roll-milling direction (longitudinal), and the adhesion between the fiber and rubber matrix was improved by the comilling of the fiber with waste rubber. The proposed process provides an economical and ecologically sound method for tire-rubber recycling. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 4087–4094, 2007

Key words: adhesion; fibers; recycling; rubber; waste

INTRODUCTION

The disposal problems created by waste-rubber vulcanizates is a serious challenge to our society because they do not decompose easily. Much research has been conducted to solve this worldwide problem,[1–5] and one approach is to devulcanize ground tire rubber (GTR)[6–9] to break up the three-dimensional network in vulcanized rubbers. The devulcanized rubber becomes soft and can be reprocessed, shaped, and revulcanized in the same way as virgin rubber.[10] One of the drawbacks of such revulcanizates is a weaker matrix. One way of overcoming this problem is the use of short fibers, which impart good strength and stiffness to the rubber matrix. Short-fiber-reinforced elastomers have been successfully used in the production of hoses, V-belts, tire treads, seals, and complex-shaped mechanical goods.[11] The properties of short-fiber-reinforced composites mainly depend on the type and concentration of the fiber, the orientation and distribution of the fiber after mixing, the aspect ratio of the fiber, and the degree of adhesion between the fiber and the matrix.[12,13] The interfacial bond is known to play an important role in composites because this interface is critical to the composite performance. Waste fibers represent another type of environmental problem and are normally disposed of in controlled dumps or subjected to expensive recycling processes. In the process of tire recycling, approximately 10% waste fibers are obtained. These large quantities of byproducts contain about a 30–35% loading of waste-rubber powder. A process that could use these types of wastes would represent an important environmental benefit and great economic savings for the community.

Recently, a new technique for pulverizing plastic pellets to fine powders and recycling GTR based on a stress-induced reaction has been developed in our laboratory.[14–16] The technique provides high-volume production of fine or ultrafine rubber powders by pulverizing large elastomer chips or particles from scrap rubber at the ambient temperature and is feasible for rubber recycling on an industrial scale. In addition, the processing properties and compatibility of the GTR powder with other polymeric compo-

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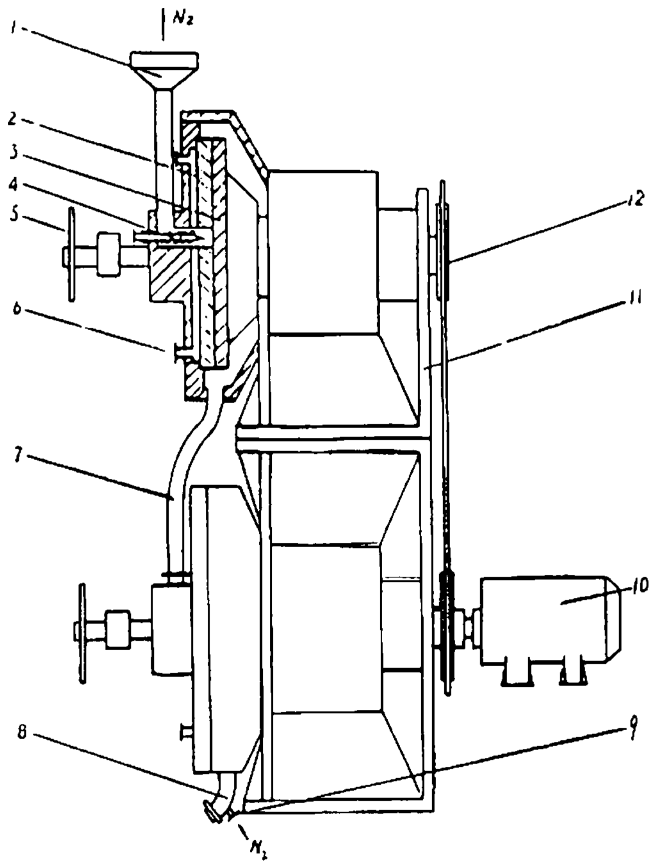


Figure 1 Schematic diagram of a pan-mill mechanochemical reactor: (1) inlet, (2) stationary pan, (3) moving pan, (4) feeding screw, (5) handle, (6) medium entrance, (7) flexible tube, (8) outlet, (9) entrance of inert gas, (10) motor, (11) stand, and (12) drive system.

nents are improved through a stress-induced reaction due to surface activation through mechanochemical devulcanization of rubber via the breakage of —S—S— bonds induced by stress. The main purpose of this study is to examine the possibility of making composite materials by recycling large amounts of waste tires and waste-tire fibers produced by rubber reclamation. The effects of the fiber content, mechanical milling by the pan-milling equipment designed in our laboratory, and fiber orientation on the mechanical properties of the composites were investigated.

EXPERIMENTAL

Materials

The reclaimed rubber powder (60 mesh) used in this study was generated by cryogenic grinding of passenger-car and light-truck tires. The waste short fiber used was the byproduct of tire reclamation. Other compounding ingredients, such as zinc oxide, stearic acid, sulfur, and *N*-cyclohexyl benzthiazyl sulfenamide (CBS) were reagent-grade and were obtained commercially.

Mechanical milling equipment

GTR and its mixture with waste short fibers were milled with a pan-mill mechanochemical reactor. Figure 1 is a simple scheme of the equipment, and Figure 2 shows the structure of its key part, the milling pan. A chain-transmission system and a screw-pressure system are set to regulate the rotation speed of the moving pan and imposed load, respectively, which can strictly control two major dynamic parameters, the velocity and force during milling. Cooling water flows through the hollow interior of the pan to take away the heat generated during milling; through the control of the flow, the milling temperature is adjustable. The milling process of the solid mass in the equipment operates as follows: the materials are fed to the center of the pan from the inlet, driven by a shear force, and move along a spiral route toward the edge of the pan until they come out from the outlet; thus, one cycle of milling is finished.

Devulcanization of GTR and comilling with waste fibers

In this study, a pan-mill mechanochemical reactor was developed to partly devulcanize GTR at the ambient temperature. Reclaimed rubber powder was milled at the ambient temperature for a certain number of cycles at a rotation speed of 30 rpm, the average residence time of coarse rubber powder during milling was 25–40 s per cycle, and the heat produced during milling was removed by water circulation. Pan-milled GTR was sampled to measure the gel fraction. To improve the adhesion between

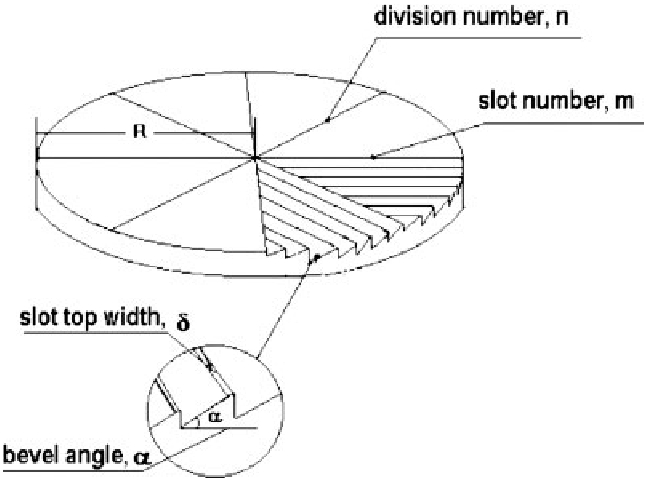


Figure 2 Schematic diagram of an inlaid mill pan.

TABLE I
Formulations of the Vulcanized Systems

Material	Weight per 100 parts of rubber powder
Reclaimed rubber powder	100 (milled or without milling)
Waste short fiber	0, 5, 10, 15
Zinc oxide	2
Stearic acid	1
CBS	0.5
Sulfur	1.5

the fiber and rubber matrix, the comilling of waste fibers with GTR was conducted.

Preparation of the rubber mixes and vulcanizates

The formulations used for the preparation of the composites are given in Table I. Mixing was carried out on a conventional laboratory two-roll mill at a friction ratio of 1 : 1.2 according to ASTM D 3184-80. The roll temperature was kept at about 50°C during mixing. Waste fiber was separated manually and added in small increments to obtain a uniform dispersion. The compounds were rolled along the milling direction and resent through the mill to obtain the maximum fiber orientation in the milling direction. The sheeted rubber compound was conditioned at room temperature for 24 h before vulcanization. Each sample was cured in a hydraulic press at 150°C under 10 MPa of pressure for 15 min.

Mechanical property testing

The green strength values were determined with dumbbell-shaped samples obtained from unvulcanized composites at a crosshead speed of 500 mm/min in an Instron 4302 universal testing machine. The stress–strain properties were measured according to ASTM D 412-80 specifications with dumbbell specimens. The tear strength was determined per ASTM D 624-81 with angular tear specimens. At least five measurements for each composition were made. The hardness of the composite was measured with a Shore A durometer according to ASTM 2240.

Determination of the gel fraction of the devulcanized rubber

The gel fractions of GTR obtained at different milling cycles were measured by the Soxhlet extraction method with toluene as a solvent. The specimens (ca. 1 g) were accurately weighed (M_i), closed in filter paper, and extracted with toluene. The extracted samples were then placed in a vacuum chamber and dried at 60°C for 4 h so that the solvent would vaporize, and the dry, insoluble part was obtained. This yielded the weight of the dried sample (M). The gel fraction was determined as follows:

$$\text{Gel fraction (\%)} = M/M_i \times 100\%$$

Electron spectroscopy for chemical analysis (ESCA) measurements

To determine the introduction of the functional groups into the GTR particles, the surfaces of the GTR particles at different milling cycles were analyzed with ESCA. The ESCA measurements were made with an XSAM-800 photoelectron spectroscope (Kratos Analytical, Manchester, UK). The instrument used a nonmonochromatic Mg Kα X-ray source.

Scanning electron microscopy (SEM) observation

The morphology of the fiber surface and fractured surface of the composite was observed under a JEOL JSM-5600 scanning electron microscope (JEOL Ltd., Akishima, Japan). A thin layer of a Pd–Au alloy was coated onto the specimen to prevent charging on the surface. The scanning electron microscope was operated at 20 kV. The fractured surface of the composites was prepared through the freezing of the composite in liquid nitrogen and then rapid breaking above the surface of liquid nitrogen.

RESULTS AND DISCUSSION

Stress-induced mechanochemical devulcanization of waste vulcanized rubber

The gel fractions and tensile properties of devulcanized rubber and revulcanized rubber are shown in Table II. Pan milling has the effect of simultaneous degradation (the breakage of the carbon bonds at

TABLE II
Gel Fractions and Tensile Properties of Devulcanized Rubber and Revulcanized Rubber

Sample	Gel fraction (%) of devulcanized rubber	Tensile strength (MPa)	Elongation at break (%)
Without milling	90.3	4.4	109.0
Milled for 5 cycles	88.4	6.6	154.3
Milled for 10 cycles	86.5	8.1	202.5
Milled for 15 cycles	81.3	4.2	122.1

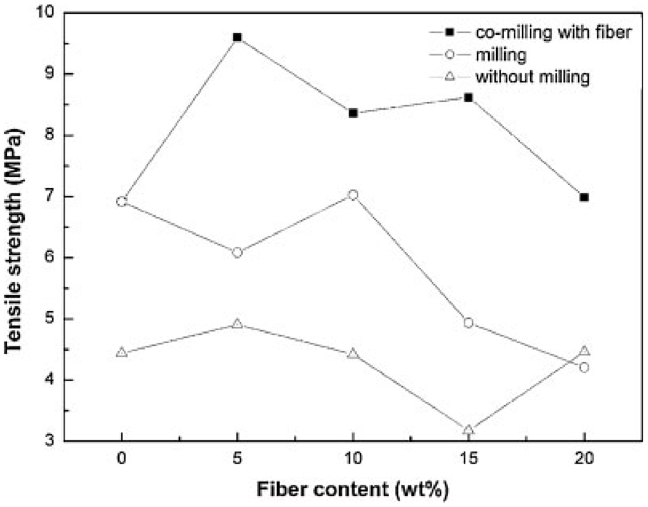


Figure 3 Effects of the waste-fiber content and pan milling on the tensile strength: (■) comilling with fiber, (○) milling, and (△) without milling.

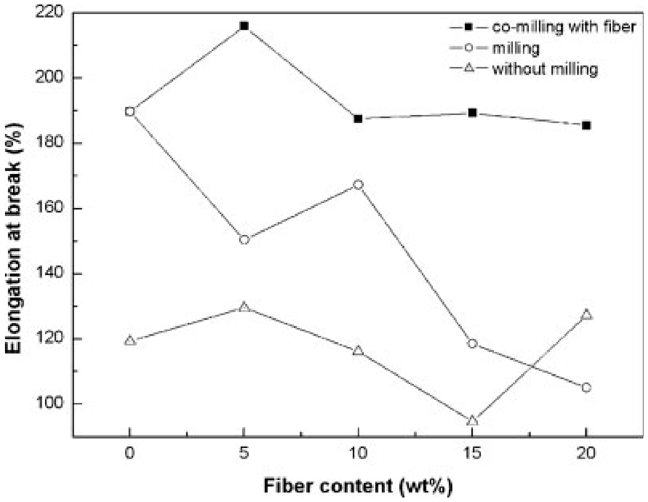


Figure 4 Effects of the waste-fiber content and pan milling on the elongation at break: (■) comilling with fiber, (○) milling, and (△) without milling.

the backbone of the rubber) and devulcanization (the breakage of the sulfur–sulfur crosslinking bond) on GTR. The results show that for 60-mesh reclaimed rubber powder, 10 cycles of milling are optimum for the devulcanization of GTR. Up to 15 cycles, the degradation of the rubber backbone is predominant, and this results in the deterioration of the mechanical properties. Therefore, 10 milling cycles were performed for all the compositions in this study.

Effects of the waste-fiber content and pan milling on the mechanical properties

The effects of the waste-fiber content and pan milling on the tensile strength and elongation at break are shown in Figures 3 and 4, respectively. In Figures 3 and 4, ''without milling'' represents blends of raw GTR and waste fiber prepared in a conventional mixing manner; that is, the waste fiber was separated manually and added to the compounds during open two-roll mixing. ''Milling'' represents blends of pan-milled GTR and waste fiber prepared in a conventional mixing manner, and ''comilling'' represents GTR/waste-fiber composites in which waste fibers were comilled with GTR. The experimental results indicate that the tensile strength and elongation at break of the blends decrease with the fiber content, except for the comilled system. The deterioration of the tensile properties of the composites prepared in a conventional mixing manner can be attributed to the poor adhesion of waste fibers to the rubber matrix. During straining, voids at the ends of the fibers will be created and hence initiate crack development. The probability of failure increases as a result of the number of voids increasing with the fiber content.[17]

In the case of the comilling system, the reinforcement of waste fiber on GTR can be observed up to a fiber content of 15 wt %. The tensile strength and elongation at break of revulcanized GTR/waste-fiber composites reached maximum values of 9.6 MPa and 215.9%, respectively, with 5 wt % fiber. Better bonding of the short fiber to the rubber matrix is the main reason for the composites. Because of its unique structure, the pan-mill equipment acts as three-dimensional scissors during milling, exerts strong shear forces, and shows multiple functions, such as pulverization, dispersion, mixing, and activation on the materials undergoing mechanical action. During the comilling of the fibers with GTR, the size reduction and surface activation of the particles are predominant in the initial milling stage. Table III exhibits the variation of the elemental concentration on the GTR surface during pan milling; this was obtained from ESCA spectra. The oxygen concentration on the GTR particle surface increases with increasing milling cycles. The increase in the number of oxygen-containing groups on the surface of GTR particles indicates that reactions occur between the oxygen in air and the free radicals generated during pan milling. The introduction of the polar groups containing

TABLE III
Variation of the Elemental Concentrations on the GTR Surface During Pan Milling

	Relative concentration (%)		
Sample	C	O	S
Without milling	96.46	3.17	0.37
Milled for 15 cycles	94.82	4.74	0.44
Milled for 25 cycles	94.43	5.10	0.47

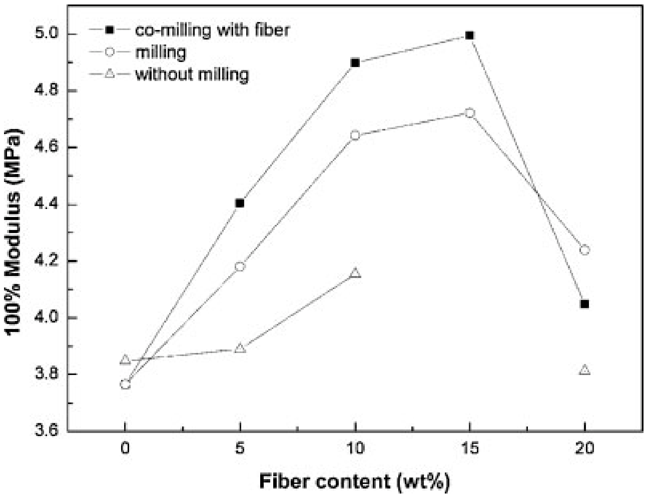


Figure 5 Effects of the waste-fiber content and pan milling on the 100% modulus: (■) comilling with fiber, (○) milling, and (△) without milling.

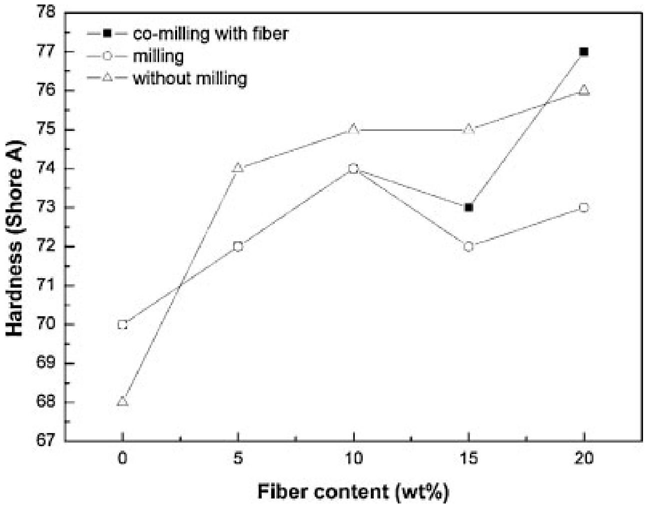


Figure 6 Effects of the waste-fiber content and pan milling on the hardness: (■) comilling with fiber, (○) milling, and (△) without milling.

oxygen facilitate interfacial interactions between GTR and waste fibers and thus enhance the interfacial adhesion. According to Hanafi,[18] strong adhesion between the fiber and rubber matrix results in higher shear strength at the interface, and a stronger force must be used to overcome the shear strength at the interface, which results in a higher tensile strength.

Another reason is that the strong shear force exerted by pan milling can homogeneously distribute fibers in the matrix. Because of the brittle nature of the short fiber, extensive breakage of the fiber occurs during pan milling, and this subsequently improves fiber dispersion.

However, the tensile strength and elongation at break show that the effective reinforcement of devulcanized GTR with waste fiber takes place only below a fiber content of 20 wt %. At higher fiber contents, the matrix cannot effectively wet all the fibers, and the strength decreases.

The results for the tensile properties given in Figures 3 and 4 show that the waste fiber without comilling with GTR cannot effectively reinforce a devulcanized GTR matrix.

Figures 5 and 6 show the results of the modulus at 100% elongation and the hardness of the GTR/waste-fiber composites, respectively. The elongation at break of the without-milling system with a fiber content of 15 wt % is smaller than 100%, so its 100% modulus cannot be obtained. The addition of waste fibers to the GTR matrix leads to an increase in the 100% modulus and Shore A hardness because of the stiff nature of the short fibers. However, the tensile modulus shows a sharp decrease at a fiber content of 20 wt %. This can be ascribed to the poor dispersion of short fibers in the rubber matrix with fiber contents up to 20 wt %; the tendency of stress transfer from the matrix to the fibers decrease, so the tensile modulus decreases.

As shown in Figure 5, the comilled composites show the highest value of the 100% modulus because of the better adhesion of waste fibers in the rubber matrix and improved fiber dispersion in the matrix. The stronger adhesion at the fiber and matrix interface causes better stress transfer from the matrix into the fibers, thus leading to a higher tensile modulus.

The effects of the waste-fiber content and pan milling on the tear strength show that the tear strength of the composites increases with increasing fiber contents up to 20 wt %. The tear strength is minimum for the composite obtained without milling (Fig. 7). The experimental results for the effects

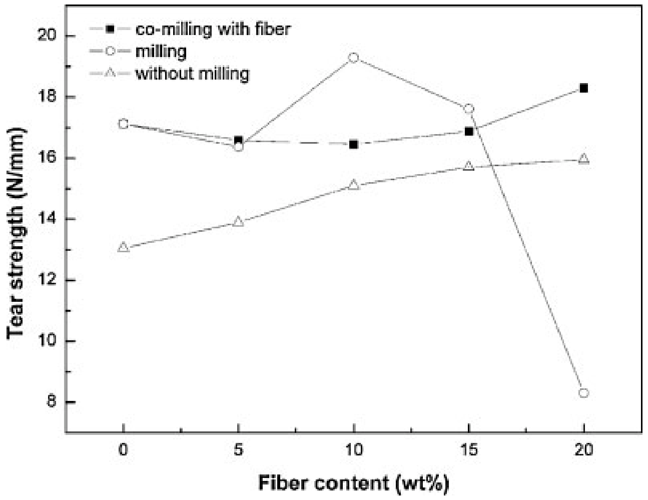


Figure 7 Effects of the waste-fiber content and pan milling on the tear strength: (■) comilling with fiber, (○) milling, and (△) without milling.

TABLE IV
Mechanical Properties of the Composites: Effect of the Fiber Orientation

Sample[a]	Tensile strength (MPa)	Elongation at break (%)	100% modulus (MPa)	Tear strength (MPa)
5 wt % L	9.6	215.9	4.4	16.6
5 wt % T	8.2	202.7	3.9	12.7
10 wt % L	8.4	187.5	4.9	16.5
10 wt % T	7.2	174.6	4.3	15.2
15 wt % L	8.6	189.3	5.0	16.9
15 wt % T	7.4	197.3	4.0	14.7
20 wt % L	7.0	185.6	4.0	18.3
20 wt % T	6.8	182.5	4.1	13.5

[a] L, longitudinal; T, transverse.

of pan milling on the mechanical properties of the composites indicate that comilling waste fibers with GTR is essential to improving the fiber dispersion in the matrix and the adhesion between the waste fiber and rubber matrix.

Effects of the short-fiber orientation on the mechanical properties

Table IV displays the effects of the short-fiber orientation on the tensile strength, elongation at break, 100% modulus, and tear strength of the composites and indicates that all of them have higher values in the longitudinal direction than in the transverse direction. The short fibers align themselves along the two-roll-milling direction, inducing anisotropy in the properties.[19] As reported by Sreeja and Kutty,[20] in the longitudinal direction, the fibers increase the overall strain resistance and hinder the growing crack front and hence higher tensile strength values; the smaller values of the tear strength in the transverse direction result from the inability of fibers aligned parallel to the crack propagation to block the advancing crack front.

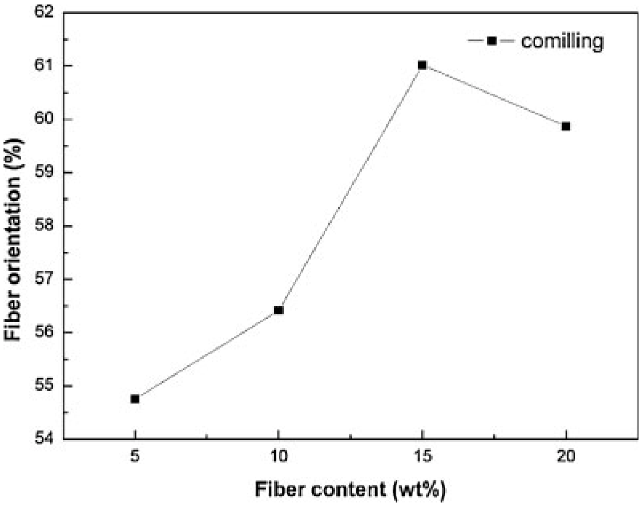


Figure 8 Variation of the fiber orientation percentage with the fiber content.

The green strength values of comilled composites obtained from unvulcanized composites also confirm the preferential orientation of the fibers in the two-roll-milling direction. The green strength of short-fiber-reinforced unvulcanized composites depends on the degree of fiber orientation, and so the latter can be obtained as follows:[21]

$$\text{Fiber orientation (\%)} = \frac{S_L/S_{G,L}}{S_L/S_{G,L} + S_T/S_{G,T}} \times 100\%$$

where S represents the green strength and subscripts G, L, and T represent gum, longitudinal, and transverse, respectively.

The variation of the fiber orientation percentage of the composites with various amounts of fiber is shown in Figure 8. The fiber orientation percentage increases with increasing fiber content up to 15 wt % and then decreases with further increasing fiber content. According to Geethamma et al.,[22] at low levels of the fiber content, the fibers can assume a multitude of alignment directions, and the freedom of

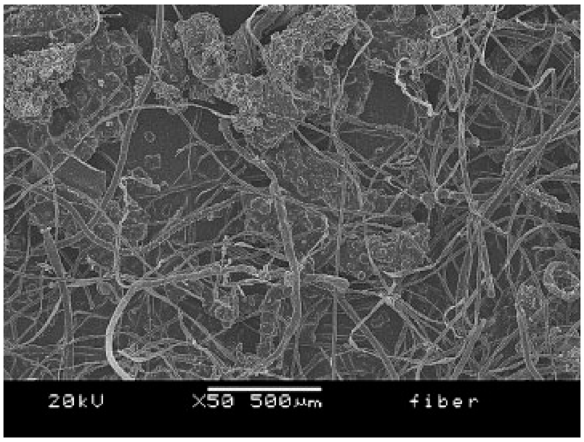
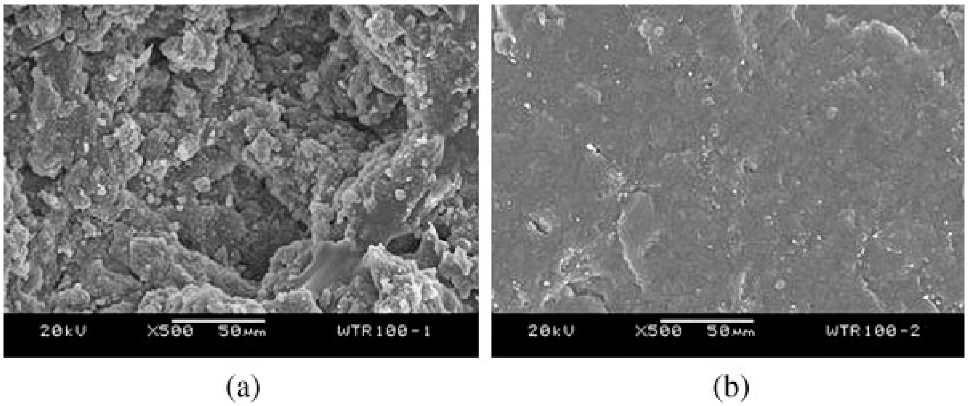


Figure 9 SEM micrograph of waste fibers.



(a) (b)

Figure 10 SEM fractographs of reprocessed GTR sheets (a) from GTR before and after (b) mechanochemical devulcanization.

movement is greater. When the fiber content is up to 20 wt %, the fibers cannot orient themselves in the unidirectional fashion that occurs in composites containing less fiber content because of entanglement as a result of the overpopulation of fibers.

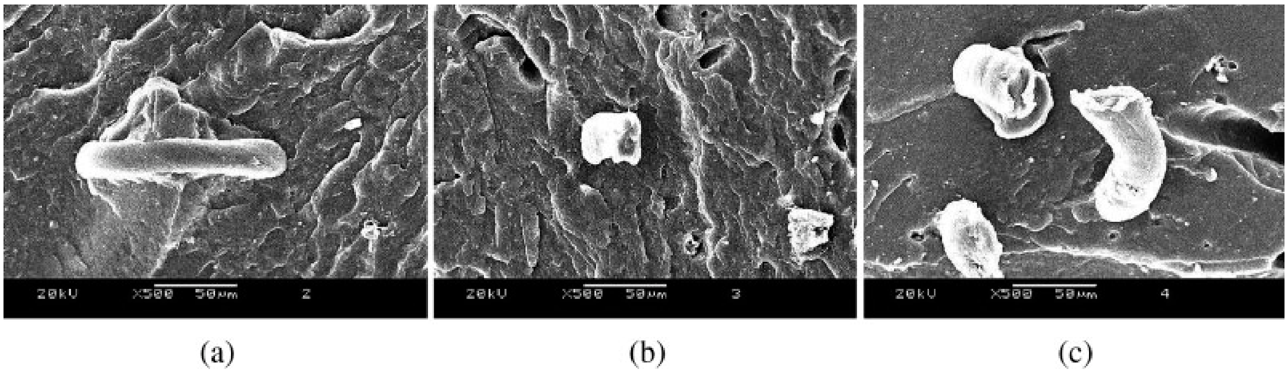
However, the degree of anisotropy in the tensile strength is lower than that in the composite of short fibers and virgin rubber reported by Geethamma et al.[22] The main reason is that the preferential orientation of fibers in the two-roll-milling direction is more prominent if the fibers are well bound to the matrix. Again, the length-to-diameter ratio of the fibers significantly decreases during pan milling, and this consequently leads to the degree of anisotropy decreasing.

SEM observations

Figure 9 shows an SEM micrograph of waste fibers used in this study and produced in waste-tire reclamation; the filaments are long and continuous. The waste fiber consists of adhered fiber and rubber particles, and this kind of structural feature will lead to the poor distribution of the fiber in the rubber matrix. This factor, together with the poor adhesion of waste fibers to the rubber matrix, is responsible for the deterioration of the mechanical properties of the composites without comilling.

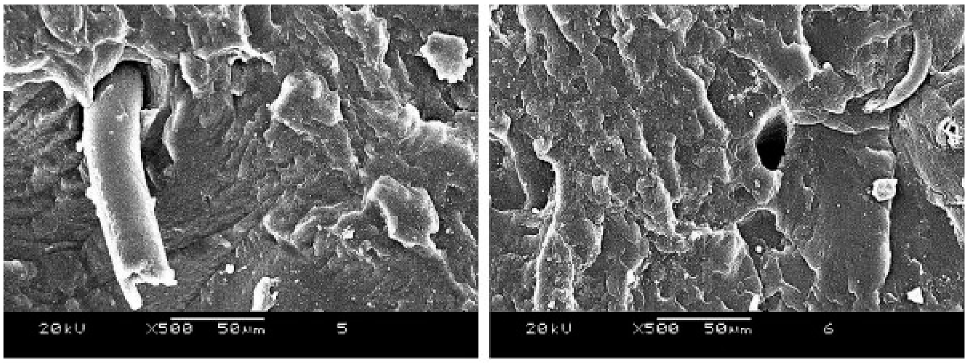
SEM fractographs of reprocessed GTR sheets from GTR before and after mechanochemical devulcanization are displayed in Figure 10(a,b), respectively. The reprocessed GTR sheets from undevulcanized GTR exhibit a rough surface, and the rubber particle adhere loosely with many voids, which lead to poor mechanical properties. As for the reprocessed rubber sheets prepared from ground GTR obtained by pan milling, the rubber particles are tightly bond and form a continual structure because of devulcanization induced by stress, which is favorable to the improvement of the mechanical properties of the milled sample.

The improvement in the mechanical properties of the rubber composites obtained through comilling is supported by the morphology of the fractured surface. SEM micrographs of the fractured surfaces of comilled composites with 5, 10, and 20 wt % fiber concentrations are shown in Figure 11(a–c), respectively. The SEM micrographs of the comilled composites show stronger adhesion occurring at the fiber/matrix interface, at which the fiber is strongly



(a) (b) (c)

Figure 11 SEM fractographs of GTR/waste-fiber composites prepared via comilling with various fiber contents: (a) 5, (b) 10, and (c) 20 wt %.



(a) (b)

Figure 12 SEM fractographs of GTR/waste-fiber composites, with fiber contents of (a) 5 wt % and (b) 10 wt %, prepared in a conventional mixing manner.

bonded to the rubber matrix, even at a fiber content up to 20 wt %. As a result, the mechanical properties of the comilled composites are improved. However, the fractured surface of similar composites prepared without comilling, displayed in Figure 12(a,b), exhibits weak interfacial adhesion between the fiber and rubber matrix. Failure will occur easily at the weak interface between the fiber and rubber matrix when stress is applied. In addition, the fiber orientation can be observed from the SEM micrographs of the composites.

CONCLUSIONS

On the basis of this investigation, it is concluded that the reinforcement of devulcanized GTR with waste-tire fibers can be achieved without any compatibilizer or fiber modification. The compatibilizing effect and adhesion between the waste-tire fiber and waste-rubber matrix can be greatly enhanced by the comilling of waste fibers with waste rubber. The variation of the elemental concentration on the GTR surface has confirmed that oxygen-containing groups are introduced onto the surface of GTR particles during pan milling and subsequently increase interfacial interactions between GTR and waste fibers. Meanwhile, the dispersion of fiber into the rubber is also improved. The mechanical properties of the composites are consequently enhanced. The reinforcement of waste-tire fiber on waste rubber is explained on the basis of the stress transfer from the matrix into the fibers according to the interfacial adhesion. The deterioration of the mechanical properties at a higher fiber loading may be attributed to the volume effect of the filler. The fiber-filled composites show anisotropy in the stress–strain properties because of the preferential orientation of the short fibers along the two-roll-milling direction (longitudinal), which is substantiated by the results for the green strength. The proposed process provides an efficient method for GTR recycling to produce rubber composites with acceptable mechanical properties.

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