Short Sisal Fiber-Reinforced Tire Rubber Composites: Dynamic and Mechanical Properties

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ABSTRACT: The world tendency toward using recycled materials demands new products from vegetable resources and waste polymers. In this work, composites made from powdered tire rubber (average particle size: 320 μm) and sisal fiber were prepared by hot-press molding and investigated by means of dynamic mechanical thermal analysis and tensile properties. The effects of fiber length and content, chemical treatments, and temperature on dynamic mechanical and tensile properties of such composites were studied. The results showed that mercerization/acetylation treatment of the fibers improves composite performance. Under the conditions investigated the optimum fiber length obtained for the tire rubber matrix was 10 mm. Storage and loss moduli both increased with increasing fiber content. The results of this study are encouraging, demonstrating that the use of tire rubber and sisal fiber in composites offers promising potential for nonstructural applications. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 670–677, 2004

Key words: sisal fibers; rubber; composites; mechanical properties; viscoelastic properties

INTRODUCTION

Economical recycling of used tires and use of new materials from renewable resources are a great challenge today. Many natural fibers have been successfully used for elastomer reinforcement in the production of low-cost composite materials.[1–4] Among natural fibers, sisal fibers are especially suitable because of their good physicochemical and mechanical properties.[5]

Almost all worn-out rubber tires are discarded and degrade very slowly because of the crosslinked structure of the rubber and the presence of stabilizers and other additives.[6,7] Commercially, one of the most popular uses of powdered tire rubber is for golf courses, industrial flooring, and roads.[8] Although several studies have been done for its applications in, for example, polymer mortar,[9] thermoplastic elastomers,[10] and as an additive to cement paste,[11] only few studies have used powdered tire rubber in natural fiber–reinforced composites.[12–14]

One of the most important factors for obtaining good reinforcement in polymer composites is the bonding between fiber and matrix, which depends on the structure and polarity of the component materials.[15] As reported by Varghese et al.,[3,15] the surface of sisal fiber can be modified by acetylation treatment, which was found to improve its adhesion properties to natural rubber. The effects of fiber orientation, content, and fiber surface treatment on the dynamic mechanical properties of sisal fiber–reinforced natural rubber composites were studied.[15]

The aim of this work was to investigate the effect of fiber length, content, and chemical treatments (mercerization and acetylation) on the dynamic mechanical and tensile properties of short sisal fiber–reinforced tire rubber composites.

EXPERIMENTAL

Materials

Sisal fibers were from the variety *Agave sisalana*, supplied by Embrapa Algodão (Embrapa/CNPA/Brazil). The average chemical composition for this variety is as follows: cellulose: 75.2 ± 0.3%; hemicellulose: 13.9 ± 0.1%; lignin: 8.0 ± 0.1%; and ash: 0.87 ± 0.01%.[16]

Fiber density was 1.31 ± 0.03 g cm^{-3}, as measured using a Micromeritics 1305 helium picnometer, and the average fiber diameter was 124 ± 26 μm (150 fibers were measured).

Powdered tire rubber having 320 μm average particle size was supplied by Borcol Indústria de Borracha Ltda (Sorocaba, S.P., Brazil), and were from buses and trucks. Natural rubber and poly(butadiene-*co*-styrene) (SBR) were the main components of the tire rubber used, and the density of particles was 1.152 ± 0.001 g cm^{-3}.[11]

TABLE I
Compositions of the Tire Rubber/Sisal Fiber Composites

Sample	Tire rubber (%)	Raw fiber (length)	Mercerized fiber (length)	Mercerized/acetylated fiber (length)
A	100	—	—	—
B	95	5% (2 mm)	—	—
C	95	5% (5 mm)	—	—
D	95	5% (10 mm)	—	—
E	95	5% (15 mm)	—	—
F	95	5% (20 mm)	—	—
G	95	5% (25 mm)	—	—
H	90	10% (10 mm)	—	—
I	95	—	5% (10 mm)	—
J	90	—	10% (10 mm)	—
K	95	—	—	5% (10 mm)
L	90	—	—	10% (10 mm)

TABLE II
Mechanical Properties of the Raw, Mercerized (5% NaOH, 80°C, 5 h), and Mercerized (5% NaOH, 80°C, 5 h)/Acetylated Sisal Fiber

| Fiber	Modulus (GPa)	Ultimate tensile strength (MPa)	Elongation at break (%)
Raw	30 ± 13	701 ± 306	3 ± 1
Mercerized	24 ± 5	596 ± 124	3 ± 1
Mercerized/acetylated	27 ± 5	557 ± 93	3 ± 1

Analytical-grade sodium hydroxide and acetic anhydride were purchased from Mallinckrodt (Paris, KY); sulfuric acid and glacial acetic acid were purchased from Synth and J. T. Baker, respectively. All reagents were used as received.

Methods

Sisal fiber samples were washed in distilled water at 80 ± 2°C for 1 h. The washed fibers were then mercerized with 5% sodium hydroxide (NaOH) at 80°C for 5 h, removed, rinsed with tap water, then neutralized with acetic acid and dried.

For the acetylation treatment, the fibers were immersed in glacial acetic acid for 1 h at room temperature (26 ± 2°C), separated, and immersed for 5 min in 50 mL of acetic anhydride containing 2 drops of concentrated sulfuric acid, according to the procedure reported by Chand et al.[17] These fibers were filtered in a Buchner funnel, rinsed with tap water to achieve a
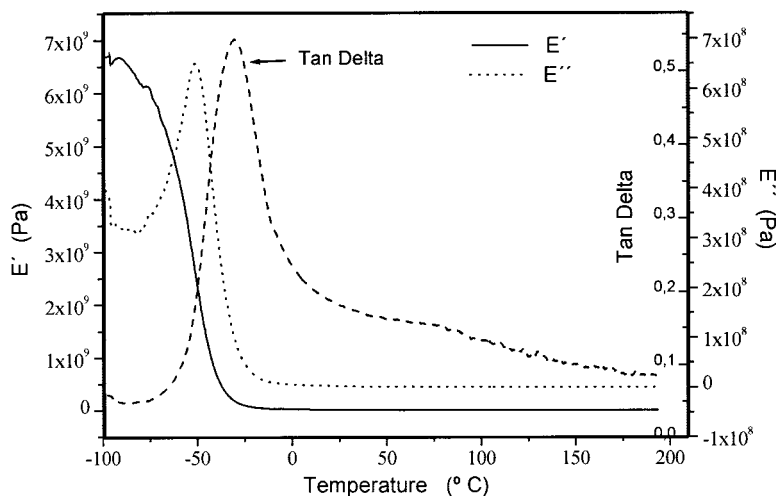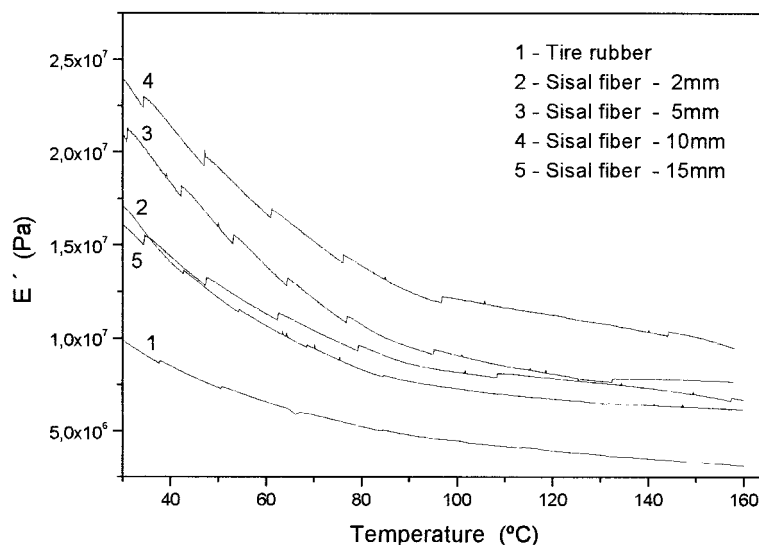

Figure 1 DMTA curves of the tire rubber depicting variation of tensile storage modulus (E'), tensile loss modulus (E''), and loss factor (tan δ) as a function of temperature (°C). Frequency 10 Hz.
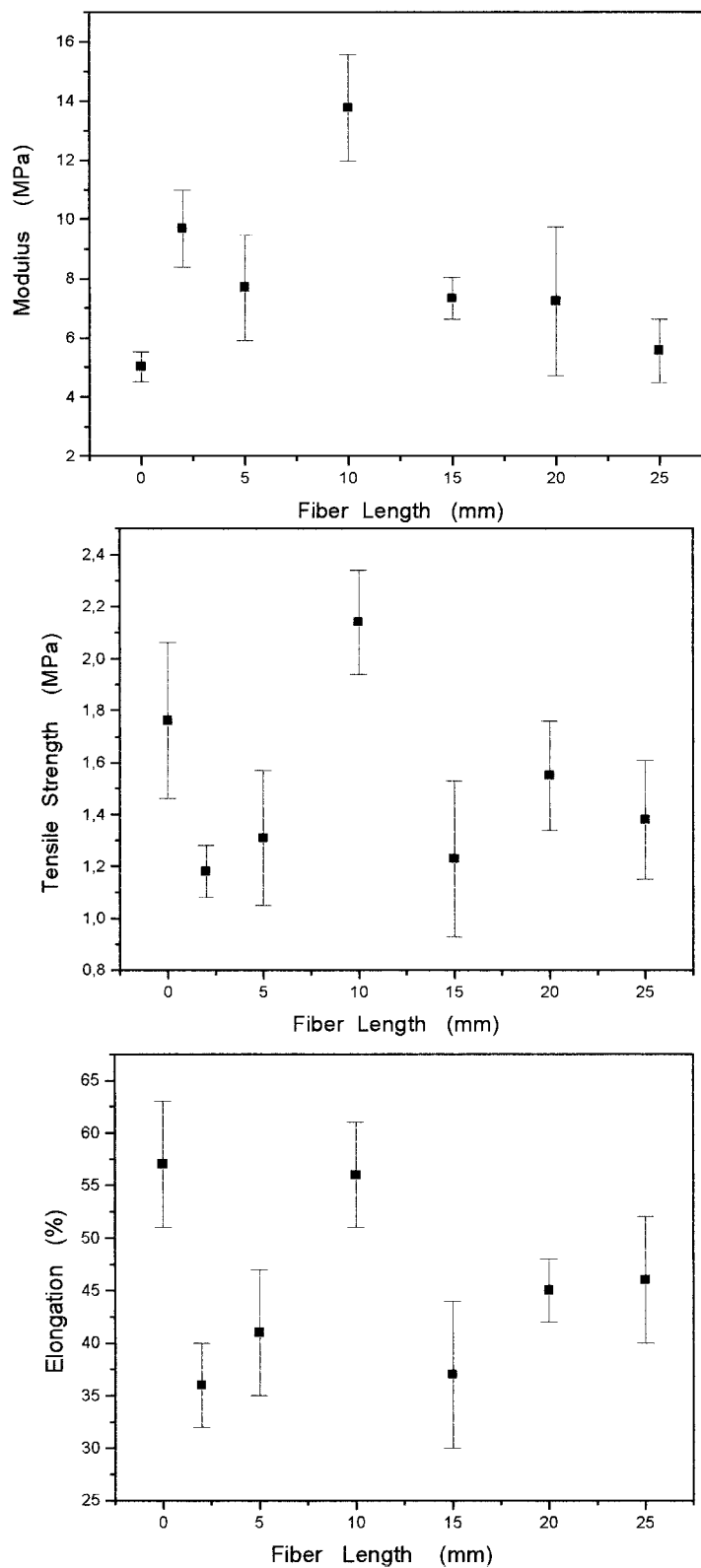
Figure 2 Mechanical properties of tire rubber/raw sisal fiber composites at different fiber lengths. Zero fiber length means the matrix without any fibers.

pH between 6 and 7, and then dried in a microwave oven for 15 min. The infrared spectra of the acetylated fibers show absorption peaks at 1740 cm^{-1} (ester C=O), 1375 cm^{-1} (ν C—CH$_3$), and 1235 cm^{-1} (ν C—O), indicating successful acetylation.[15,17–19] Infrared spectra of treated and raw sisal fibers were re-

Figure 3 DMTA curves of tire rubber/5% raw sisal fiber composites at different fiber lengths depicting variation of tensile storage modulus (E') as a function of temperature (°C). Frequency 10 Hz.

corded on a Perkin–Elmer spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT), in KBr pellets.

For tensile measurements, the fiber samples and the composites were conditioned at 20 ± 2°C and $50 \pm 5\%$ relative humidity for at least 48 h before testing, which were done on an Instron universal testing machine (model 5569; Instron, Canton, MA). For the fibers, tensile measurements were done according to ASTM D 2256-95,[20] at a speed of 30 mm/min, gauge length of 250 mm, with at least 100 samples. Measurements of the mechanical properties of the composites followed ASTM D 412-92,[21] at a speed of 500 mm/min and gauge length of 70 mm.

Compositions of the composites under investigation are shown in Table I. Raw and treated fibers were manually cut and mixed with rubber particles by hand in the proper amounts. Randomly oriented composite sheets ($150 \times 160 \times 3$ mm) were prepared by hot-press molding at 10,000 kgf, at 200°C for 3 h.[14]

The dynamic tensile storage modulus (E'), tensile loss modulus (E''), and loss factor (tan δ) of the specimens ($15 \times 8 \times 3$ mm) were measured as a function of temperature at a frequency of 10 Hz using a dynamic mechanical thermal analyzer (DMTA IV; Rheometric Scientific). The properties were determined over a temperature range from 30 to 150°C, with a tensile strain amplitude of 0.06 mm and at a heating rate of 1°C/min.

RESULTS AND DISCUSSION

Tensile measurements were performed to determine the mechanical performance of raw and treated sisal fibers. As shown in Table II, a slight decrease may be observed

in tensile strength and Young's modulus after the chemical treatments, with significant variability, which decreases after fiber treatment. It is well known that the properties of natural fibers depend on the source, age, and internal structure of the fibers.[1] Because all fibers from the present investigation were collected from the same place, and have the same age, it can be assumed that the first two factors do not vary significantly, and the variations on the properties can thus be attributed to the changes on the structure of fibers.

Figure 1 shows the dynamic mechanical results for the tire rubber. These tests were obtained to investigate the viscoelastic behavior of the rubber used. The relaxation peak at about −30°C has been associated with the glass-transition temperature. As expected, this value is higher than that for unused natural rubber and SBR (−65 and −52°C, respectively,[22]), indicating that in the powdered tire rubber chain flexibility decreases because of the crosslinked structure of the waste tires.

The properties of short fiber–reinforced material composites depend on the degree to which an applied load is transferred to the fibers, which is a function of fiber length and fiber/matrix interaction. Above a critical fiber length, the load transfer from matrix to fiber is maximum.[23] The optimum fiber length for different elastomer composites was previously determined by Kumar et al.[23] and Geethamma et al.[24] They found that the optimum length was 10 mm for sisal fiber–reinforced natural rubber, and 6 mm for sisal fiber/SBR composites.

To determine the optimal fiber length to obtain the maximum performance of the composites, mechanical and dynamic mechanical measurements were done for composites containing fibers with 0, 2, 5, 10, 15, 20,
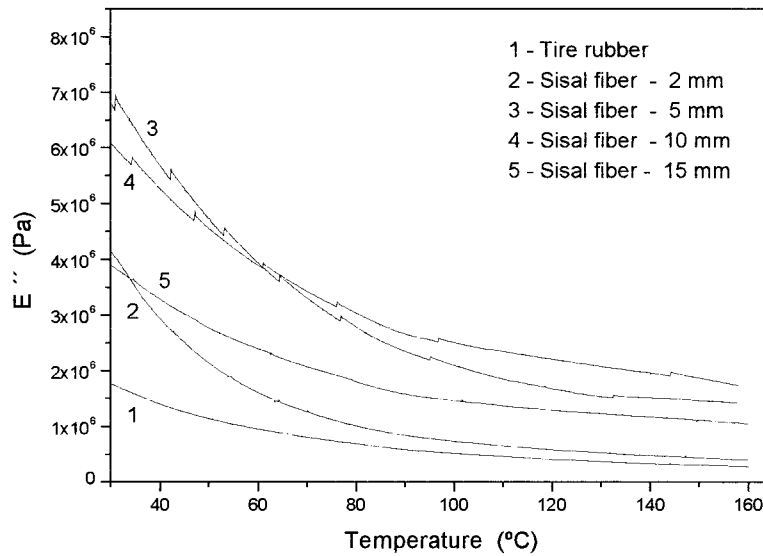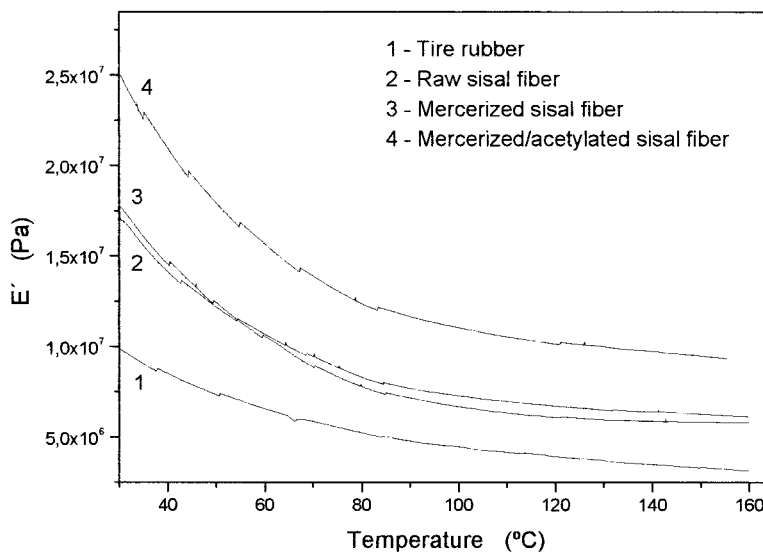
Figure 4 DMTA curves of tire rubber/5% raw sisal fiber composites at different fiber lengths depicting variation of tensile loss modulus (E'') as a function of temperature (°C). Frequency 10 Hz.

and 25 mm fiber length (Figs. 2–4). Performance of the composites reaches its maximum value when the fiber length is 10 mm and decreases for longer fibers, probably because of fiber entanglements.[15] At higher fiber length, its dispersion within the rubber matrix became very difficult and was not uniform. The modulus of the composite, with 10 mm fiber length, increased approximately 180% and tensile strength about 25% compared to that of the matrix without fibers (Fig. 2).

Figures 3 and 4 show the effect of temperature on the storage and loss moduli of the composites. It may be observed that the addition of fibers increases both storage and loss moduli and in all cases they decrease with temperature increase, as expected. The same behavior was observed for virgin natural rubber/sisal fiber composites.[15] The maximum storage modulus was obtained for composites having a fiber length of 10 mm (Fig. 3). From the results of the effect of fiber length (Figs. 2 and 3), the optimum length for obtaining maximum tensile properties and maximum dynamic modulus is 10 mm. Based on these results, the study of the influence of chemical treatments and fiber content on the performance of composites was carried out with the 10-mm fiber length composites.

Many studies have been reported[1–5,15] on the tensile and dynamic mechanical behavior of sisal fiber–rein-

Figure 5 DMTA curves of treated and untreated sisal fiber/tire rubber composites (5% fiber content and 10 mm length) depicting variation of tensile storage modulus (E') as a function of temperature (°C). Frequency 10 Hz.
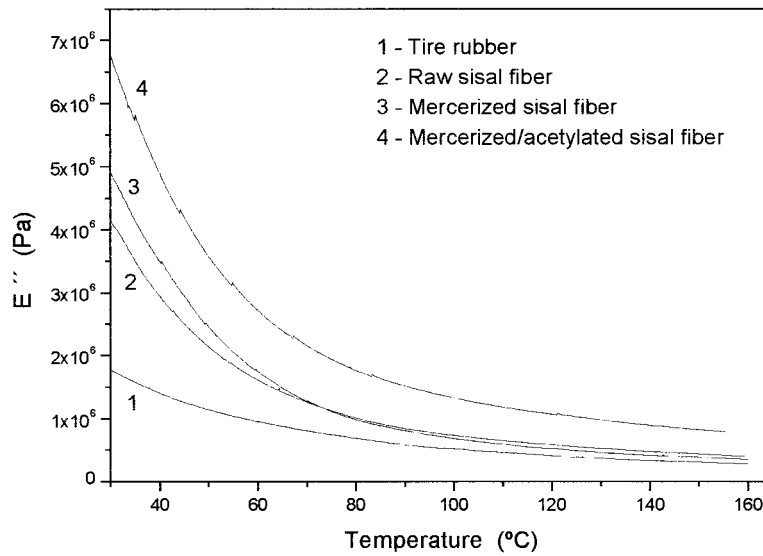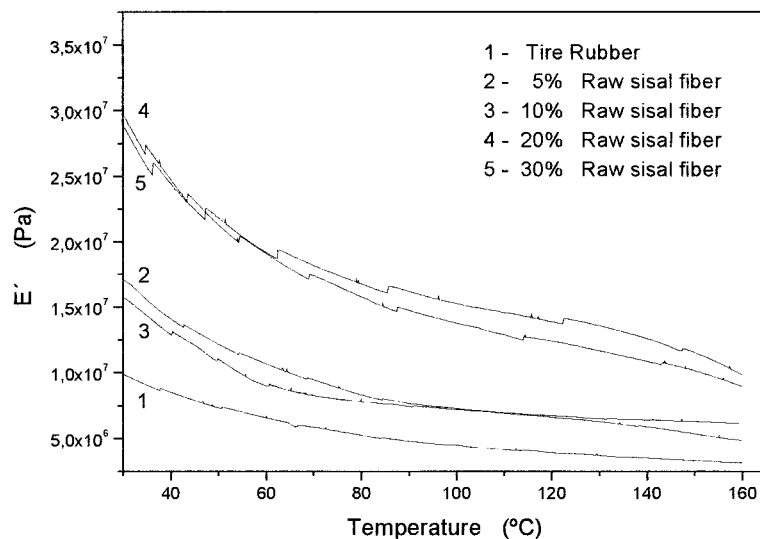
Figure 6 DMTA curves of treated and untreated sisal fiber/tire rubber composites (5% fiber content and 10 mm length) depicting variation of tensile loss modulus (E'') as a function of temperature (°C). Frequency 10 Hz.

forced polymer–matrix composites, in which the authors observed that the chemical treatment of the fibers can improve some properties of the composites. Figures 5 and 6 show the effect of chemical treatments (mercerization and acetylation) of the fibers on tire rubber composites. It may be seen that E' and E'' are lower for tire rubber than for sisal/tire rubber composites because of the incorporation of the fibers into the rubber matrix, thus increasing its stiffness and hardness.[15] The mercerized fiber/tire rubber composites present a behavior similar to that of the raw sisal fiber/tire rubber composites, whereas the mercerized/acetylated fiber/tire rubber composites show

higher storage and loss moduli, indicating a stronger fiber–rubber adhesion.

Figure 7 shows the effect of temperature on the storage modulus (E') of the composites with raw sisal fiber at different fiber contents. At any given temperature, the storage modulus increases with fiber content. This can be attributed to the reinforcement imparted by the fibers that allowed greater stress transfer at the interface.[25] It was also observed that the storage modulus increased with the addition of up to 20% fiber, but no significant change occurred with 30%. This may be a consequence of the increased fiber-to-fiber interaction and orientation with increased fiber

Figure 7 DMTA curves of tire rubber/raw sisal fiber composites at different fiber contents (10 mm length) depicting variation of tensile storage modulus (E') as a function of temperature (°C). Frequency 10 Hz.
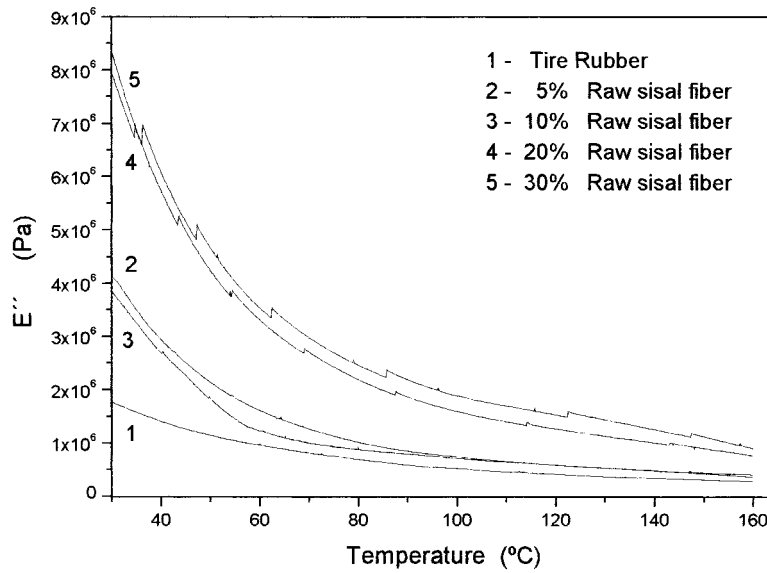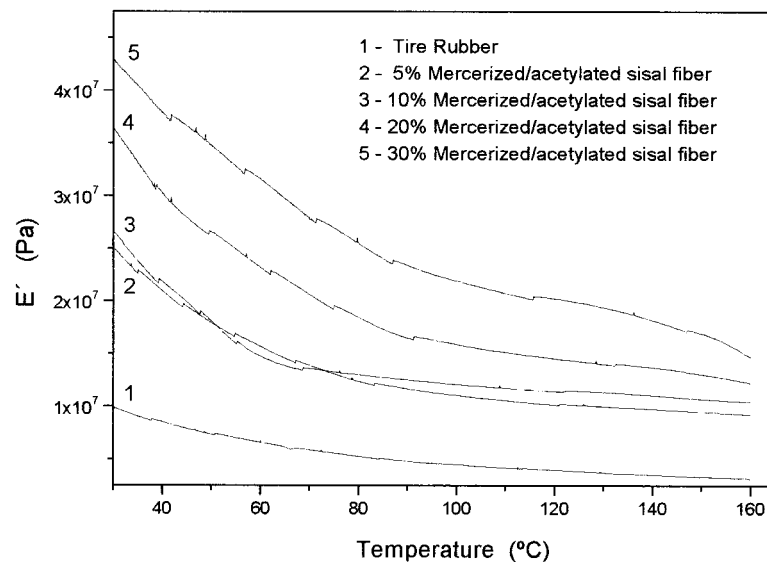
Figure 8 DMTA curves of tire rubber/raw sisal fiber composites at different fiber contents (10 mm length) depicting variation of tensile loss modulus (E'') as a function of temperature (°C). Frequency 10 Hz.

content. Similar behavior was observed by Joseph et al.[26] in their investigation of the dynamic mechanical properties of short sisal fiber–reinforced low-density polyethylene composites. They observed that the storage modulus increased sharply by the addition of 10% fiber, followed by a leveling off at higher fiber content.

When the applied energy is not stored elastically, it must be either lost or converted to heat through molecular friction, that is, viscous dissipation within the material, as measured by loss modulus.[25] Figure 8 shows the effect of temperature on the loss modulus (E'') of raw sisal fiber/tire rubber composites at differ-

ent fiber contents. As in the case of the storage modulus, the loss modulus of all composites shows the same behavior upon increase of the fiber content. Similarly, for the mercerized/acetylated fiber–tire rubber composites, the storage modulus E' (Fig. 9) increased sharply upon fiber addition and decreased at higher temperature. The loss modulus of the mercerized/acetylated fiber–tire rubber composites (Fig. 10) shows the same performance of the storage modulus.

The addition of both raw and mercerized/acetylated fiber increases both the storage and the loss moduli. This effect is more pronounced in the case of

Figure 9 DMTA curves of tire rubber/mercerized and acetylated sisal fiber composites at different fiber contents (10 mm length) depicting variation of tensile storage modulus (E') as a function of temperature (°C). Frequency 10 Hz.
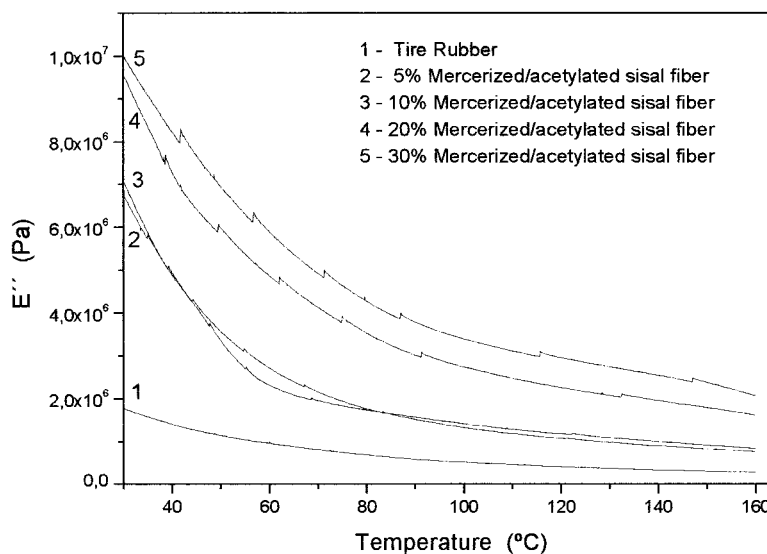
Figure 10 DMTA curves of tire rubber/mercerized and acetylated sisal fiber composites at different fiber contents (10 mm length) depicting variation of tensile loss modulus (E'') as a function of temperature (°C). Frequency 10 Hz.

mercerized/acetylated fibers than in that of raw fibers at the same fiber content, which can be attributed to greater reinforcement of the matrix by the addition of treated fibers that are well bonded to the rubber matrix. This indicates the importance of fiber/matrix adhesion in improving the viscoelastic properties of short fiber composites.[15]

CONCLUSIONS

The mercerization/acetylation treatment of the fibers improves the performance of the tire rubber/sisal fiber composites. The storage and loss moduli of mercerized/acetylated treated composites were found to be higher than those of the raw and only mercerized treated composites. This can be attributed to the improvement in the fiber/matrix interfacial adhesion. In all cases the addition of short sisal fibers to the tire rubber matrix increased both the storage and the loss moduli. This study showed that 10 mm is the optimum fiber length for obtaining maximum dynamic modulus and tensile properties in short sisal fiber/tire rubber composites.

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