

Viscoelastic and Thermal Properties of Woven-Sisal-Fabric-Reinforced Natural-Rubber Biocomposites

Maya Jacob,¹ Jesmy Jose,² Seno Jose,² K. T. Varughese,³ Sabu Thomas²

¹*Polymers and Composites Competence Area, Materials Science and Manufacturing, Council for Scientific and Industrial Research, Port Elizabeth, South Africa*

²*School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam, Kerala 686 560, India*

³*Polymer Laboratory, Central Power Research Institute, Bangalore 560 080, India*

Received 26 August 2009; accepted 11 October 2009

DOI 10.1002/app.31598

Published online 22 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Textile–rubber biocomposites were prepared by the reinforcement of natural rubber with woven sisal fabric. The viscoelastic properties of the composites were analyzed at different frequencies. Sisal fabric was subjected to different chemical modifications, such as mercerization, silanation, and thermal treatment, and the influences of the modifications on the dynamic mechanical properties were analyzed. The storage modulus was found to increase with reinforcement of natural rubber with woven sisal fabric. The chemical modification of the sisal fabric resulted in a decrease in the stor-

age modulus. The damping factor was found to decrease with chemical treatment, and the gum compound exhibited maximum damping characteristics. The thermal stabilities of the composites were also analyzed by thermogravimetric studies. Scanning electron microscopy studies were performed to evaluate the morphology of the fabric–matrix interface. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 614–621, 2010

Key words: activation energy; composites; thermal properties

INTRODUCTION

Developments in composite technology have encouraged rapid progress in natural-fiber-reinforced composites, such as lignocellulosic composites. In this branch of science and technology, lignocellulosic fibers are especially important because of their lower specific gravity and easier processability compared to many other natural and synthetic fibers. Lignocellulosic-fiber-reinforced polymer composites are also attractively lightweight. Applications for plant-fiber-reinforced composites are numerous and range from consumer needs to engineering industries. Also, the development in textile technologies, such as weaving, knitting, and braiding, has resulted in the formation of textile composites that have superior mechanical properties, as no discontinuous orientation of fibers is entailed at any point.

The dynamic mechanical properties of a composite material depend on the fiber content, the presence of the additives such as filler, compatibilizer, fiber orientation, and mode of testing. Three important

parameters that can be obtained during dynamic mechanical analysis are (1) storage modulus, which is a measure of the maximum energy stored in the material during one cycle of oscillation; this gives an idea of the stiffness behavior and load-bearing capability of a composite material; (2) loss modulus, which is proportional to the amount of energy that has been dissipated as heat by the sample; and (3) the mechanical damping term $\tan \delta$, which is the ratio of the loss modulus to the storage modulus and is proportional to the degree of molecular mobility in the polymer material.¹

O'Donnell et al.² characterized the dynamic mechanical properties of natural-fiber-reinforced and acrylated epoxidized soybean oil resin composites, which were manufactured by vacuum-assisted resin transfer molding. The different natural fibers used were flax, hemp, cellulose, and recycled newspaper. The authors observed that the recycled-newspaper-reinforced resin composites exhibited a storage modulus value that was almost five times greater than that of the resin. The composites were also found to possess high damping characteristics; this makes them a probable choice as material for antivibration parts in the automotive industry.

The effect of alkali treatment on the dynamic mechanical properties of kenaf- and hemp-fiber-reinforced polyester composites was analyzed by

Correspondence to: M. Jacob (mjohn@csir.oc.za or mayajacobkunnel@yahoo.com).

Aziz and Ansell.³ The authors observed that the treated fiber composites had higher storage modulus values and lower damping parameters; this indicated a greater interfacial bond strength and adhesion between the polyester resin matrix and the fiber and inferior impact properties compared to the untreated fiber composites. They also noticed a similar pattern of results when cashew nut shell liquid was used as the matrix.⁴

In an interesting study, Guigo et al.⁵ analyzed the viscoelastic properties of green nanocomposites based on silicate/clays/lignin/natural fibers. They observed that the use of organophilic montmorillonite resulted in a higher glass-transition temperature (T_g) and enhanced thermal stability. The properties of manmade cellulose and abaca fibers were investigated by Bledzki et al.⁶ The storage modulus of poly(lactic acid) based composites was found to be much higher than of unreinforced poly(lactic acid) because of better stress transfer in the reinforced composites. T_g derived from the loss modulus shifted to higher temperatures compared to the matrix polymer.

In a study concerning hybrid biofiber systems, the dynamic mechanical properties of sisal/oil-palm-hybrid-fiber-reinforced natural rubber composites were analyzed by Jacob et al.⁷ The authors noticed that there was an increase in the storage modulus with fiber reinforcement, whereas the damping characteristics registered a decrease. The chemical modification of sisal and oil palm fibers resulted in an increase in the storage modulus.

As described previously, it is evident that a number of investigations have been carried out on short-fiber-reinforced composites. Nevertheless, the viscoelastic and thermal properties of textile-rubber composites have not been attempted to date. This study explores the dynamic mechanical behavior of woven-sisal-fabric-reinforced natural rubber composites. The influence of chemical modification on the viscoelastic properties was also determined. Moreover, the effect of frequency on the viscoelastic properties of the textile composites was also examined.

EXPERIMENTAL

Materials

Sisal fabric was obtained from local sources. The natural rubber used for the study was procured from the Rubber Research Institute of India (Kottayam, India). The other ingredients used to vulcanize the natural rubber were zinc oxide, stearic acid, 2,2,4-trimethyl-1,2-dihydroquinoline, *N*-cyclohexylbenzothiazyl sulfenamide, and sulfur, and these were obtained from local rubber chemicals suppliers. The sisal fabric used in this study had a unidirectional

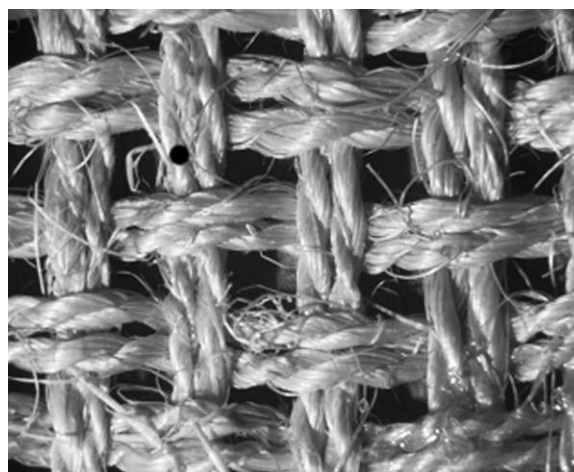


Figure 1 Weave pattern of the sisal fabric.

tional type of fabric weave having a count of 20 (see Fig. 1). The properties of the woven sisal fabric are given in Table I.

Fabrication of the composites

Natural rubber was masticated on a mill for 2 min followed by the addition of the ingredients. The rubber sheet was prepared in a laboratory two-roll mill ($150 \times 300 \text{ mm}^2$) (Kottayam, India). The nip gap, mill roll, speed ratio, and number of passes were kept the same for all of the mixes. A bonding system, consisting of resorcinol and hexamethylene tetramine, was also incorporated. We prepared the sisal fabric/natural rubber textile composites (thickness = 3 mm) by sandwiching a single layer of sisal fabric between two layers of preweighed rubber sheets; this was then compression-molded at 150°C under a pressure of 120 bar for 8 min (see Fig. 2). The formulations of the different composites are given in Table II.

Chemical modification of the sisal fabric

The different chemical modifications performed were as follows.

Alkali treatment

Sisal fabric was treated for 1 h with a 4% NaOH solution. The fabric was further washed with water

TABLE I
Properties of the Sisal Fabric

Yarn distance: weft	3 mm
Yarn distance: warp	5 mm
Twist	10 turns/mm
Areal density	1500 g/m ²

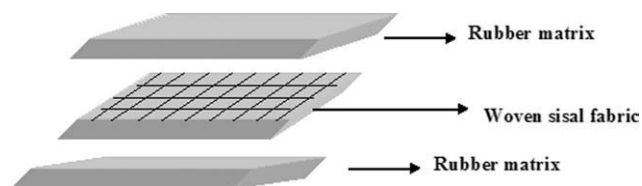


Figure 2 Schematic sketch of the sisal fabric/natural rubber composite.

containing acetic acid. Finally, the fabric was washed again with fresh water and dried in an oven.

Silane treatment

The silane coupling agents used were Silane A1100 (3-aminopropyl triethoxysilane) and Silane A174 (γ -methacryloxypropyltrimethoxysilane). A 0.4% silane solution was prepared by the mixture of 4 g of the respective silane in an ethanol (600 mL)/water (400 mL) mixture and was allowed to stand for 1 h. The pH of the solution was maintained at 4 with the addition of acetic acid. Sisal fabric was dipped in this solution and was allowed to stand for 1.5 h. The ethanol/water mixture was drained out, and the fabric was dried in air and then in an oven at 70°C until it was completely dry.

Thermal treatment

We carried out the thermal treatment by keeping the woven sisal fabric in the oven for 8 h at 150°C. The fabric, directly from the oven, was used for composite preparation.

Measurements

Dynamic mechanical analysis measurements were carried out on a Universal V2.6D (TA Instruments). The test specimen was clamped between the ends of two parallel arms, which were mounted on low-force flexure pivots restricting the motion only in

the horizontal plane. The samples were measured at operating frequencies of 0.1, 1, and 10 Hz and at a heating rate of 2°C/min. The samples were evaluated in the temperature range –100 to 150°C.

Thermogravimetric analysis of the fabric-reinforced composites was carried out with a Universal V2.3C instrument (TA Instruments) with the temperature programmed at a 20°C/min heating rate from room temperature to 700°C in the presence of nitrogen gas with a flow rate of 20 mL/min.

Scanning electron microscopy (SEM) studies were conducted with a JEOL JSM 5800 (Tokyo, Japan) to analyze the fracture behavior of the composites. The fracture ends of the tensile specimens were mounted on aluminum stubs and gold-coated to avoid electrical charging during the examination.

RESULTS AND DISCUSSION

Viscoelastic properties

Storage modulus

The storage modulus provides valuable insight into the stiffness of a material with reference to temperature. It measures the elastic response of a material. Figure 3 shows the variation of storage modulus with the temperature of the gum and untreated and treated samples, at a frequency of 1 Hz. The composite containing untreated sisal fabric exhibited an increase in the storage modulus compared to the gum compound. The storage modulus mainly depends on the stiffness and rigidity of a composite. Any factor that increases the stiffness of the system will result in an increase in the storage modulus. The gum compound, composed of only the rubber phase, gave the material more flexibility, which resulted in a low degree of stiffness and, hence, a low storage modulus. When sisal fabric (which was tightly knit) was incorporated into the otherwise flexible rubber matrix, the stiffness of the composite increased; this resulted in a high storage modulus.

TABLE II
Formulations of the Mixes

Ingredient	Gum	T	TB	TBA	TBAS	TBMS	TT
Natural rubber	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Resorcinol	—	—	7.5	7.5	7.5	7.5	7.5
Hexamethylene tetramine	—	—	4.8	4.8	4.8	4.8	4.8
TDQ	1	1	1	1	1	1	1
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulfur	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Sisal fabric	—	✓	✓	✓	✓	✓	✓
Treatment	—	—	—	4% NaOH for 1 h	Aminosilane	Methylsilane	Heat

CBS = *N*-cyclohexylbenzothiazyl sulfenamide; TDQ = 2,2,4-trimethyl-1,2-dihydroquinoline.

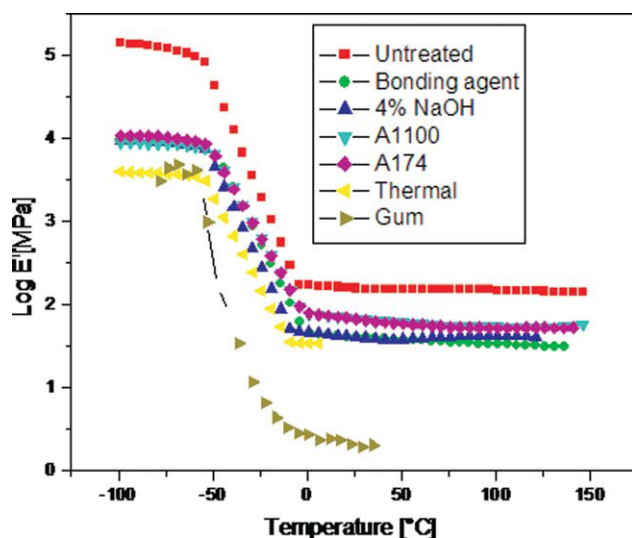


Figure 3 Variation of the storage modulus (E') with the temperature as a function of chemical modification. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Also, the addition of woven fabric allowed greater stress transfer at the interface, which consequently increased the storage modulus.

Also, chemical modification of the sisal fabric resulted in a decrease in the storage modulus. The mechanics of textile composites are different from those of short-fiber composites. Generally, it has been seen that chemical treatments increase the properties of the short fiber composite. In fact, the incorporation of mercerized sisal and oil palm fibers increase the tensile strength of natural rubber composites.⁸ The major contribution to strength in textile composites is the alignment of yarns in the warp and weft direction. Chemical treatment results in the partial unwinding of yarns (as hemicellulose dissolves off), and hence, the alignment gets antagonized. This resulted in a decrease in the strength of the composites. Another reason was that as sisal fabric was composed of thick strands and knots, the alkali and silane coupling agents did not penetrate into the fabric, and therefore, the interfacial properties between the sisal fabric and rubber matrix did not improve enough. Hence, chemical treatment was ineffective, because of which the high stiffness obtained in the former case was antagonized when the fabric was subjected to conventional chemical treatment of the fibers.

Among the treated composites, the composite containing silane (A174)-treated fabric exhibited the highest storage modulus. This was attributed to increased adhesion in these composites. The interfacial adhesion in the chemically modified textile composites could be further understood by examination of the fracture topography of the system. SEM is a useful method for analyzing the degree of fiber/

matrix adhesion. Figure 4(a–f) presents the tensile fracture surfaces of the untreated and various chemically modified composites. In Figure 4(a), we can see the presence of cavities. This was due to the fact that individual strands of fiber were pulled out of the rubber matrix upon application of the stress. This indicated that the adhesion between the rubber matrix and sisal fabric was not satisfactory in the absence of a bonding agent or chemical modification. Figure 4(b) exhibits the SEM of the composite in the presence of a bonding agent. Here, there is clear evidence of fiber breakage. The strong bonding between the fabric and rubber matrix resulted in fibers being broken off rather than unwinding themselves from the matrix. We clearly observed broken ends of fibers protruding from the matrix. Figure 4(c) shows the SEM of the tensile fracture surface of the composite containing alkali-treated sisal fabric. Generally, mercerization treatment results in the removal of lignin and hemicellulose; for this to take place, it is essential that the alkali penetrate each and every nook of the fabric. In this particular study, we observed from the SEM that this did not occur. This was because the woven sisal fabric was composed of thick yarns, and when it was subjected to mercerization, the alkali did not penetrate the individual fiber strands. As a result, the bonding was not uniform or effective. Hence, the composites prepared from the alkali-treated fabric showed impaired properties.

The SEM of the tensile fracture surfaces of the composites containing silane-treated fabric is presented in Figure 4(d,e). The individual strands of the fabric had a smoother appearance. The silanyl groups from the silane coupling agent promoted better interaction between the rubber matrix and fabric [Fig. 4(d)]. As shown in Figure 4(e), there was the presence of fiber breakage, which suggested good bonding. Traces of silanyl coupling agent adhered to the strands of the fabric surface. As shown in Figure 4(f), the broken ends of fiber projecting from the matrix indicated a strong interface. Upon thermal treatment, the hydrophilic nature of the fibers decreased, whereas the crystallinity of the fiber increased. As a result, the adhesion between the rubber matrix and sisal fabric increased and gave rise to a stronger interface, as shown in the figure. Therefore, we can state that there was no fiber pullout when the composites were thermally treated.

Loss modulus and damping characteristics

The loss modulus represents the viscous response of a material. Figures 5 present the variation of loss modulus with the temperature as a function of chemical modification. The maximum loss modulus was exhibited by the composite containing untreated

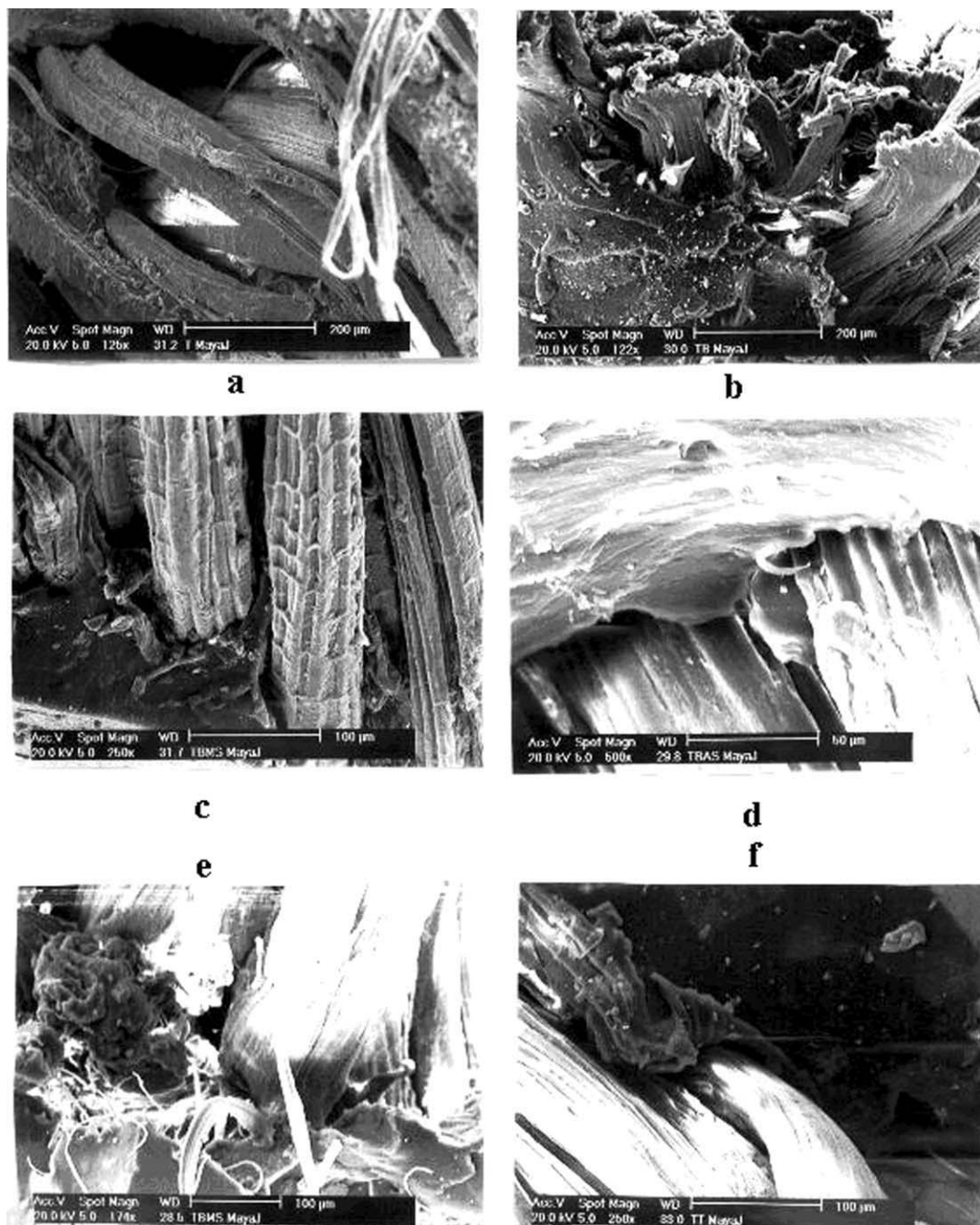


Figure 4 SEM micrographs of tensile fracture surfaces of the chemically modified textile composites: (a) the composite containing untreated sisal fabric, (b) the composite with the bonding agent, (c) the composite containing alkali-treated fabric (4% NaOH), (d) the composite containing aminosilane-treated fabric (A1100), (e) the composite containing methylsilane-treated fabric (A174), and (f) the composite containing thermally treated fabric.

sisal fabric, and upon chemical modification, the loss modulus value decreased. The height and area of the peak regions were also indications of the energy absorbed by the system. Compared to the untreated composite, the peak height decreased for the composites composed of chemically modified sisal fabric.

Damping is an important parameter related to the study of the dynamic behavior of fiber-reinforced composite structures. $\tan \delta$ relates to the impact resistance of a material. As the damping peak occurs

in the region of the glass transition where the material changes from a rigid to a more rubbery state, it is associated with the segmental mobility within the polymer structure, all of which are initially frozen in. Therefore, higher the $\tan \delta$ peak value is, the greater is the degree of molecular mobility.¹

Figure 6 presents the variation of $\tan \delta$ with the temperature of the textile composites. The gum compound exhibited maximum damping characteristics, and damping decreased upon reinforcement with

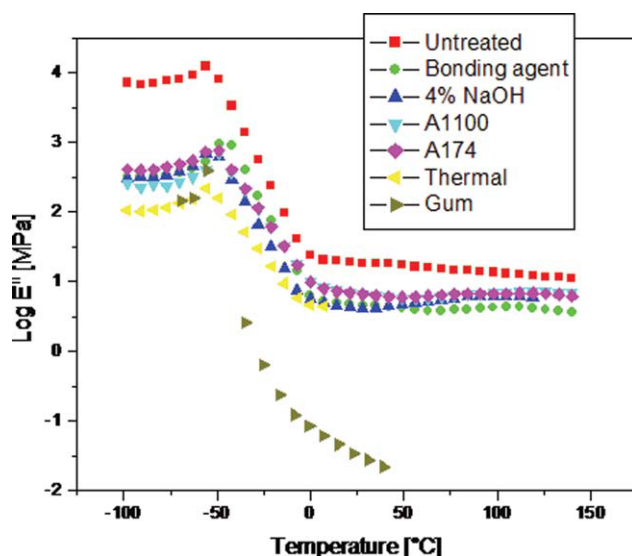


Figure 5 Variation of the loss modulus (E'') with the temperature as a function of chemical modification. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sisal fabric. The incorporation of fabric resulted in barriers being formed, which restricted the mobility of rubber chains and led to lower flexibility, lower degrees of molecular motion, and hence, lower damping characteristics. Another reason for the decrease was that there was less matrix by volume to dissipate the mechanical energy. When compared to the untreated composite, one can see that the chemically modified composites exhibited lower damping characteristics.

Table III presents the T_g values from the loss modulus peak and $\tan \delta$ peak. It was evident that the incorporation of sisal fabric resulted in an increase in T_g . This was attributed to the decrease in mobility

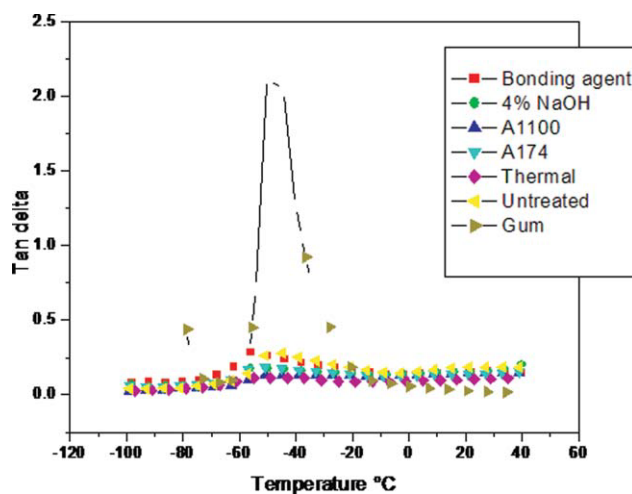


Figure 6 Variation of $\tan \delta$ with the temperature as a function of chemical modification. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
 T_g Values of the Composites

Sample	T_g ($^{\circ}\text{C}$)	
	Loss modulus peak	$\tan \delta$ peak
Gum	-54	-50
T	-45	-48
TB	-55	-58
TBA	-52	-55
TBAS	-50	-53
TBMS	-52	-55
TT	-52	-56

of the rubber–fabric system. Also, the T_g values decreased to lower temperatures upon chemical treatment. This decrease was due to ineffective interfacial bonding, which enhanced the mobility of the molecular chains and resulted in the transition state being pushed to lower limits.

Frequency dependence of the textile composites

The mechanical behavior of viscoelastic materials is dependent on time (or frequency) and temperature. The variation of the dynamic properties of sisal-fiber-reinforced polypropylene with frequency was investigated by Joseph et al.⁹ The authors observed that the storage modulus increased with frequency, and this increase was prominent at higher temperatures. Figures 7 and 8 represent the variation of storage modulus of the untreated and thermally treated composites with temperature at three different frequencies: 0.1, 1, and 10 Hz. It was clear that the storage modulus increased with frequency, and this increase was prominent only at low temperatures. This was attributed to the lesser mobility of the

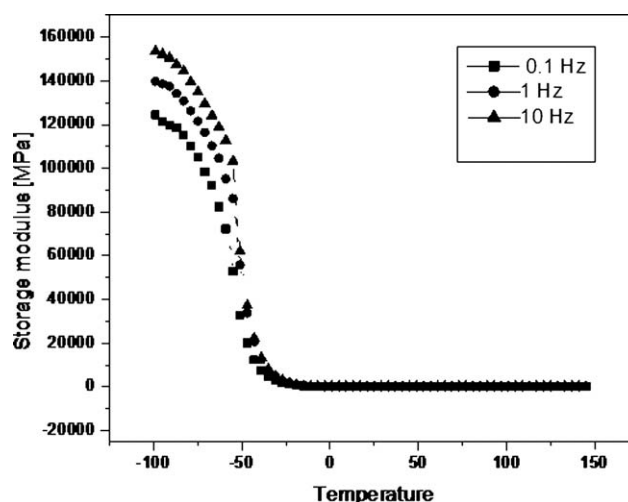


Figure 7 Variation of the storage modulus of the untreated composite with the temperature at different frequencies.

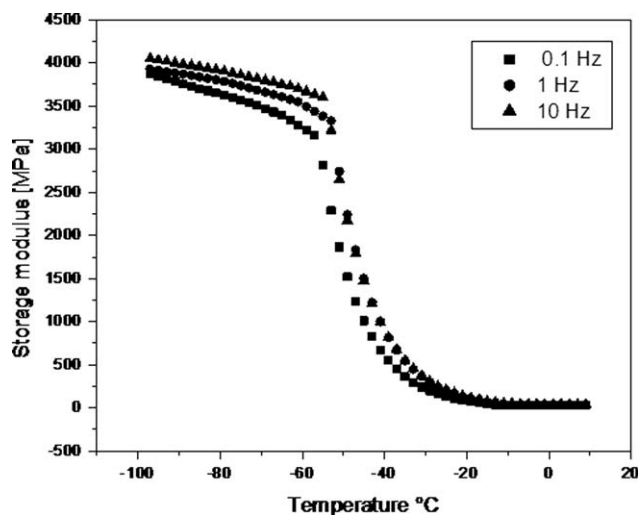


Figure 8 Variation of the storage modulus of the thermally treated composite with the temperature at different frequencies.

rubber chains when the speed of cyclic stress was too fast to bring about deformation.

Thermogravimetric analysis

Generally, the incorporation of plant fibers into different matrices increases the thermal stability of the system. In an interesting study, thermogravimetric analysis of biodegradable composites composed of poly(propylene carbonate) and the short, lignocellulose fiber *Hildegardia populifolia* was performed by Li et al.,¹⁰ and the investigation revealed that the introduction of the fiber led to a slightly improved thermooxidative stability of poly(propylene carbonate).

However, anomalous results were noticed in some other natural-fiber-reinforced composites. The

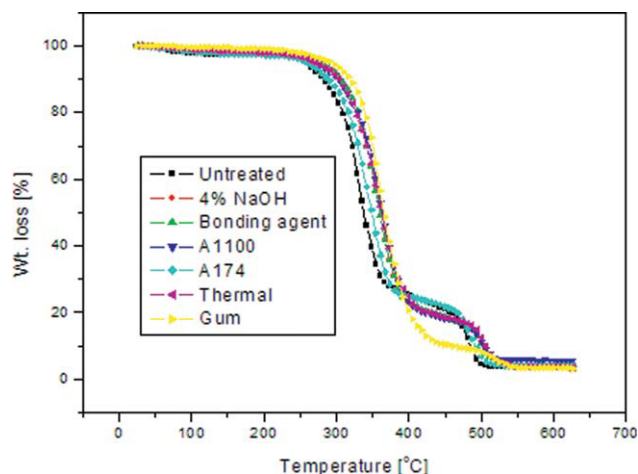


Figure 9 TG thermograms of the composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

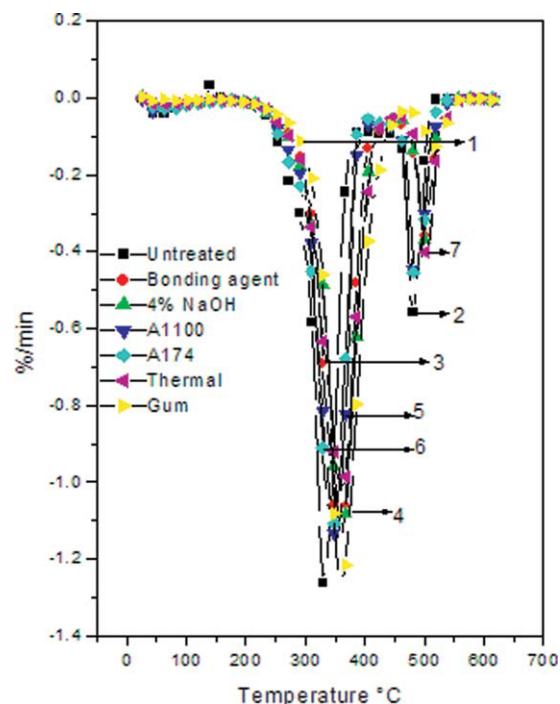


Figure 10 DTG thermograms of the composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

thermal properties of several lignocellulosic-fiber-reinforced polyester composites was investigated by Hassan and Nada.¹¹ The fibers used were rice, straw, bagasse, and cotton stalk. They observed that all of the lignocellulosic-fiber-reinforced polyester composites were slightly less thermally stable than the neat polyester composite. The thermal properties of rubberwood fiber/thermoplastic natural rubber composites were determined by Sameni et al.¹² The authors observed an increasing degradation temperature in the samples with rubberwood fiber.

Thermogravimetry (TG) and derivative thermogravimetry (DTG) thermograms of the untreated and treated sisal-fabric-reinforced rubber composites are shown in Figures 9 and 10. Table IV gives the peak temperatures and percentage weight loss of the

TABLE IV
Peak Temperatures of the Composites

Sample	Temperature (°C)		wt % at 700°C
	Peak I	Peak II	
Gum	360.5	—	3.2
T	329.3	480.2	3.4
TB	355.8	501.3	3.6
TBA	357.9	501.7	5.4
TBAS	353.0	487.2	3.3
TBMS	348.9	482.5	3.9
TT	360.0	504.0	3.5

various composites. For the gum composite, the peak at 360.5°C corresponded to the maximum degradation of the rubber matrix. In the case of the composite containing woven sisal fabric, the peak temperatures decreased to 329.3°C, and a new peak appeared at 480.2°C due to hemicellulose and α -cellulose degradation. For the composite containing fabric treated with bonding agents and alkali, the peak temperatures increased to 501.3 and 501.7°C, respectively. This means that mercerization resulted in a greater thermal stability for the composites. For the composites containing silane-treated sisal fabric, the peak temperatures shifted to 487.2 and 482.5°C; this indicated that the silane-treated composites were thermally less stable than the alkali-treated composites. Thermal stability was at a maximum for the composite containing the thermally treated sisal fabric; this was evident from the peak temperature at 504°C. The amount of residual char left after 600°C increased for the composite containing the alkali-treated sisal fabric. A similar observation was reported by Ray et al.¹³ for alkali-treated jute fibers; they explained that mercerization reduced the hemicellulose to a considerable extent and gave rise to a lignin-cellulose complex, which made the product more stable than the raw sample. This was reflected in the increased amount of char left behind.

CONCLUSIONS

An investigation into the viscoelastic properties with thermal resistance and morphology of woven-sisal-fabric-reinforced natural rubber composites was presented. The storage modulus was found to increase upon reinforcement of the natural rubber with sisal fabric. This was attributed to the increase of stiffness in the rubber-fabric network. The chemical modification of the sisal fabric resulted in a decrease in the storage modulus. This was due to the partial unwinding and loosening of individual fiber strands, which disrupted the alignment of yarns in the warp

and weft directions. The damping parameter registered a decrease upon chemical modification because of a decrease in the mobility of the polymer chains. The storage modulus was also found to increase with frequency for the untreated and treated composites. Thermogravimetric analysis revealed that composites containing chemically treated fabric were thermally more stable than the untreated composite, and among the composites containing chemically treated fabric, the thermally treated composites were found to be more stable. This was substantiated by the increase in the decomposition temperatures of hemicelluloses and α -cellulose for the treated composites. Morphologically, we noticed that there was poor adhesion in the alkali-treated composites, as the alkali was unable to penetrate into the thick sisal fabric.

References

1. Kuzak, S. G.; Shanmugam, A. *J Appl Polym Sci* 1999, 73, 649.
2. O'Donnell, A.; Dweib, M. A.; Wool, R. P. *Compos Sci Technol* 2004, 64, 1135.
3. Aziz, S. H.; Ansell, M. P. *Compos Sci Technol* 2004, 64, 1219.
4. Aziz, S. H.; Ansell, M. P. *Compos Sci Technol* 2004, 64, 1231.
5. Guigo, N.; Vincent, L.; Mija, A.; Naegele, H.; Sbirrazzuoli, N. *Compos Sci Technol* 2009, 69, 1979.
6. Bledzki, A. K.; Jaszkievicz, A.; Scherzer, D. *Compos A* 2009, 40, 404.
7. Jacob, M.; Thomas, S.; Varughese, K. T. *Polym Compos* 2006, 27, 671.
8. Jacob, M.; Thomas, S.; Varughese, K. T. *Compos Sci Technol* 2004, 64, 955.
9. Joseph, P. V.; Mathew, G.; Joseph, K.; Groeninckx, G.; Thomas, S. *Compos A* 2003, 34, 275.
10. Li, X. H.; Meng, Y. Z.; Wang, S. J.; Rajulu, A. V.; Tjong, S. C. *J Polym Sci Part B: Polym Phys* 2004, 42, 666.
11. Hassan, M. L.; Nada, A. M. A. *J Appl Polym Sci* 2003, 87, 653.
12. Sameni, J. K.; Ahmad, S. H.; Zakaria, S. *Polym Plast Technol Eng* 2003, 42, 139.
13. Ray, D.; Sarkar, B. K.; Basak, R. K.; Rana, A. K. *J Appl Polym Sci* 2002, 85, 2594.