Effect of Bis(3-triethoxysilylpropyl) Tetrasulfide on the Crosslink Structure, Interfacial Adhesion, and Mechanical Properties of Natural Rubber/Cotton Fiber Composites

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ABSTRACT: Bis(3-triethoxysilylpropyl) tetrasulfide (TESPT) was used to improve the interfacial adhesion between cotton fiber and natural rubber (NR). The crosslink density, interfacial adhesion, mechanical properties, dynamic mechanical properties, and morphology of NR/cotton fiber composites were investigated. The composites with TESPT had higher crosslink density, better mechanical properties, higher initial modulus, and higher yield strength than the composites without TESPT because of the difference in interfacial adhesion. The results of an interfacial adhesion evaluation, the high storage modulus and low damping values of the composites with TESPT, and the coarse surfaces of the pullout fibers implied the enhancement of interfacial adhesion. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 437–443, 2009

Key words: adhesion; fibers; rubber

INTRODUCTION

Cotton fiber is a natural fiber based on cellulose that has some biological reactivity. Cotton fiber can be used as a reinforcing filler for polymers frequently termed *polymeric biocomposites*, which have properties such as hydrophilicity, biocompatibility, stereoregularity, and multichirality and reactive hydroxyl groups.[1]

However, a typical problem involving natural-fiber-reinforced polymers is the limited compatibility between the hydrophilic hydroxyl groups of the natural fibers and the hydrophobic polymer matrix.[2] Some chemical and physical methods, that is, calandering[3] and thermal treatments,[4] have been used to reduce the interfacial energy of the contacting phases, leading to the good dispersion of fibers during processing.

Bis(3-triethoxysilylpropyl) tetrasulfide (TESPT) is an organic silane with ethoxy and tetrasulfane groups (S_4 ring). The modification of silica with TESPT has been widely investigated[5–7] because the reaction between ethoxy groups and hydroxyl groups favors the reinforcement of silica on rubber. However, few studies dealing with the modification of fibers with TESPT in a rubber/fiber system have been reported. In this study, natural rubber (NR)/cotton fiber composites were prepared. TESPT was used as a coupling agent between the fiber and matrix to enhance the interfacial adhesion. The interfacial adhesion was evaluated, and the effects of the fiber content on the crosslink density, mechanical properties, stress–strain behavior, dynamic mechanical properties, and morphology of NR/cotton fiber composites were investigated as well.

EXPERIMENTAL

Materials

NR (RSS1) was supplied by Hainan Nongken (Hainan, China). Cotton fiber was produced by Wujin Hua Dong Particular-Kind Fiber Manufacture Co., Ltd. (Changzhou, China). The chemical constituents and physical properties of the cotton fibers are listed in Table I. TESPT was reagent-grade and was produced by Nanjing Shuguang Chemical Group Co., Ltd. (Nanjing, China). Stearic acid (activator) was reagent-grade and was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Commercially available *N*-cyclohexy1-2-benzothiole sulfonamide (CZ-80; accelerator), ZnO-80 (activator), and sulfur (S-80; cure agent) with an active content of 80% were industrial-grade and were obtained from Rhein Chemic Corp. (Qingdao, China).
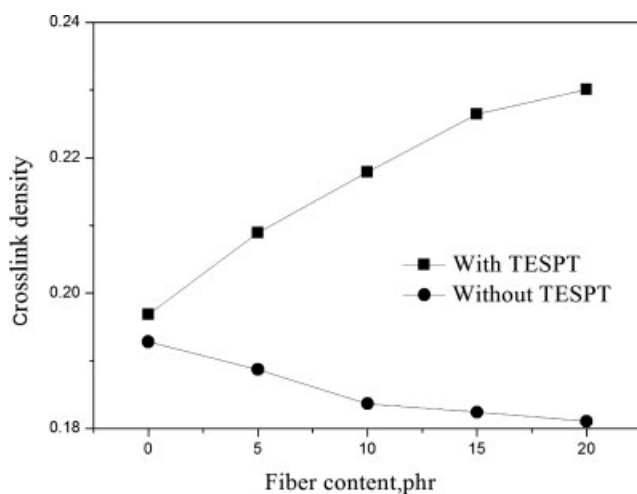
Sample preparation[8–11]

Cotton fibers were dried in an oven at 80°C for 24 h to remove moisture. The composites were prepared

Chemical constituents (wt %)	
Cellulose	83
Hemicellulose	6
Lignin	1
Wax	1
Ash	3
Physical properties	
Diameter (μm)	20–50
Density (g/cm^3)	1.4
Elongation at break (%)	7.0–8.0
Tensile strength (MPa)	287–597
Young's modulus (GPa)	5.5–12.6

Figure 2 Reaction mechanism between TESPT and NR during vulcanization.

with a laboratory two-roll mill. The nip gap (1 mm), speed ratio (1 : 1.27), and time of mixing (12 min) were kept the same in all the mixes. NR was milled for 2 min at 80°C, and this was followed by the addition of TESPT and other ingredients. Then, the fibers were added to the compounds and mixed for 10 min. The compounds were milled again for 10 min under the same experimental conditions 24 h later. We paid attention to maintain the direction of the compound flow and make sure that most fibers were aligned in the same direction. During the sample preparation, the hydroxyl groups should have formed through the hydrolysis of TESPT, and then the condensation reaction should have occurred between these newly formed hydroxyl groups or with the hydroxyl groups of the fibers. All the samples were press-cured with a thickness of 2 mm at 150°C for 20 min. The amount of TESPT used in the composites was 2 phr, except for the section on mechanical properties.

Determination of the crosslink density[12,13]

The crosslink density was determined by the equilibrium swelling method. Press-cured samples were swollen in toluene at 25°C for 72 h to achieve equilibrium swelling. Then, the weight of the swollen samples was measured. The swollen samples were dried in a vacuum oven at 80°C for 36 h to remove the residual solvent. The volume fraction of the rubber in the swollen gel (V_r), used to represent the crosslink density of the composite, was determined with eq. (1):

$$V_r = \frac{m_0 f(1-\alpha)/\rho_r}{m_0 f(1-\alpha)/\rho_r + (m_1 - m_2)/\rho_s} \qquad (1)$$

where m_0 is the sample mass before swelling; m_1 and m_2 are the sample masses before and after drying, respectively; f is the mass fraction of rubber in the composite; α is the mass loss of the gum NR composite during swelling; and ρ_r and ρ_s are the rubber and solvent densities, respectively.

Figure 1 Effect of the fiber content on the crosslink density of composites with and without TESPT.

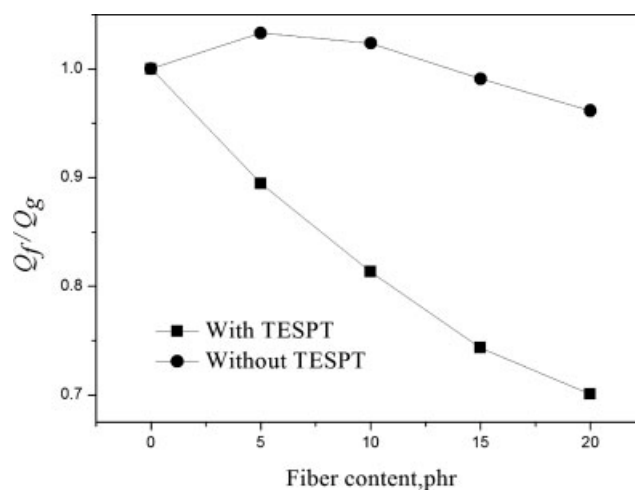**Figure 3** Lorenz–Park plot for NR/fiber composites swollen in toluene.

TABLE II
Effect of the TESPT Content on the Mechanical Properties of Composites with 10 phr Fibers

TESPT content (phr)	Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)	Modulus at 300% elongation (MPa)
0	63 ± 0.7	12.9 ± 0.5	602 ± 4	2.2 ± 0.1	2.9 ± 0.1
2	67 ± 0.9	15.0 ± 1.0	575 ± 6	2.4 ± 0.1	3.4 ± 0.1
4	67 ± 0.4	14.9 ± 0.9	565 ± 7	2.4 ± 0.2	3.6 ± 0.1
6	68 ± 0.4	14.6 ± 0.8	551 ± 5	2.3 ± 0.1	3.6 ± 0.2
8	68 ± 0.5	14.7 ± 1.2	543 ± 6	2.3 ± 0.1	3.6 ± 0.1

Scanning electron microscopy (SEM)

The morphology of the composites was observed with a Hitachi (Tokyo, Japan) S-2150 scanning electron microscope. The fractured surface of a failed tensile sample was coated with a thin gold layer before observation.

Mechanical properties

An Instron (Canton, MA) series IX 4465 material tester was used to measure the tensile properties according to ASTM D 412-1998. The tensile properties were measured with dumbbell specimens (with a 6-mm-wide cross section) at the crosshead speed of 500 mm/min. Shore A hardness was measured with a hand-held Shore A durometer according to ASTM D 2240-2004. All the specimens were tested in the longitudinal direction. Values of the mechanical properties were determined from at least five measurements for each specimen.

Dynamic mechanical analysis (DMA)

DMA was performed in a dynamic mechanical analyzer (Rheometric Scientific, Inc., New Castle, DE). Measurements were performed in the double-cantilever mode with a frequency of 1 Hz over a temperature range of −90 to 0°C at a heating rate of 3°C/min. The specimens were rectangular strips [10 × 4 × 1 mm^3 (length × width × thickness)]. The strain amplitude remained at 0.01%.

RESULTS AND DISCUSSION

Crosslink density

The crosslink density of the composites, shown in Figure 1, has been calculated with eq. (1). For the composites without TESPT, the crosslink density slightly decreases with increasing fiber content, and this can be ascribed to the adsorption of the accelerator (CZ-80) by the hydroxyl groups.[14] The crosslink density of the composites with TESPT monotonously increases with increasing fiber content, and they show a higher crosslink density than those without TESPT at the same fiber content. This can be attributed to two factors. First, a reaction between TESPT and hydroxyl groups of fibers occurs during compounding, and then fewer accessible hydroxyl groups lead to less adsorption of the accelerator (CZ-80).[15] Second, the S_4 ring of TESPT opens during vulcanization to react with the allylic hydrogen or the double bonds of the rubber to form crosslinks.[16] As shown in Figure 2, TESPT acts as an effective coupling agent to enhance the interfacial adhesion between the fiber and matrix.

Evaluation of fiber–matrix interfacial adhesion

The interfacial adhesion between the fiber and matrix has been evaluated with the Lorenz–Park equation:[17]

TABLE III
Effect of the Fiber Content on the Mechanical Properties of Composites

| Fiber content (phr)		Hardness (Shore A)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 100% elongation (MPa)	Modulus at 300% elongation (MPa)
0	With TESPT	45 ± 0.2	23.5 ± 1.1	635 ± 6	1.08 ± 0.1	2.7 ± 0.1
	Without TESPT	44 ± 0.5	23.3 ± 1.3	643 ± 4	1.06 ± 0.1	2.6 ± 0.1
5	With TESPT	57 ± 1.0	18.2 ± 0.6	609 ± 11	1.7 ± 0.1	3.0 ± 0.2
	Without TESPT	55 ± 0.8	14.2 ± 0.4	630 ± 9	1.4 ± 0.2	2.3 ± 0.1
10	With TESPT	67 ± 0.9	15.0 ± 1.0	575 ± 6	2.4 ± 0.1	3.4 ± 0.1
	Without TESPT	63 ± 0.7	12.9 ± 0.5	602 ± 4	2.2 ± 0.1	2.9 ± 0.1
15	With TESPT	75 ± 0.3	12.3 ± 0.6	554 ± 5	3.0 ± 0.1	3.6 ± 0.2
	Without TESPT	72 ± 0.8	10.3 ± 0.8	570 ± 8	3.0 ± 0.1	3.5 ± 0.1
20	With TESPT	78 ± 0.3	11.7 ± 1.4	537 ± 10	3.5 ± 0.1	3.7 ± 0.1
	Without TESPT	74 ± 0.7	8.58 ± 1.1	551 ± 4	3.2 ± 0.2	3.0 ± 0.2
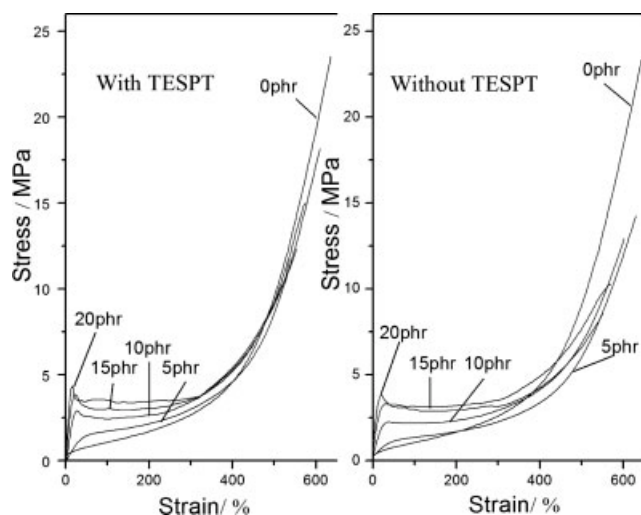
Figure 4 Stress–strain curves of NR/fiber composites.

$$\frac{Q_f}{Q_g} = ae^{-z} + b \qquad (2)$$

where Q is the weight of toluene uptake per gram of rubber hydrocarbon; subscripts f and g represent the composite and matrix, respectively; Z is the ratio by weight of the fiber to the rubber hydrocarbon in the composite; and a and b are constants for a specific system. In this work, Q has been calculated as follows:[18]

$$Q = \frac{\text{swollen weight} - \text{dried weight}}{\text{original weight} \times 100/\text{formula weight}} \qquad (3)$$

The lower the Q_f/Q_g values are, the stronger the interfacial adhesion is between the fiber and matrix. As shown in Figure 3, the composite with TESPT shows lower Q_f/Q_g values than that without TESPT at the same fiber content, and this indicates that the interfacial adhesion between the fiber and matrix is enhanced in the presence of TESPT.

Mechanical properties

The effect of the TESPT content on the mechanical properties of composites with fibers at a concentration of 10 phr is shown in Table II. The TESPT content has little effect on the hardness, tensile strength, or modulus at a definite elongation of the composites. The tensile strength reaches the maximum value when 2 phr TESPT is added. This proves that 2 phr TESPT can react with most of the accessible hydroxyl groups of 10 phr fibers and that excessive TESPT does not favor the reinforcement of fibers on rubber. With the addition of TESPT, the increment of the crosslink density leads to a reduction of the elongation at break.

Table III shows the effect of the fiber content on the mechanical properties of the composites with and without 2 phr TESPT. As shown in Table III, the tensile strength and elongation at break decrease with increasing fiber content independently of the presence of 2 phr TESPT. When the specimens are at high strain, the elongation completely surpasses the fiber length. Therefore, the formation of holes when fibers are pulled out of the matrix instead of adhering to the matrix[19] and the strain-induced crystallization ability of NR are disrupted by the addition of fibers,[20] and this leads to the reduction of the tensile strength and elongation at break. The hardness and modulus at a definite elongation increase with increasing fiber content because of the much higher modulus of the fibers versus that of the matrix. In addition, an increase in the hardness, tensile strength, and modulus at a definite elongation with the addition of TESPT has been observed, and this can be ascribed to an enhancement of interfacial adhesion. When fibers are added at a concentration of 20 phr, the modulus at 300% elongation and tensile strength of the composites with TESPT are 23.3% and 36.3% higher than those of the composites without TESPT, respectively.
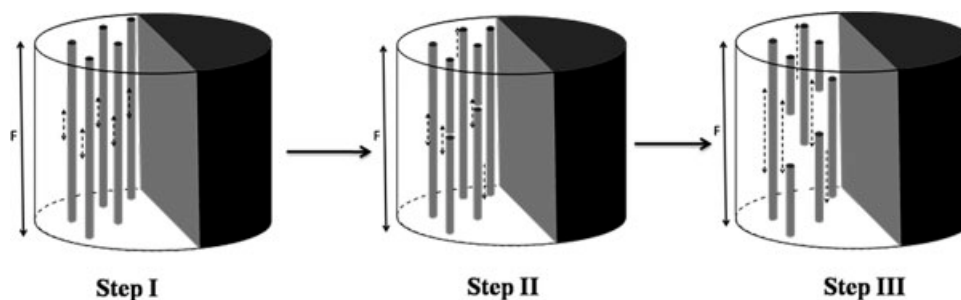
Stress–strain behavior

Figure 4 shows the stress–strain curves for composites with and without TESPT, respectively. The two curves look similar. For the composites with a fiber content less than 5 phr, the stress increases monotonously along with the tensile process. However, for the composites with a fiber content greater than 10 phr, stress-yielding points occur; this is similar to the stress-yield behavior of plastics. Then, the stress continues to increase until the sample fails. The yield strength and initial modulus (measured by a straight line being fit to the data at a low strain) increase with increasing fiber content, and this reflects the characteristics of a high modulus accompanied by a low strain. It also can be seen from Table IV that the composites with TESPT show a high yield strength and initial modulus.

TABLE IV
Effect of the Fiber Content on the Initial Modulus and Yield Strength of the Composites

Fiber Content (phr)	Initial modulus (MPa): with TESPT/ without TESPT	Yield strength (MPa): with TESPT/ without TESPT
0	0.90/0.90	—
5	4.33/2.68	—
10	14.1/9.16	2.92/2.25
15	22.9/17.7	3.85/3.30
20	35.6/33.3	4.33/3.80

Scheme 1 Schematic tensile process from commencement to fracture.

All this can be explained by the tensile process of composites. The process can be divided into three steps according to strain as shown in Scheme 1:

Step I. The fibers and matrix are under stress at a low strain simultaneously, and the initial modulus increases with increasing fiber content because of the filling effect of the fibers. The good interfacial adhesion leads to the high initial modulus of the composites with TESPT.

Step II. At a high strain, the fibers are pulled out of the matrix or undergo breakage, and this leads to the sharp reduction of stress because only the rubber matrix is under stress; then, stress-yielding points occur in the stress–strain curves. The composites with TESPT show higher yield strength than those without TESPT because the better fiber–matrix affinity enhances the difficulty of fiber pullout or breakage.

Step III. Only the rubber matrix is under stress until failure at a high strain. The stress–strain curves of this step are similar to those of unfilled composites.
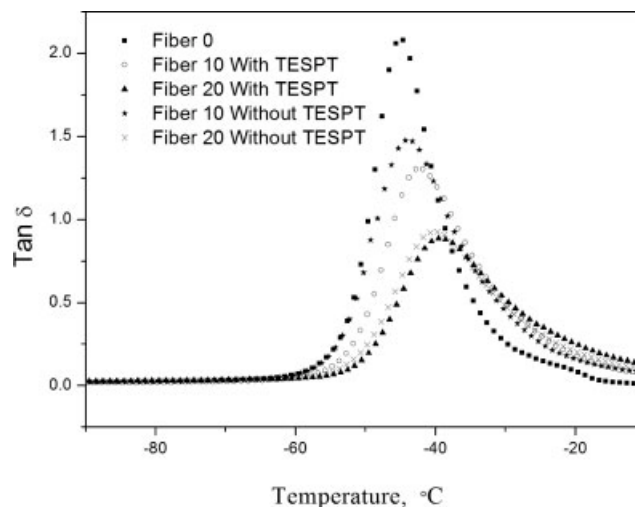
Dynamic mechanical properties

The variation of the storage modulus (G') with the temperature at different fiber contents is shown in Figure 5. G' increases with increasing fiber content. The increment is especially apparent in the glassy region but is marginal in the rubbery plateau. The composites without TESPT have lower G' values than those with TESPT because of the poor interfacial adhesion between the fiber and matrix due to the hydrophilic nature of the fiber, and this leads to lower stiffness of the composites.[21] With the addition of TESPT, the increment of the crosslink density also leads to higher G' values of the composites. An interesting phenomenon is that NR/fiber (10 phr) composites with TESPT even exhibit higher G' values than NR/fiber (20 phr) composites without TESPT.

Figure 6 shows plots of tan δ as a function of temperature for NR/fiber composites, and Table V shows the glass-transition temperature (T_g) and tan δ_{max} values. The addition of fibers significantly decreases the height of tan δ, and this indicates that fibers could act as barriers to the molecular chain
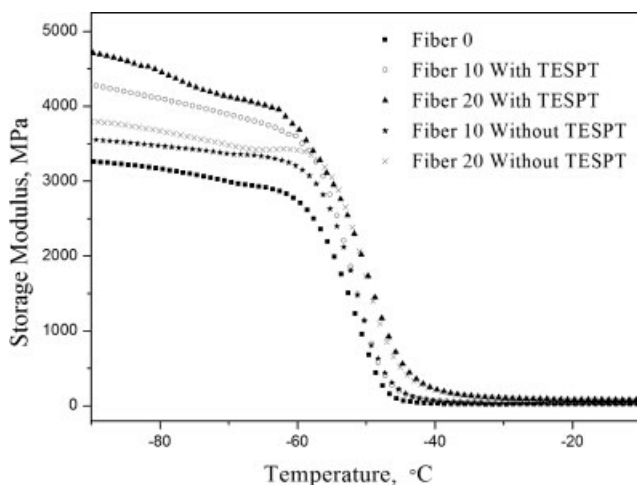
Figure 5 G' versus the temperature for NR/fiber composites with and without TESPT.

Figure 6 Tan δ versus the temperature for NR/fiber composites with and without TESPT.

TABLE V
Parameters of the Dynamic Mechanical Properties of the Composites

Sample	T_g (°C)	tan $\delta_{\max}$	V_f	B
Fiber 0	−44.6	2.077	0	—
Fiber 10 with TESPT	−41.7	1.302	0.0569	6.456
Fiber 10 without TESPT	−43.2	1.470	0.0578	5.056
Fiber 20 with TESPT	−39.5	0.886	0.1072	9.921
Fiber 20 without TESPT	−40.4	0.924	0.1098	9.604

V_f, fiber volume fraction.

mobility and flexibility. The composites with TESPT have lower tan δ values, and the dynamic mechanical behavior suggests that TESPT is able to improve the interfacial adhesion between the fiber and matrix and hence lower damping characteristics. For the composites with and without TESPT, the T_g values are shifted to a slightly higher temperature, which is exhibited as a well-defined relaxation peak, in comparison with the unfilled composites. For the composites with TESPT, T_g is shifted to a higher temperature at the same fiber content, and this is attributed to the presence of TESPT restraining the molecular chain mobility.[22]

If the matrix and fiber are identical, then an interfacial adhesion indicator (B) can be used to characterize the interfacial adhesion,[23] and it is calculated with eq. (4):

$$B = \frac{(1 - \frac{\tan\delta_c}{\tan\delta_m})}{f} \qquad (4)$$

where subscripts c and m represent the composite and matrix, respectively, and f represents the fiber volume fraction. The larger the value of B is, the better the interfacial adhesion is. As shown in Table V, the composites with TESPT show high B values at the same fiber content, and this further demonstrates that TESPT could act as a good coupling agent for the fiber and matrix.

Morphological analysis

The interaction between the fiber and matrix is clear from SEM images of typical tensile fracture surfaces of composites, as shown in Figure 7. It can be seen in Figure 7(b) that the surfaces of fibers pulled out of composites with TESPT are relatively coarse, and plenty of NR remains on the rough fiber surface.[24] Good adhesion is clear from the matrix traces sticking to the surfaces of the fibers. It can be ascribed to the better transfer of frictional shear stress across the interface until the frictional resistance over the entire embedded fiber length is overcome.[25] As shown in Figure 7(a), the fiber surfaces are smooth with little adhering matrix. This is due to the poor affinity between the fiber and matrix without TESPT. Thus, the SEM studies further testified to the improved interfacial adhesion with the addition of TESPT.

CONCLUSIONS

The addition of TESPT can influence the crosslink structure of NR/cotton fiber composites. The composites with TESPT show a higher crosslink density than those without TESPT at the same fiber content.

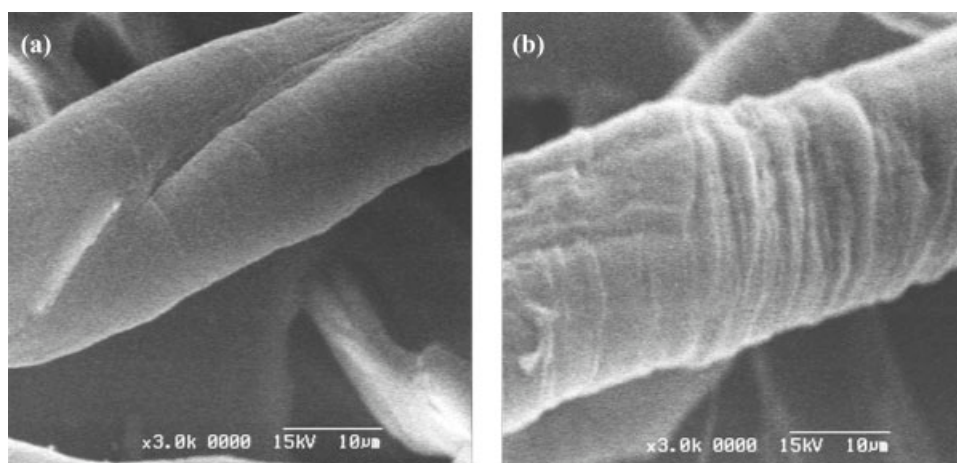The results of the Lorenz–Park equation and SEM images prove that the interfacial adhesion is

Figure 7 SEM micrographs of the tensile fracture surfaces of composites with 10 phr fiber: (a) without TESPT and (b) with TESPT.

improved between the fiber and matrix with the addition of TESPT.

NR/cotton fiber composites with TESPT show lower tan δ values and higher G' and T_g values than those without TESPT at the same fiber content. The composites with TESPT exhibit better mechanical properties than those without TESPT in terms of higher tensile strength and modulus at a definite elongation, initial modulus, and yield strength.

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