

Improvement of Interfacial Adhesion of Poly(*m*-phenylene isophthalamide) Short Fiber–Thermoplastic Elastomer (SEBS) Composites by N-Alkylation on Fiber Surface

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ABSTRACT: A composite of short-fiber, poly(*m*-phenylene isophthalamide), and thermoplastic elastomer styrene (ethylene–butylene) styrene (SEBS), was investigated. The fiber surface was modified by N-alkylation (heptylation and dodecylation) to improve their compatibility with a less polar SEBS matrix. Observation of fiber-surface morphology by SEM revealed surface roughness after N-alkylation. Nearly complete coating of the polymer matrix on the fiber was observed on a fractured surface of the composite, which is evidence for the improvement of fiber–matrix adhesion. It was found that the modulus of the composites grew with increasing fiber loading to approximately the same extent for both unmodified and modified fiber composites. Tensile strength of the modified fiber composites was found to improve significantly over that of the unmodified fiber composite. This suggests that the presence of the alkyl group on the fiber surface is responsible for an improvement of interfacial adhesion. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2414–2422, 1999

Key words: short-fiber composite; aramid; poly(*m*-phenylene isophthalamide) thermoplastic elastomer; SEBS

INTRODUCTION

Aramid short fibers such as poly(*p*-phenylene terephthalamide) (under the trade name of Kevlar by Du Pont Co.) and poly(*m*-phenylene isophthalamide) (under the trade name of Nomex by Du Pont Co. or the trade name of Conex by Teijin Co. Ltd.) are important as reinforcing fibers for plastics and elastomers due to their high strength, good thermal stability, sufficient flexibility, and light weight. However, the problem of fiber dispersion in the matrix often arises due to inertness of the fiber surface and the agglomera-

tion of fibers due to hydrogen bonding. In order to overcome this problem, chemical or physical bonding between the fiber and the matrix is usually introduced through the addition of a suitable coupling agent^{1–2} or chemical modification of the fiber surface.^{3–6} Plasma treatment has also been used to create a functional group on Kevlar and hence to provide bonding with the matrix.^{7–10}

One chemical method used to modify the surface of aramid fiber is the metalation reaction of the fiber surface to form polyanions, which is then followed by reaction with some functional groups or the grafting of suitable polymer segments.^{11–15}

Short-fiber reinforced thermoplastic elastomers have recently gained much attention due to their attractive properties.^{16–17} The advantages of thermoplastic elastomers are ease and economy in processing, high strength, and rigid-

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ity and recyclability, but some of their disadvantages are low thermal and low-dimensional stability at elevated temperatures. Incorporation of short fibers with high thermal stability and high strength, such as aramid fibers, in order to enhance dimensional stability is therefore interesting. We have investigated a system of poly(*m*-phenylene isophthalamide) (Conex) short-fiber reinforced styrene (ethylene–butylene) styrene (SEBS) thermoplastic elastomer composite. An improvement of interfacial adhesion of this composite system by partial hydrolysis on the fiber surface and the addition of a reactive compatibilizer, maleic anhydride–grafted SEBS, was reported.¹⁸ In this study another method of surface treatment was carried out by N-alkylation to reduce the interaction through hydrogen bonding between fibers and to reduce the polarity of the highly polar surface. The alkyl groups on the fiber surface are expected to be compatible with the EB block in the SEBS matrix, which should facilitate the enhancement of interfacial adhesion and therefore will result in the improvement of tensile properties of the composite.

EXPERIMENTAL

Materials

Materials used in this study were a styrene (ethylene–butylene) styrene block copolymer (SEBS, Kraton G1652), provided by Shell chemical Co. Ltd., with 29% styrene content as thermoplastic elastomer matrix, and poly(*m*-phenylene isophthalamide), Teijin-Conex, provided by Teijin Co. Ltd. in the form of short fibers with an approximate length of 3 mm and a diameter of 12–15 μm . The fibers were first washed with acetone, followed by distilled water to remove possible contamination, and they were then dried at 50°C to a constant weight in a vacuum oven. Anhydrous dimethyl sulfoxide (DMSO) and alkyl bromides were used as received. Sodium hydride (60% suspension in paraffin oil) was washed three times with dried hexane before use.

Surface Modification of Conex Fiber by N-alkylation

The technique used for N-alkylation of Conex fibers was similar to that reported earlier by Takayanagi et al.¹¹ The reaction scheme is presented in Figure 1. Since only slight modification on the fiber surface is needed, a small amount of

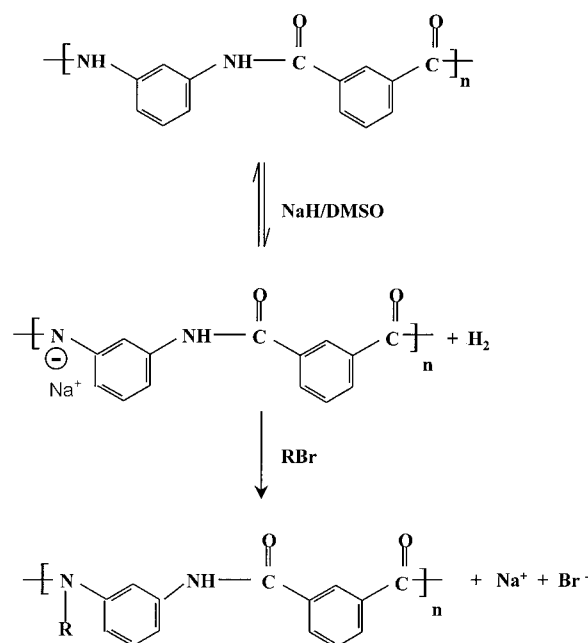


Figure 1 N-alkylation reaction on poly(*m*-phenylene isophthalamide) (Conex) short fiber.

the reagents and short reaction times were employed. In the first step, i.e. a metalation reaction, about 1,000 mL of anhydrous DMSO and 0.05 mol of purified NaH were reacted for 40 min at 70°C in a nitrogen atmosphere. After cooling to 30°C, 30 g of fiber were added into the reactor and stirred mechanically for 10 min. At this stage, the skin color of the fiber changed from off-white to pale yellow. Then about 0.25 mol of heptyl bromide was added and stirred for a further 3 h. The reaction was stopped by transferring the fibers into a large quantity of distilled water. The products were washed with acetone and water several times and dried at 60°C to a constant weight in a vacuum oven. For dodecylation, only 0.025 mol of NaH was used; otherwise the resulting fibers became hard and stuck together, and hence were difficult to disperse in the matrix.

The alkyl group on the fiber surface was characterized by Fourier transform infrared (FTIR) spectroscopy recorded on a Perkin-Elmer PE2000 spectrometer using diffuse reflectance accessory (DRIFT). Two hundred scans at a resolution of 2 cm^{-1} were performed to obtain a good spectrum.

Preparation of Composites

The composites were prepared by a melt blending technique, using a laboratory-size internal mixer (Haake Rheomix 90) at the set temperature of 175°C at a rotor speed of 90 rpm. To obtain good

dispersion, the fiber was first preopened in a Moulinex blender for a few seconds, then put in the mixing chamber in which the rotor was operated for 30 sec before the SEBS was added. After mixing for 10 min, the composite was discharged from the mixer and immediately rolled into a single sheet using a small laboratory two-roll mill. The composite sheet was then compression molded into a sheet 2 mm thick under a pressure of 15 MPa at 180°C for 10 min. The molded sheets were kept in a desiccator for 24 h prior to tensile measurement.

Fiber loading was varied from 0 to 7% by weight. We studied low-fiber content composites so as to maintain an important property of elastomers—their high percentage of extension. Another reason for studying such composites is that at low-fiber concentration, there is less of a problem of fiber agglomeration, so we can evaluate the results by focusing only on the effect of adhesion at the interface.

Measurement of Tensile Properties

The composite sheets were cut into dumbbell-shaped specimens with a cutting die of size 115 × 6 mm, parallel to the direction passing through the two-roll mill. According to ASTM D638, tensile properties were measured using an Instron 4301 tensile tester with a cross-head speed of 500 mm min⁻¹ and a full-scale load cell of 100 kg. All values presented were averages of at least five measurements.

Morphology Study

A scanning electron microscope (SEM, Hitachi S-2500) was utilized to characterize the surface morphology of Conex short fibers before and after modification, as well as the fractured surface of composites. The fractured surfaces of the composites were prepared by freezing the sample in liquid N₂ and breaking it rapidly. The samples were then coated with palladium (Hitachi E102 ion sputter) and observed using an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION

N-Alkylation of Conex Fiber Surface

In this study, the aramid (Conex) fiber surface was modified by a deprotonation reaction with NaH in DMSO, followed by N-alkylation.

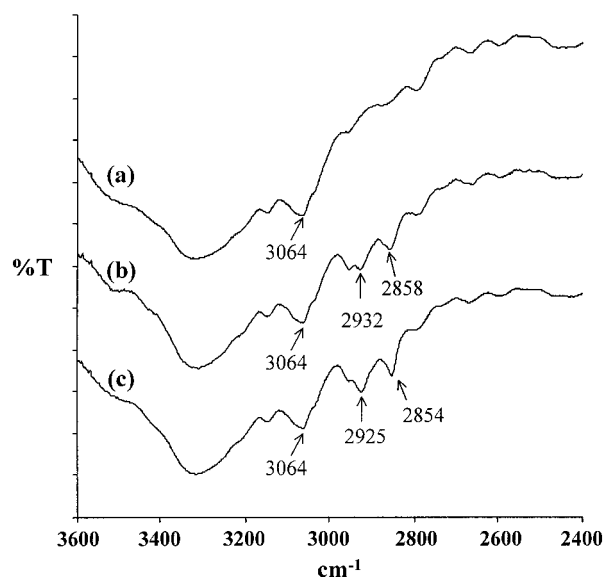


Figure 2 Infrared spectra (DRIFT) of (a) unmodified, (b) heptylated, and (c) dodecylated Conex fibers.

Infrared spectra of unmodified, heptylated, and dodecylated Conex fibers are presented in Figure 2 as curves a, b, and c, respectively. The C—H stretching vibration peaks at 2,858 and 2,932 cm⁻¹ are of the heptyl group, the peaks at 2,854 and 2,925 cm⁻¹ are of the dodecyl group, and the N—H stretching peak appears in all spectra at 3,064 cm⁻¹. Therefore, the partial N-alkylation on the fiber surface is considered successful.

SEM micrographs demonstrating surface morphology of the fibers before and after modification are shown in Figure 3. The surface of controlled fiber (unmodified) shown in Figure 3(a) is relatively smooth. Figure 3(b) shows the fiber taken from the reaction just after deprotonation for 10 min, that is, without alkyl groups on the surface, still shows a relatively smooth surface. It is seen that the ionization step does not affect the appearance of the fiber surface. In contrast, heptylated and dodecylated fibers exhibit high surface roughness, as shown in Figures 3(c,d), respectively. Takayanagi et al.¹¹ reported that deprotonated and N-heptylated Kevlar were soluble in DMSO. In our case, the Conex fiber surface was only partially deprotonated and then N-alkylated. During the alkylation reaction time of 3 h, some parts of modified fiber surface might be swollen in DMSO. When the reaction had been terminated with distilled water, the swollen parts might re-deposit on the fiber surface and hence might cause the surface roughness as seen in Figure 3(c,d). Apart from the expected compatibility of the alkyl group and the EB block in the SEBS

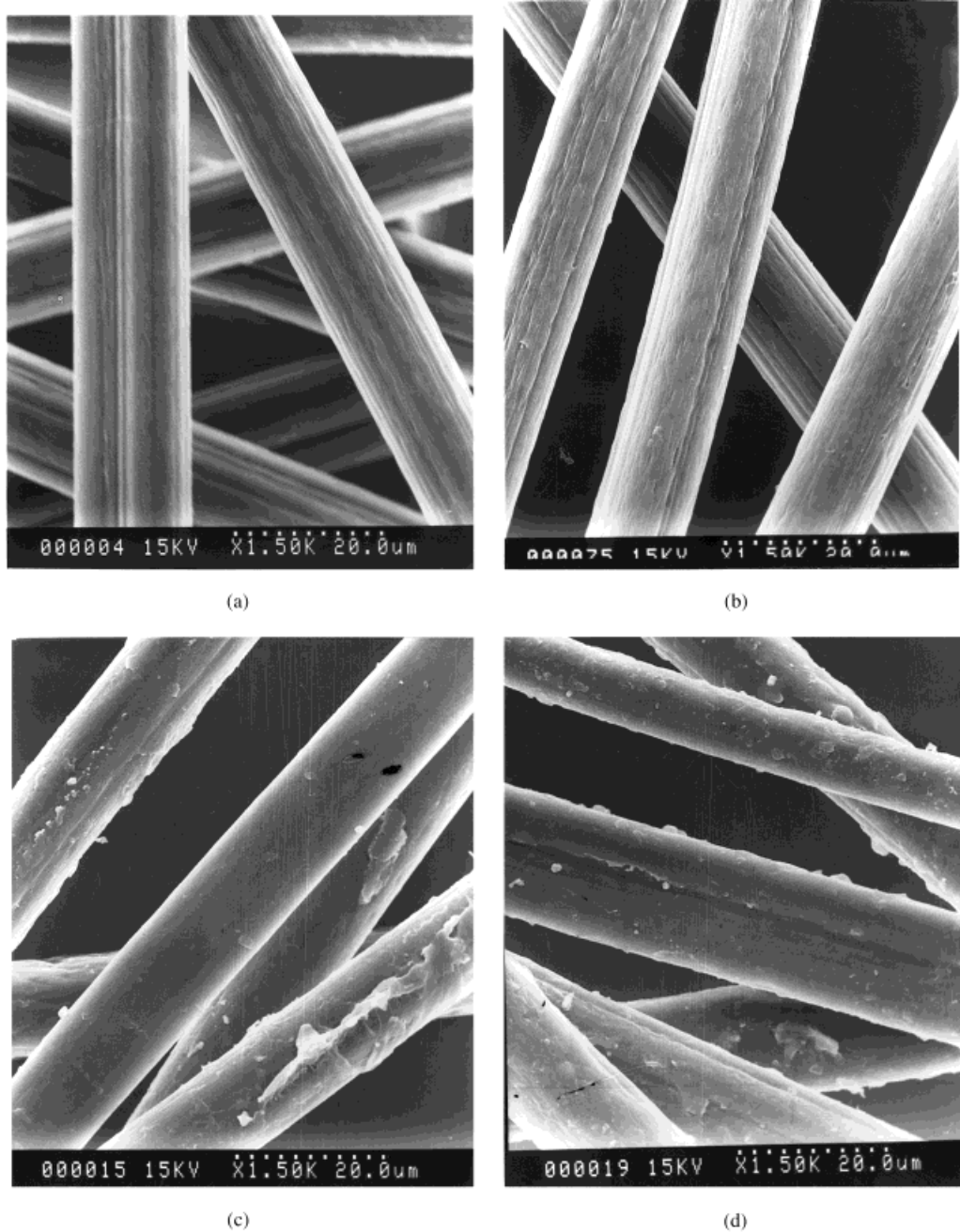


Figure 3 SEM micrographs of various Conex fibers (a) unmodified, (b) deprotonated, (c) heptylated, and (d) dodecylated Conex fiber.

matrix, this surface roughness of the alkylated Conex fibers will, in theory, also enhance the interfacial bonding between the fibers and polymer matrix via a physical interlocking or a friction mechanism.

Mechanical Properties of Composites

Plots of tensile properties of the composites containing unmodified and alkylated fibers—i.e.,

100% modulus, 300% modulus, tensile strength, and elongation at break as a function of fiber loading—are shown in Figures 4–7, respectively. The values of modulus at 100% and 300% extensions (Figs. 4 and 5, respectively) increase almost linearly with fiber loading at approximately the same extent for composites filled with unmodified and modified fibers. The increase in modulus of the composites with an increasing amount of fiber

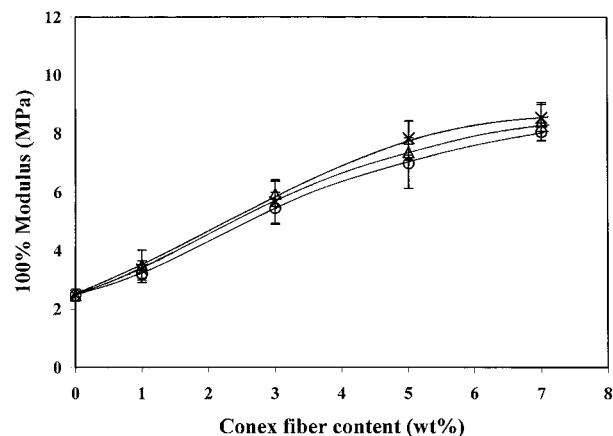


Figure 4 Tensile modulus at 100% strain versus fiber content of composites with (a) unmodified (Δ), (b) hetylated (\times), and (c) dodecylated (\circ) Conex fibers.

is mainly a result of the modulus of Conex fibers, which is far greater than that of SEBS. The higher the fiber loading is, the larger the volume fraction of high-modulus phase and thus the greater will be the bulk modulus of the composites. It can be seen that the tensile modulus is not affected significantly by N-alkylation at low-fiber loading. A slight improvement in 300% modulus is observed at 7 wt % fiber loading. Tensile strength is decreased, however, with increasing fiber loading due to the dilution effect of the matrix (see Fig. 6). However, the tensile strength of N-alkylated Conex composites is significantly higher than that of the composite filled with the unmodified fiber, particularly at high-fiber load-

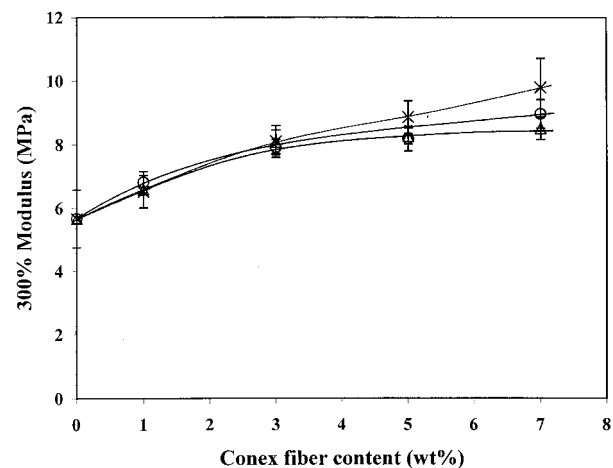


Figure 5 Tensile modulus at 300% strain versus fiber content of composites containing (a) unmodified (Δ), (b) hetylated (\times), and (c) dodecylated (\circ) Conex fibers.

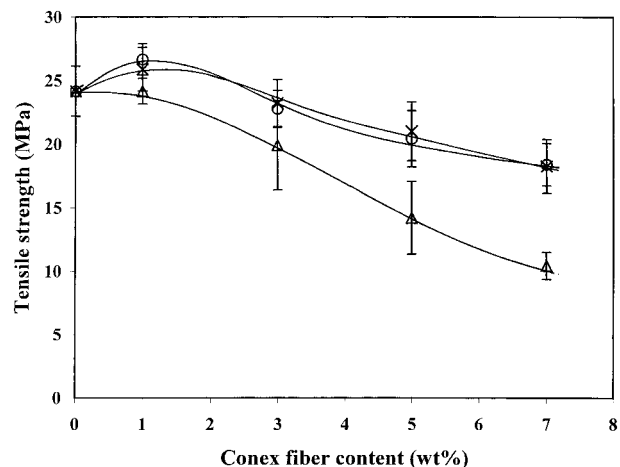


Figure 6 Tensile strength versus fiber content of composites containing (a) unmodified (Δ), (b) hetylated (\times), and (c) dodecylated (\circ) Conex fibers.

ing. At 7 wt % fiber loading, tensile strength of N-alkylated fiber-filled composites (18 MPa) is about 80% higher than that of the composite with unmodified fiber (10 MPa). On the other hand, elongation at break, shown in Figure 7, is only slightly decreased with increasing fiber loading. A slight increase of elongation at break is observed for N-alkylated fiber-filled composites, particularly at higher fiber content. No effect of the length of the alkyl groups on tensile properties of the composites can be noticed. The remarkable enhancement in tensile strength might be due to an increase in interfacial adhesion between fiber and polymer matrix via improvement of the com-

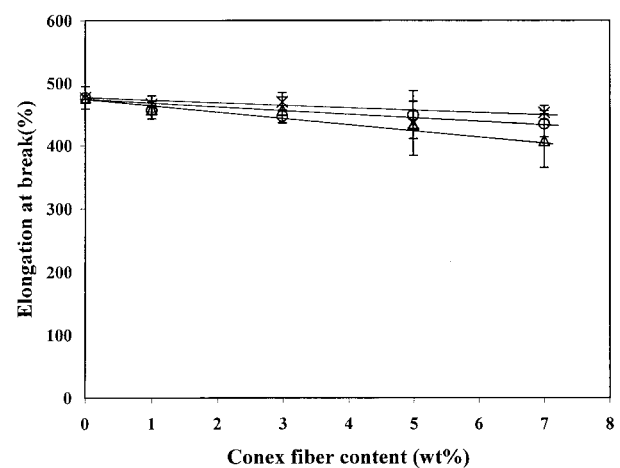


Figure 7 Elongation at break versus fiber content of composites containing (a) unmodified (Δ), (b) hetylated (\times), and (c) dodecylated (\circ) Conex fibers.

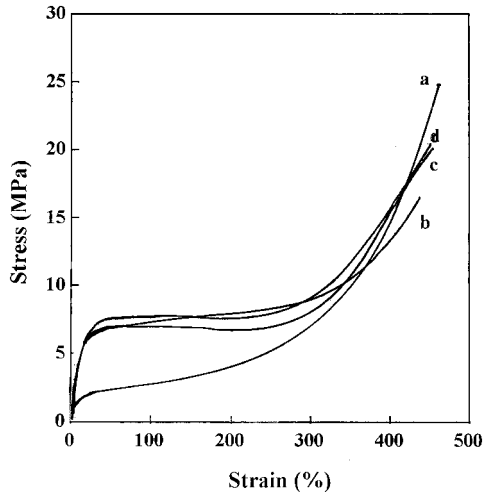


Figure 8 Stress-strain behavior of (a) neat SEBS, (b) 5 wt % unmodified Conex-SEBS, (c) 5 wt % heptylated Conex-SEBS and (d) 5 wt % dodecylated Conex-SEBS composites.

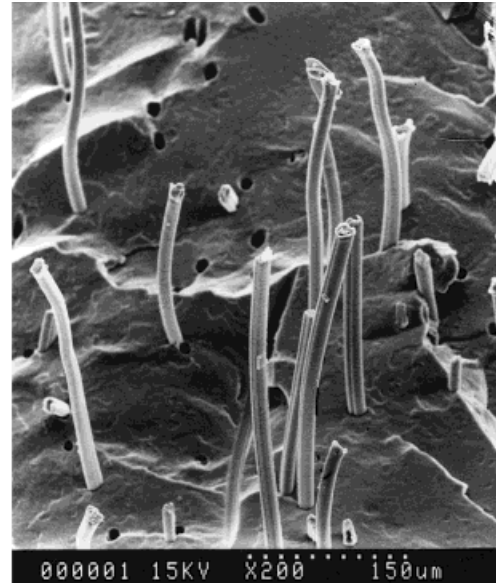
patibility between the alkyl group on the fiber surface and the EB block in SEBS matrix. In other words, the alkyl groups could assist the wetting of the fiber by the matrix. In addition, the bonded clumps on the surface could help enlarge the contact area between the fibers and the polymer matrix and hence enhance their interfacial bond strength. The evidence for improvement of adhesion at the interface can be clearly seen in SEM micrographs of fractured surfaces illustrated in the next section.

For comparison, the stress-strain behavior of unfilled SEBS and composites containing 5 wt % of unmodified and modified fibers is illustrated in Figure 8. It can be seen clearly that the unfilled SEBS (curve a) possesses the lowest tensile modulus at low strain and shows a strain-hardening effect (strain crystallization) at high strain. The thermoplastic elastomer SEBS exhibits similar behavior as a conventional strain crystallizing rubber due to the strong intermolecular interaction between the chains in the hard phase.¹⁷ Obviously, the strain hardening of SEBS decreases, causing tensile strength to decrease, as 5 wt % of unmodified fiber is added (curve b). This is due to the dilution effect of the matrix, and the high-stress concentration at the fiber ends destroys adhesion at the interface. As heptylated and dodecylated fibers are incorporated (curves c and d), strain crystallization increases again, this is, tensile strength becomes higher than that of the composite with unmodified fiber. Since the

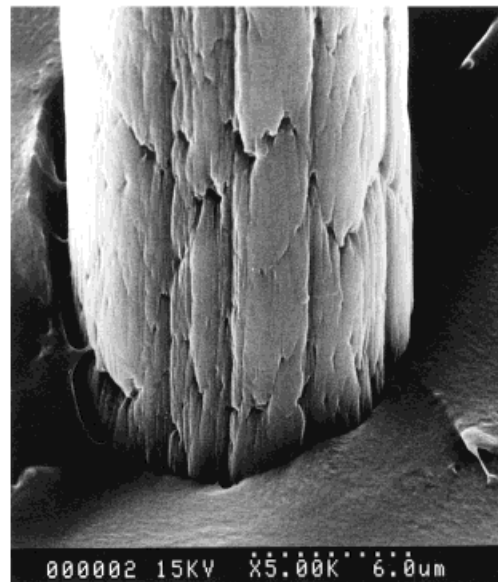
stress-strain curves rise steeply near the break point, the elongation at break is therefore not much affected.

Morphology of Composites

To obtain more information on the effect of fiber surface, the composites were studied using SEM. The micrographs of fractured surfaces of compos-

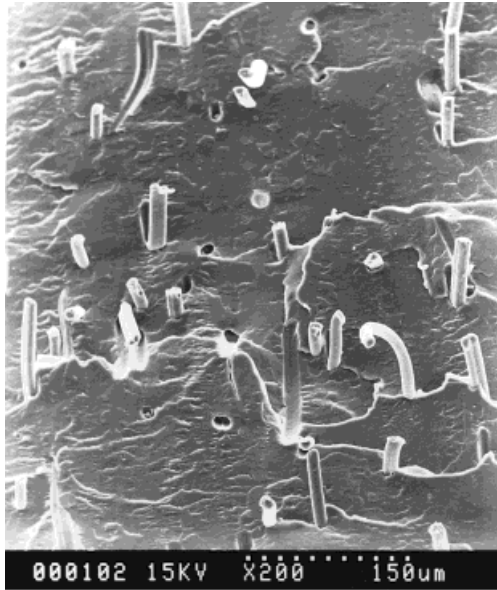


(a)

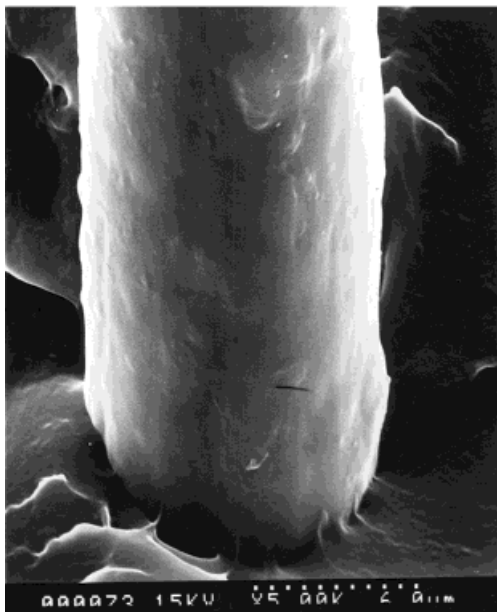


(b)

Figure 9 SEM micrographs of fractured surface of unmodified Conex composite at magnifications of (a) $\times 200$ and (b) $\times 5,000$.



(a)

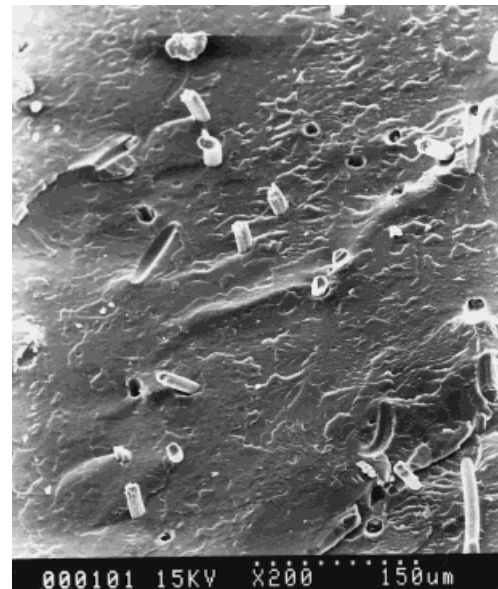


(b)

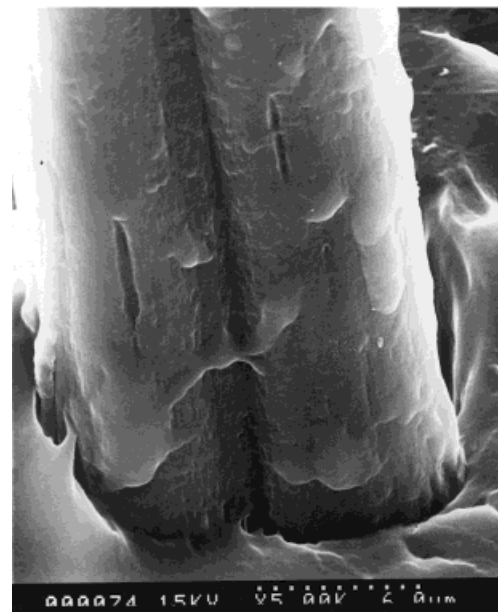
Figure 10 SEM micrographs of fractured surface of heptylated Conex composite at magnifications of (a) $\times 200$ and (b) $\times 5,000$.

ites filled with unmodified and alkylated Conex fibers are shown in Figures 9(a)–11(a) at magnification $\times 200$ and in Figures 9(b)–11(b) at magnification $\times 5,000$. Evidently, long fiber pullout is seen on the fractured surface of unmodified Conex–SEBS composite [Fig. 9(a)], indicating poor interfacial adhesion between fiber surface and

polymer matrix. Magnification of this specimen at $\times 5,000$, shown in Figure 9(b), indicates a number of grooves and cracks on the fiber surface. By contrast, the composites filled with heptylated and dodecylated short fibers, presented in Figures 10(a) and 11(a), respectively, show fiber breakage rather than pullout phenomena, which are evi-



(a)



(b)

Figure 11 SEM micrographs of fractured surface of dodecylated Conex composite at magnifications of (a) $\times 200$ and (b) $\times 5,000$.

dent in that the N-alkylation of the Conex fibers improves interfacial adhesion between Conex fiber and SEBS matrix. Clearer evidence of strong interfacial adhesion can be seen from micrographs at higher magnification power shown in Figures 10(b) and 11(b). In these figures, the surface of the fibers is coated by SEBS layer, thus no grooves and cracks can be observed. Also at the proximal end of the fiber that is buried in the matrix, there is good sticking between the matrix and the fiber. This evidence clearly supported the conclusion that the interaction force responsible for adhering the fiber to the matrix is the purely physical force acting through the alkyl groups since no chemical bonding between the fiber and the matrix is expected. The resulting improvement of interfacial adhesion is supported by a significant increase in tensile strength of the modified fiber-filled composites as discussed in the previous section.

Since the fibers were modified by using two successive steps—deprotonation followed by N-alkylation—we had to find out which step was more effective. To do this, deprotonated fibers were prepared by stopping the reaction in the first step with distilled water. The fibers obtained at this stage are shown in Figure 3(b). The other procedures used for preparation of the composites were the same as those described in the experimental sections. Tensile properties of deprotonated Conex–SEBS composites were measured (data not shown here). Modulus and elongation at break were found to be about the same as those of unmodified fiber. However, the tensile strength was found to be slightly higher than that of the unmodified Conex–SEBS system but lower than that of the alkylated Conex–SEBS system. These results ensured that the presence of the alkyl group was essential for the improvement of the composite properties.

Since the results from tensile measurements and the morphology shown in SEM micrographs are in good agreement, it can be concluded that the application of the N-alkylation process described to Conex fibers can significantly enhance the interfacial adhesion between the fibers and SEBS, and thus the mechanical properties of these Conex short-fiber-filled SEBS composites.

CONCLUSIONS

The partial N-alkylation onto short-fiber surface of poly(*m*-phenylene isophthalamide (Conex) was car-

ried out by a metalation reaction with NaH in DMSO solution followed by the addition of alkyl bromide (heptyl and dodecyl). The presence of alkyl groups on the fiber surface was detected by FTIR DRIFT technique. Original and modified fibers were melt-blended with thermoplastic elastomer styrene (ethylene–butylene) styrene (SEBS). Tensile properties of compression-molded specimens were measured. The morphology of the modified fibers and the fractured surfaces of the composites were investigated using SEM. The results obtained were as follows:

1. N-Alkylated Conex fibers show characteristic C—H stretching of alkyl groups in the DRIFT spectra. The result reveals that the fiber surface is successfully modified.
2. By comparison with the unmodified Conex short fibers, the alkylated fibers enhance tensile strength of the composites, probably due to the improvement in interfacial adhesion between the fibers and the SEBS matrix. This result is evident by SEM micrographs of fractured surface, which show nearly complete coating of matrix on the fiber surface.
3. From the systems studied, no difference has been observed from the effect of the length of the alkyl groups, i.e. 7- and 12-carbon atoms on the fiber surface, on tensile properties of the composites.

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