Fiber–Matrix Interactions in Aramid-Short-Fiber-Reinforced Thermoplastic Polyurethane Composites

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ABSTRACT: The mechanical and dynamic mechanical properties of thermoplastic polyurethane (TPU) elastomers reinforced with two types of aramid short fibers, *m*-aramid (Teijin-Conex) and copoly(*p*-aramid) (Technora), were investigated in this study with respect to the fiber loading. In general, both types of composites exhibited very similar stress–strain behaviors, except that Technora–TPU was stronger than Conex–TPU. This was primarily due to the intrinsic strength of the reinforcing fibers. Both types of fibers reinforced TPU effectively without any surface treatment. This could be attributed to good fiber–matrix interactions, which were revealed by the broadening of the tan δ peak in dynamic mechanical analysis. Furthermore, the morphologies of cryogenically fractured surfaces of the composites and extracted fibers, investigated with scanning electron microscopy, revealed possible polar–polar interactions between the aramid fibers and TPU matrices. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1059–1067, 2003

Key words: fibers; matrix; thermoplastics; polyurethanes

INTRODUCTION

Short-fiber-reinforced thermoplastic elastomers have recently gained much attention because of their attractive properties. Thermoplastic elastomers combine the processing advantages of thermoplastics, such as extrusion and injection, and the property advantages of elastomers without the addition of any vulcanizing agents, but there are some disadvantages, including low thermal and dimensional stability at elevated temperatures. The incorporation of short fibers with high thermal resistance and high strength, such as aramid fibers (i.e., Kevlar, Conex and Technora), to improve the dimensional stability of thermoplastic elastomers is, therefore, interesting. We have reported systems of aramid-fiber/thermoplastic elastomer composites, such as Kevlar–Styrene (Ethylene-Butylene) Styrene (SEBS),[1] Conex–SEBS,[2,3] and Kevlar–Santoprene.[4] The mechanical properties of short-fiber/elastomer composites depend on the fiber content, fiber aspect ratio, fiber dispersion, fiber orientation, and fiber–matrix interactions.

Fiber-to-matrix adhesion plays an important role in the reinforcement of a short fiber in the polymer matrix. The fiber–matrix interfacial adhesion is important in determining the mechanical, dynamic mechanical, and rheological characteristics of composites because the stress transfer occurs at the interface from the matrix to the fiber.[5] The chemical structures of both the fiber and the matrix determine the extent of the interfacial adhesion and, therefore, the strength of the composites. In the composite systems that we previously studied, between the polar aramid fiber and the nonpolar matrix, the fiber–matrix interaction was poor. Therefore, we carried out various fiber surface modifications and/or the addition of reactive compatibilizers, such as a maleic anhydride-grafted polymer with a chemical structure resembling that of the matrix, to improve the interfacial adhesion. For Kevlar/thermoplastic polyurethane (TPU), many researchers have reported good fiber–matrix interactions.[6–8]

In this study, two types of aramid short fibers, Conex and Technora, were used to reinforce TPUs. The effects of the fiber loading on the mechanical and dynamic mechanical properties and the morphology of the composites were investigated. Particular attention was paid to the fiber–matrix interactions.

EXPERIMENTAL

Materials

The elastomer used was a polyester-based TPU (Desmopan 385, Bayer AG, Leverkusen, Germany). The TPU was composed of a 4,4′-diphenylmethane diisocyanate hard segment with a softening temperature of 141–179°C and a polyester-based soft segment with a glass-transition temperature (T_g) of −30°C (determined by differential scanning calorimetry). It had a

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TABLE I
Properties of Materials Used for This Study

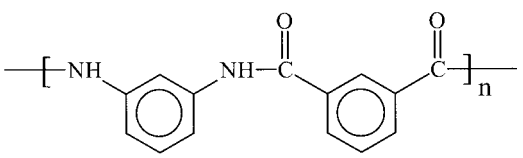
Polyester-based TPU (Desmopan 385)	Hardness (shore A)	85
	Tensile strength (MPa)	40
	Elongation at break (%)	450
Poly(m-phenylene isophthalamide) (Conex)	Young's modulus (GPa)	8–10
	Tensile strength (GPa)	0.6–0.7
	Elongation at break (%)	35–45
Copoly(3,4′-diphenylene ether/p-phenylene terephthalamide) (Technora)	Young's modulus (GPa)	20–21
	Tensile strength (GPa)	3.0–3.2
	Elongation at break (%)	5–7

density of 1.20 g/cm^3 and a hardness of 85 shore A. Two types of aramid short fibers (3 mm long) with different structures, poly(*m*-phenylene isophthalamide) (Conex) with a diameter of 15 μm and copoly(3,4′-diphenylene ether/*p*-phenylene terephthalamide) (Technora) with a diameter of 12 μm, were used in this study as reinforcements. They were kindly provided by Teijin, Ltd., Osaka, Japan. The properties of these materials are given in Table I, and their chemical structures are presented in Figure 1.

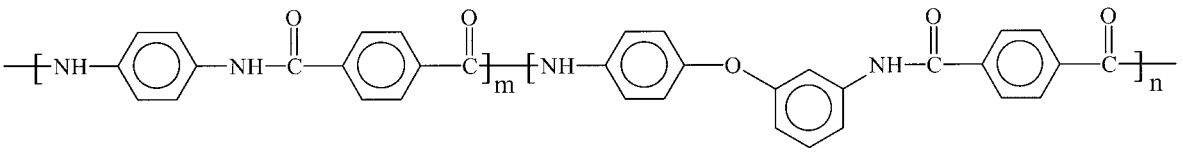
Processing

Before being used, the TPU pellets were dried in a circulating air oven at 100°C for 2 h for the removal of moisture. Both Conex and Technora short fibers were first washed with methylene chloride, then with methanol, and finally with deionized water for the removal of surface contaminants. The fibers were dried at 60°C in a vacuum oven for 24 h for the removal of moisture before use. So that fiber agglomeration would be avoided, dried fibers were first opened with a Moulinex blender (France) for a few seconds.

In the mixing procedure, an intermeshing corotating twin-screw extruder (Prism 16-TC, Staffordshire, UK) with a screw diameter of 16 mm and a length/diameter ratio of 25 was used. The processing was performed at a screw speed of 50 rpm, at a temperature of 175°C at the hopper zone, at temperatures of 195, 200, and 195°C at three barrel zones, and at a temperature of 185°C at a circular die 4 mm in diameter. The extrudate was immediately quenched in a water bath and then pelletized into granules 3 mm long as a maximum size; these were later vacuum-oven-dried at 70°C. The composites were shaped with an injection-molding machine (Dr Boy 22S, Fernthal, Germany). The processing conditions were a screw speed of 150 rpm and temperatures of 185, 195, and 185°C at the hopper, barrel and nozzle zones, respectively. The dumbbell-shape mold used was according to ISO 527 Type B. After their preparation, the composite specimens were kept in a desiccator to minimize moisture absorption.



Conex



Technora

Figure 1 Chemical structures of the Conex and Technora fibers.

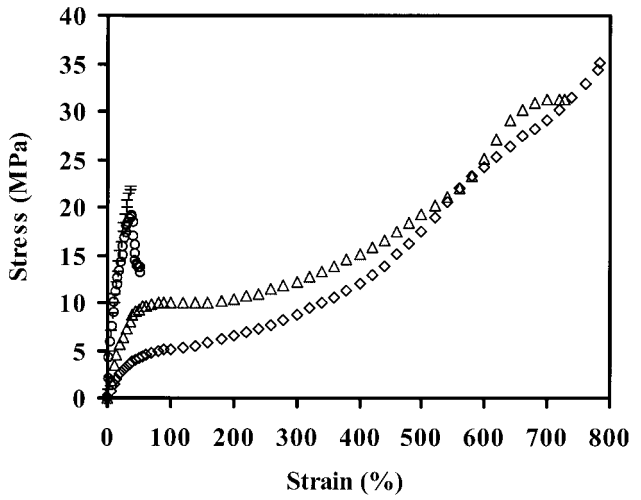


Figure 2 Stress–strain curves of Conex-short-fiber/TPU composites as a function of the fiber loading: (◇) 0, (△) 3, (○) 7, and (+) 10% fiber.

Characterization

Mechanical properties

Tensile testing was carried out on an Instron 4301 (Bucks, UK) tensile tester with a load cell of 5 kN and at a crosshead speed of 500 mm/min in agreement with ASTM D 638. The hardness of the composites was measured with a hardness tester (Zwick D-7900, Ulm, Germany) with a shore A durometer according to ASTM D 2240-91.

Dynamic mechanical thermal analysis

The dynamic mechanical properties were measured on a Polymer Laboratories MKII (Loughborough, UK) dynamic mechanical thermal analyzer in a bending mode at a frequency of 3 Hz. The sample length was 5 mm, and the displacement was 64 μm peak to peak. The measurements were carried out from -60 to 100°C at a heating rate of 5°C/min.

Scanning electron microscopy (SEM)

The fracture surfaces of the composites were prepared by cryogenic fracturing in liquid nitrogen. The samples were then coated with palladium (Hitachi E102 ion sputterer, Ibaraki, Japan) and observed under a scanning electron microscope (Hitachi S2500) with an accelerating voltage of 15 kV. In addition, the composites were also extracted with tetrahydrofuran in a Soxhlet apparatus for 72 h. The extracted fibers were collected, dried in a vacuum oven at 70°C for 24 h, and observed under SEM as described previously.

RESULTS AND DISCUSSION

Mechanical properties of the composites

In general, the Conex–TPU and Technora–TPU composites exhibited very similar stress–strain behaviors. Figure 2 summarizes the stress–strain behaviors of neat TPU and its Conex composites. TPU, like other rubbers, deforms easily under low stress. When the strain is increased, the stress rises steeply, and the material breaks at a strain of about 800% and at a stress of about 35 MPa. The increase in the stress at a high strain is known as *strain-induced crystallization* or *strain hardening*. When 3 wt % Conex fiber was added to TPU, the stress in the low-strain region (50–200%) increased to a value about twice that of TPU. The high-strain behaviors of neat TPU and a 3 wt % Conex/TPU composite were very similar. When 7 wt % Conex fiber was added, the initial stress increased further and then dropped sharply, and the material failed at a very low strain (ca. 50%). For reasons discussed later, this may appropriately be called *yieldlike behavior*. With about 10 wt % fiber, the initial stress seemed to saturate, and the material again failed at a very low strain (ca. 25%) without a drop in stress.

Figure 3 displays the mechanical properties of the Conex–TPU and Technora–TPU composites in terms of the modulus, tensile strength, elongation at break, and hardness. A linear relationship between the fiber content and modulus measured at a 10% strain was observed. There was, however, a difference in the moduli of the two composites. Technora–TPU composites exhibited higher moduli than Conex–TPU composites over the entire range. This was simply due to the higher modulus of the reinforcing Technora, which was about twice that of the Conex (see Table I).

The tensile strengths of both types of composites decreased with increasing fiber content. A minimum tensile strength close to a fiber content of 7% was found, and beyond this point, the strength rose again. Technora–TPU composites again exhibited higher tensile strengths than Conex–TPU. The pattern with a minimum point in the tensile strength suggested that there were two different mechanisms that determined the failure stress of the composites. Without reinforcing fibers, the TPU matrix exhibited rather high strength because of strain hardening. When a small amount of fiber was added, the strength of the composite was still governed by that of the TPU matrix. Under these circumstances, it can be envisaged that a fiber would dilute the system (a dilution effect).[9] As a result, in the low-fiber-content region ($<7\%$), the tensile strength of the composite decreased with increasing fiber content. At the same time, the addition of the fiber also increased the initial stress (in the low-strain region) or modulus of the composites. This was expected to increase with increasing fiber content. The dilution (of the strain-hardening matrix) and reinforcing effects occurred simultaneously, and their effect was to give a minimum tensile strength, as observed. Similar behaviors of short-fiber-reinforced composites have been reported previously.[6,7,10]

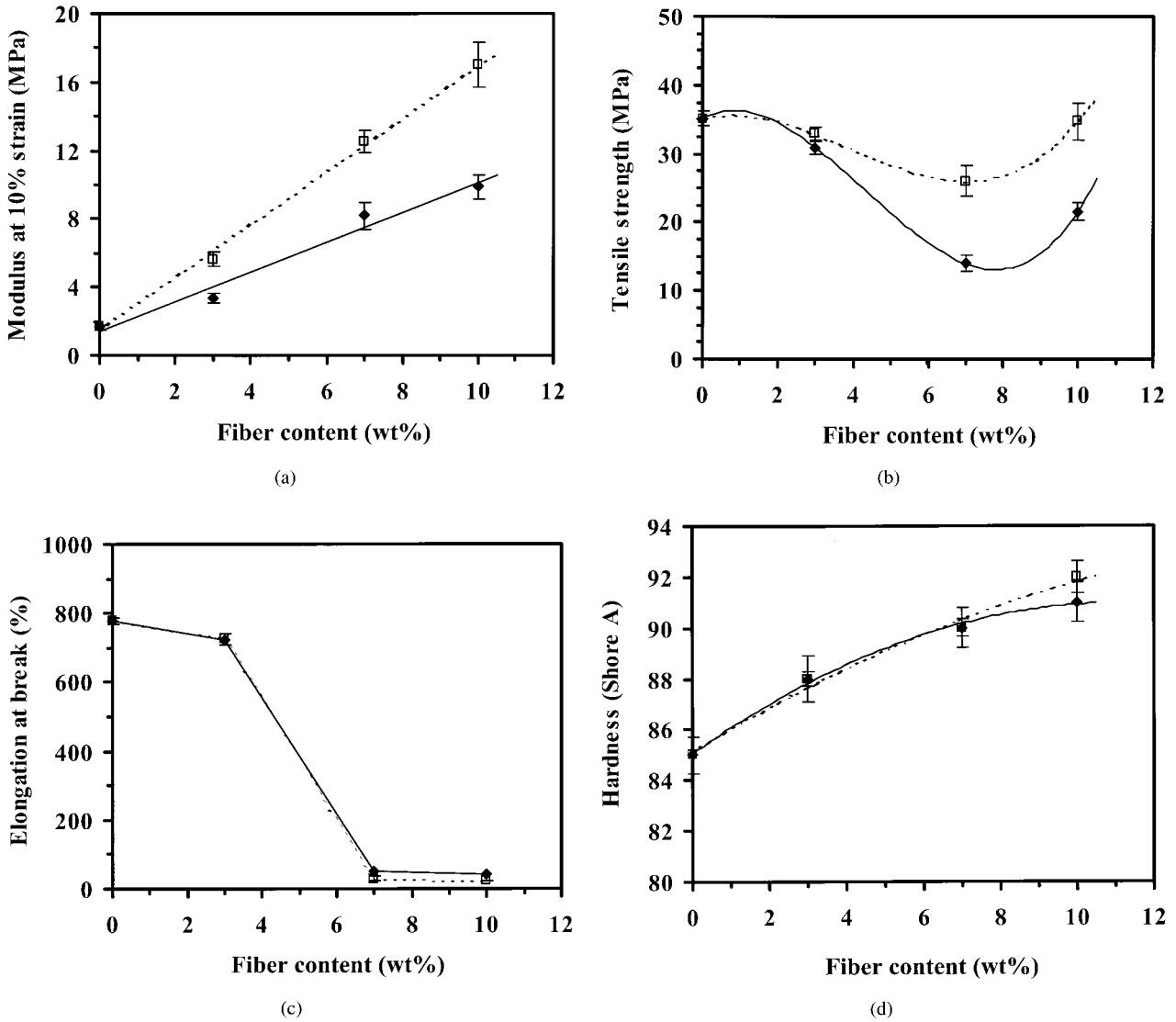


Figure 3 Mechanical properties of aramid-short-fiber/TPU composites as a function of the fiber loading for (♦) Conex and (□) Technora: (a) the modulus at 10% strain, (b) the tensile strength, (c) the elongation at break, and (d) the hardness.

For the elongation at break, at a low level of the reinforcing fiber, the composites failed at a strain similar to that of TPU itself. At an approximately 7% Conex fiber content and beyond, the failure strain dropped sharply to a value of about 25%. It is very likely that the debonding of the TPU–fiber interface occurred in this region. Such debonding would result in a drop in stress (see Fig. 2). This was not a yield process in the normal sense, as neither the TPU matrix nor reinforcing fibers exhibited yielding.[11] At a 10% fiber content, no drop in stress before failure was seen. The disappearance of this yieldlike behavior was likely caused by catastrophic failure of the matrix just after debonding. The elongation at break displayed a dramatic decrease with increasing fiber content. This was by no means unexpected. TPU, because of its elastomeric nature, is capable of undergoing great strain. Any modification that leads to inhomogeneity (e.g., the incorporation of fibers) in the materials is very likely to reduce the breaking strain. Therefore, the breaking strain was expected to decrease with increasing fiber content.

The composites showed an increase in hardness with increasing fiber content. No difference was seen between Conex and Technora composites. The simi-

TABLE II
Storage Modulus (E') at 25°C of Conex–TPU and Technora–TPU Composites

	E' (MPa) at 25°C	
Fiber content (wt %)	Conex	Technora
0	28.6	28.6
3	43.0	52.7
7	71.4	81.7
10	78.5	103.3

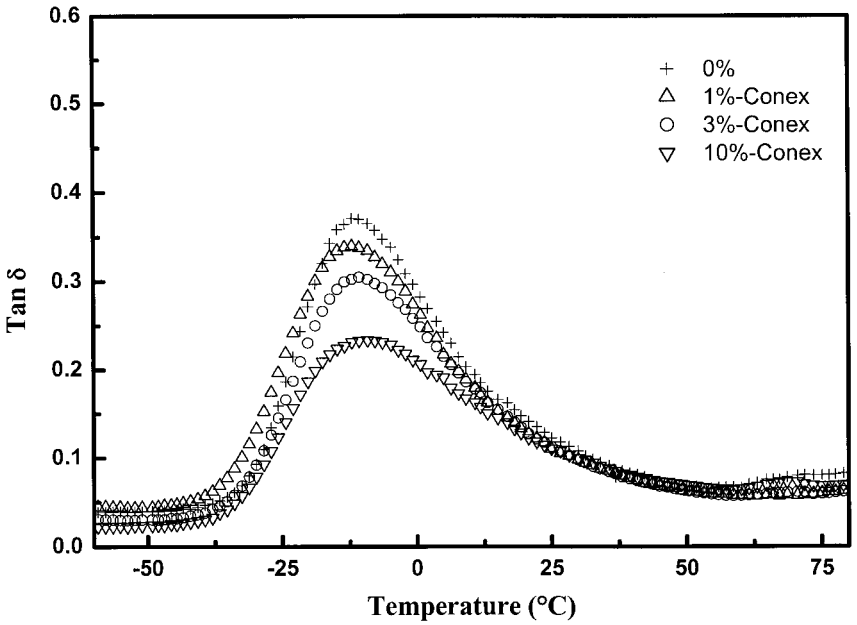


Figure 4 Temperature versus tan δ for Conex–TPU composites as a function of the fiber loading.

larities observed in the two composites, despite a significant difference in their moduli, could be explained as follows. Hardness is a property measured laterally, whereas modulus is measured longitudinally. The composite samples were prepared by injection molding, and as a result, the fiber was expected to align in the particular direction (along the dumbbell axis). Therefore, the difference in the mechanical properties of the two types of reinforcing fibers showed up under tensile testing conditions. For hardness measurements, the composite was pressed against an indenter in the lateral direction of the injection-molded specimen. In this direction, the fiber properties might not have differed significantly and, therefore, led to the same hardness values.

From these results, it is clear that the mechanical properties of TPU could be improved by the addition of either Conex fiber or Technora fiber. Compared with other systems of a similar nature investigated by our group,[2–4] TPU composites offer significantly better stiffness and strength at all levels of reinforcement being investigated. This may be due mainly to the

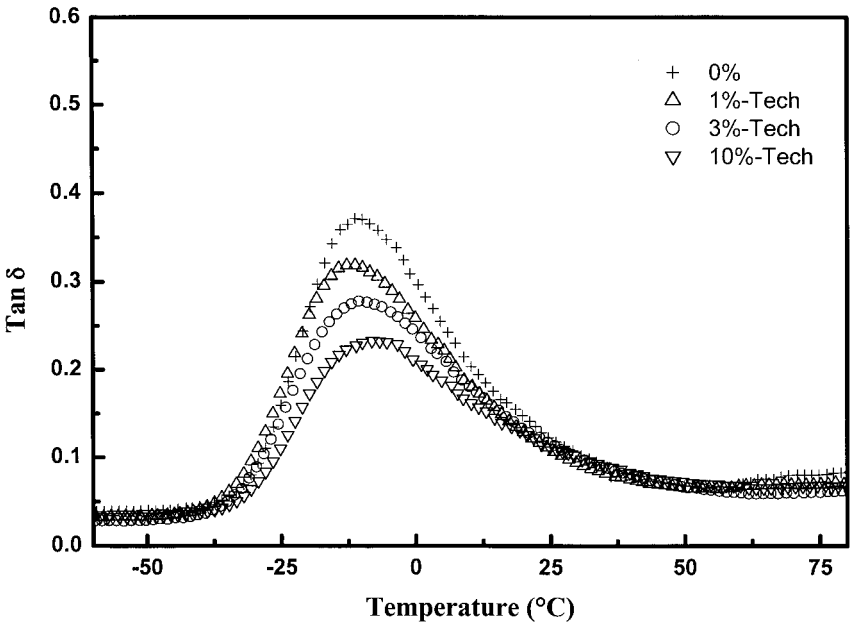


Figure 5 Temperature versus tan δ for Technora–TPU composites as a function of the fiber loading.

TABLE III
Tan δ_{max} and T_g from the Plot of Tan δ with Temperature of Conex–TPU and Technora–TPU Composites

Fiber content (wt %)	Tan δ_{max}		T_g(°C)	
	Conex	Technora	Conex	Technora
0	0.37	0.37	−11.2	−11.2
3	0.31	0.28	−10.7	−10.6
7	0.25	0.25	−9.4	−7.5
10	0.23	0.23	−9.3	−7.4

good adhesion between TPU and the fibers. Good adhesion means that stress can be transferred efficiently to the reinforcing fiber and that adhesion is maintained up to a very high stress.

Dynamic mechanical analysis

The storage moduli of both the Conex–TPU and Technora–TPU composites at various temperatures were studied with dynamic mechanical analysis. It confirmed that, at the same fiber content, the Technora–TPU composite had a higher modulus than the Conex–TPU composite. Results at 25°C are shown in Table II: the Technora–TPU composites had storage moduli approximately 25% higher than those of the Conex–TPU composites.

In addition, the interaction between the TPU matrix and reinforcing fibers was also studied. Figures 4 and 5 display the loss factor (tan δ) as a function of temperature for the Conex–TPU and Technora–TPU composites, respectively. The observed peak at about −10°C corresponds to T_g of the TPU soft segment. Neat TPU exhibited the greatest tan δ value, and the magnitude of this peak decreased with increasing fiber content (dilution effect). Table III displays the measured maximum loss factor (tan δ_{max}) and its positions for TPU and its composites. T_g shifted slightly toward higher temperatures with increasing fiber content, that is, from −11.2°C for TPU to −7.4°C for a 10 wt % Technora–TPU composite and to −9.3°C for a 10 wt % Conex–TPU composite. In other words, the shift in T_g in the Conex–TPU composite was slightly less than that in the Technora–TPU composite.

In addition to the shift in the tan δ position, the breadth of the tan δ peak became wider with increasing fiber content. This can be easily seen by scaling or normalizing of the tan δ peaks to the same height, as shown in Figures 6 and 7. The broadening of the peak was not symmetric. It occurred only on the high-temperature side of the peak. This implies that T_g of a certain fraction of TPU remained unchanged, whereas that of another fraction shifted to a higher temperature. This observation was attributed to the wall effect (immobilizing effect) introduced by the fibers, which reduced the matrix mobility, as discussed by Rebenfeld et al.[12] and Correa et al.[8] The polymer matrix in the immediate vicinity of a fiber is thought to be in a different state in comparison with the bulk matrix. This would affect the relaxation behavior of the matrix molecules. A shift as high as 5°C was observed. Similar behaviors were also found in other systems.[6,13]

Fractured surfaces of the composites

The cryogenically fractured surfaces of the composites investigated by SEM are shown in Figures 8(a) and

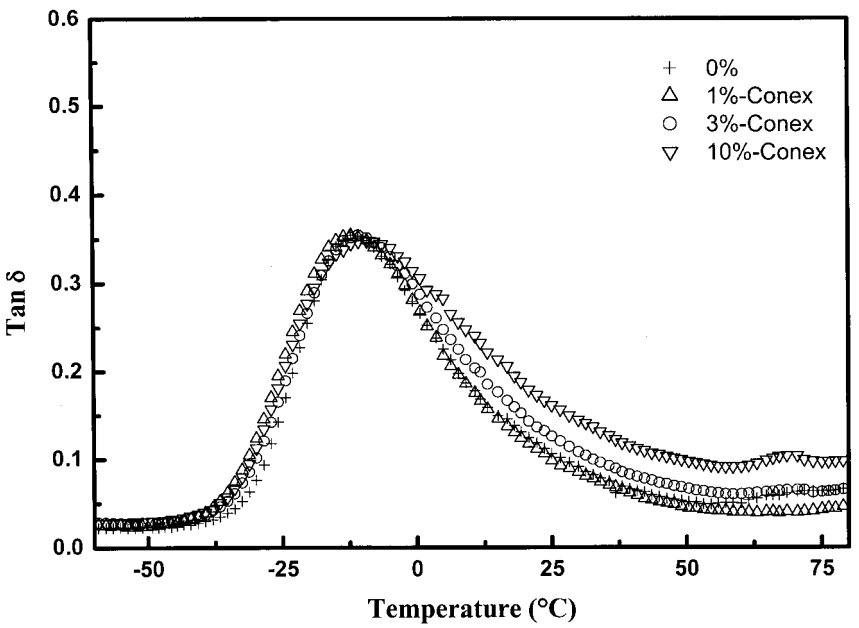


Figure 6 Normalized tan δ versus the temperature for Conex–TPU composites as a function of the fiber loading.

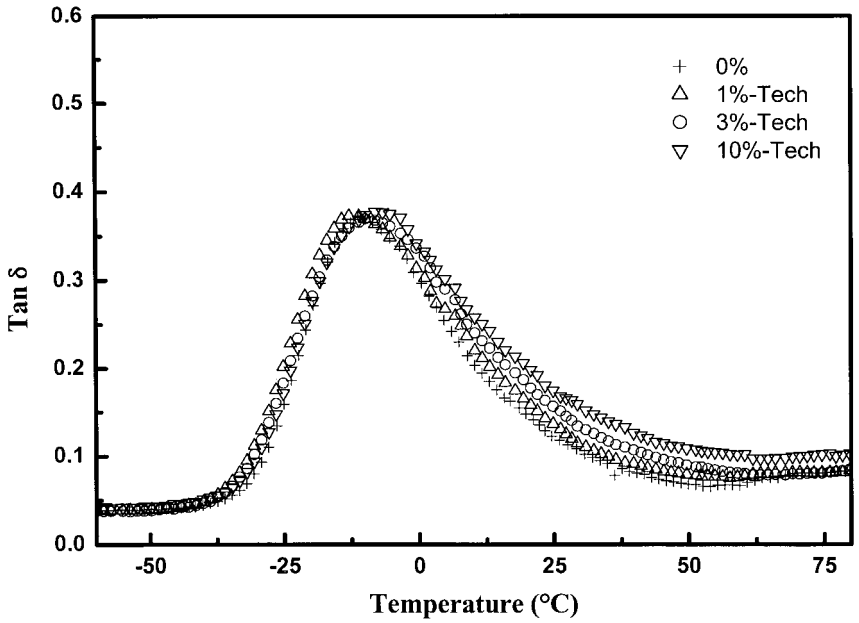


Figure 7 Normalized tan δ versus the temperature for Technora–TPU composites as a function of the fiber loading.

9(a) for Conex and Technora, respectively, at a magnification of ×200. They reveal that the composite with Conex fibers had fiber breakage, whereas the Technora system showed long fiber pullout as a result of the higher strength of the Technora fibers. However, in both cases, the proximal ends of the fibers were buried in the matrix with good sticking between the fibers and the matrix, as shown in Figures 8(b) and 9(b) for Conex and Technora, respectively, at a magnification of ×4000. This evidence clearly reveals good adhesion at the interface between the fibers and the matrix.

Surface morphology of the extracted fibers

To prove whether the fiber–matrix adhesion resulted from polar–polar interactions or covalent bonds between the aramid fibers and TPU matrix, we attempted to investigate the amount of bound rubber (unextracted rubber due to covalent bonds between the fiber and matrix) remaining on the fiber surfaces after the solvent extraction of the composites. Figure 10(a,b) shows SEM micrographs of extracted fibers from Conex–TPU and Technora–TPU composites, respectively. The extracted fiber surfaces were clean;

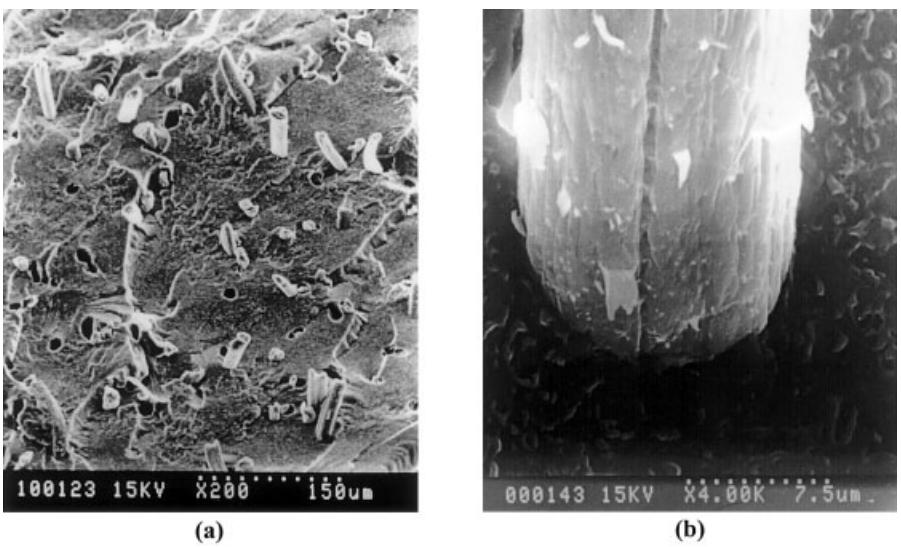


Figure 8 SEM micrographs of the fracture surface of a 7 wt % Conex composite at magnifications of (a) ×200 and (b) ×4000.

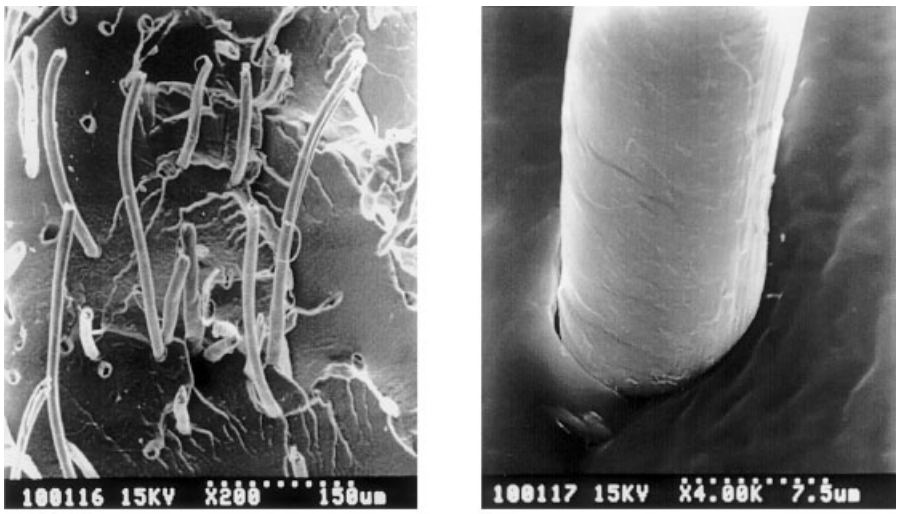


Figure 9 SEM micrographs of the fracture surface of a 3 wt % Technora composite at magnifications of (a) ×200 and (b) ×4000.

that is, there were no traces of bound rubber. Therefore, it can be concluded that the interfacial interactions between the aramid fibers and TPU matrix were mainly due to physical polar–polar interactions. It is noteworthy that the extracted Conex fibers were still in good condition, whereas the extracted Technora fibers seemed to be damaged and peeled off. This was due to the fact that the Technora was more rigid than the Conex.

CONCLUSIONS

The reinforcement of TPU elastomers with Conex and Technora fibers was achieved without any surface treatment or addition of a compatibilizer. Up to a 10 wt % fiber loading, the modulus of the composites was linearly increased with increasing fiber content. Both the modulus at 10% strain (from tensile testing) and the storage modulus (from dynamic mechanical analysis) of the Technora–TPU composite were significantly higher than those of the Conex–TPU composite. This might be due to the fact that the modulus of the Technora fiber was about twice that of the Conex fiber.

The results from dynamic mechanical analysis measurements revealed that T_g of the TPU soft segment shifted toward higher temperatures and that the width of the tan δ peak slightly increased with increased fiber loading. This suggests a reduction of the mobility of the matrix molecules in the vicinity of the fibers due to good interfacial adhesion. SEM micro-

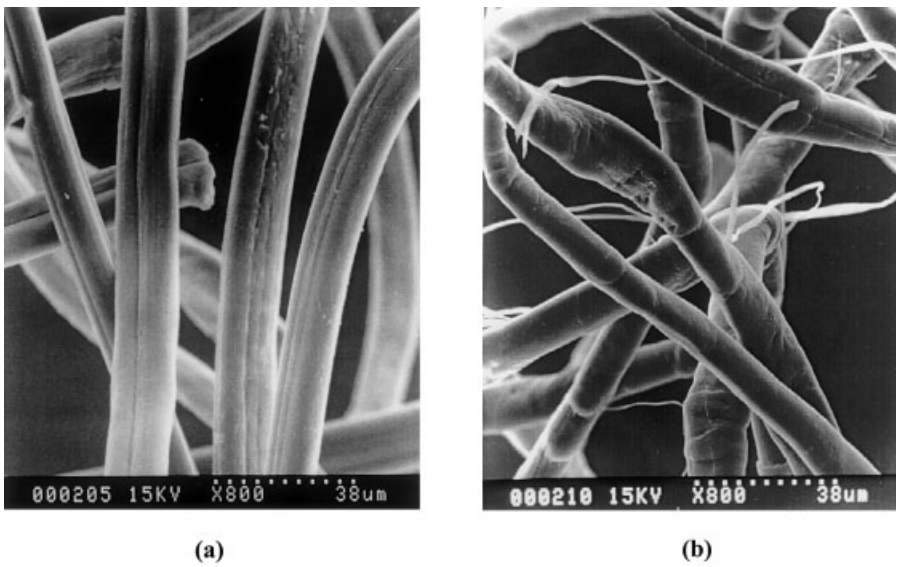


Figure 10 SEM micrographs of extracted fibers: (a) Conex and (b) Technora.

graphs of the fractured surfaces also provided evidence for good adhesion between the fibers and matrix as fiber breakage and sticking of the matrix at the proximal ends of the fibers were seen.

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