

Influence of the Nature and the Content of Carbon Fiber on Properties of Thermoplastic Polyurethane–Carbon Fiber Composites

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ABSTRACT: Three carbon fibers (CF) of different characteristics and properties were used to determine the most suitable characteristics for a carbon fiber to reinforce a thermoplastic polyurethane elastomer (TPU) matrix. The TPU was synthesized with a moderate amount of hard segments to bring polarity to the matrix without losing flexibility. On the other hand, the CF were chosen with respect to their different mechanical properties, diameter, and length to study the influence of those parameters on the TPU matrix. Additionally, the fibers were used in different amounts as well as after different oxidation treatments (i.e., different polarity). The mechanical properties and surface character-

istics of the composites were analyzed using several experimental techniques (SEM, X-ray photoelectron spectroscopy, dynamic mechanical thermal analysis, and tensile tests). The results obtained showed that the surface polarity, diameter, and length of the CFs are related to the reinforcement of a medial polar TPU matrix, whereas the mechanical properties of the CF do not influence those of the composite. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2676–2683, 2003

Key words: thermoplastics; composites; carbon fibers; elastomers; reinforcement

INTRODUCTION

The reinforcement of elastomers with short or discontinuous fibers gives composites that, combining the rigidity of the fiber with the elasticity of the elastomer, have a series of properties that make them suitable for many specific applications. In addition, they present a benefit in contrast to the composite prepared with continuous fibers: instead of using slow processes for incorporating continuous fibers, short fibers are incorporated as one of the recipe ingredients, with the stipulation that, during the mixing process, the direction of the cylinder rotation is constant (to get maximum uniformity in the orientation of the fiber in the matrix^{1,2}).

Several factors should be considered to achieve an adequate reinforcement with short fibers, although the levels reached with continuous fibers can never be attained,^{3–5} including preservation of highly uniform fiber orientation in the matrix, preservation of an appropriate length/diameter ratio (aspect ratio) in the fiber, and establishment of the strongest possible fiber–matrix bond. The aspect ratio can be directly measured, the orientation of the fiber in the matrix can be

forced during the composite preparation and assessed by green strength measurements, and the matrix–fiber bond may be improved using an adhesive system. Regarding this last factor, many systems have been studied to increase fiber adhesion to the matrix,⁶ of which the dry three-components (silica, phenol, and formaldehyde) procedure and the immersion method (impregnation of the fiber with RLF) are the most widely used.

In the composite systems where a polymeric matrix is used, an important question may arise: why not use an elastomer with both good mechanical and adhesion properties? This would solve the problem of the fiber–matrix interaction without the need of any additional component except for the polymer matrix and the fiber, thus decreasing both the economic cost and the preparation time. On the other hand, among polymers most widely used as adhesives, polyurethanes stand out for their good adhesion and mechanical properties; in addition, their properties are determined by the synthesis conditions and composition,^{7–13} which provide polymers with the desired behavior.

In view of these advantages, combined with the increasing use of polyurethane composites in different applications such as construction materials, electronics, vehicle interiors, aircraft, and sporting goods,^{14–16} our research has focused on the preparation and study of thermoplastic polyurethane (TPU)–short-fiber composites. The fibers chosen were carbon fibers (CFs)

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TABLE I
Main Characteristics of the Carbon Fibers

Carbon fiber	Length (mm)	Diameter (μm)	Critical length (mm)	Tensile strength (MPa)	Classification
H	6	5	0.13	4500	HPCF ^a
D	0.15	13	0.30	800	MGPCF ^b
K	6	18	0.34	670	GPCF ^c

^a High-performance carbon fiber.

^b Milled general purpose carbon fiber.

^c General-purpose carbon fiber.

because of their good conductive and mechanical properties. Several characteristics were considered in the choice of CF: mechanical properties, surface polarity, and dimensions (diameter and length).

The main objective of this work was to study the influence of the nature and content of carbon fibers on the properties of TPU-carbon-fiber composites.

EXPERIMENTAL

Materials

Preparation of TPUs

TPU was prepared from diphenylmethane-4,4'-diisocyanate (MDI, 98% purity; Aldrich, Gillingham, Dorset, UK), poly(ϵ -caprolactone) ($M_n = 3000$ g/mol) as macroglycol (from Solvay Interox, Cheshire, UK), and 1,4-butanediol (99% purity; Aldrich) as chain extender. Moisture in the macroglycol was removed by heating overnight at 70°C under a 5 Torr (1 Torr = 133.33 Pa) pressure. The NCO content in the prepolymer was obtained by titration with *n*-butylamine (ASTM D 2572-80).

The synthesis method used to prepare the TPU was the prepolymer method. The prepolymer was obtained by reacting the macroglycol with MDI in excess (NCO groups/OH groups = 3), under stirring and at temperature below 80°C. Further, the prepolymer was reacted (12 h at 80°C in an oven, after mixing), to complete the polymerization with a stoichiometric amount of 1,4-butanediol. The NCO/OH ratio used was chosen to achieve polarity in the TPU without decreasing its elasticity. More details on the properties of the TPU are given elsewhere.^{10,11}

Preparation of TPU-carbon-fiber composites

To prepare the composites three different carbon fibers were used: H (Hércules Aerospace España S.A.), D (Osaka Gas Co., Osaka, Japan), and K (Kureha Chemical Industry Co., Tokyo, Japan), the characteristics of which are shown in Table I, and surface composition, determined by XPS, shown in Table II. The CFs were chosen considering their different mechanical properties [a high-performance carbon fiber (HPCF) and a general-purpose carbon fiber (GPCF)] and dimensions [including a milled general-purpose carbon fiber (MGPCF)]. To prepare some of the composites, the fibers were oxidized with 35 or 70 wt % nitric acid (to modify their surface polarity), using a method described elsewhere.¹⁷ The composites are referred to as F0N, F35N, and F70N, where F is the fiber used (H, D, or K) followed by the oxidation treatment (0, 35, and 70 wt % of nitric acid N, respectively).

All composites were obtained using a two-roll laboratory mill (30.5-cm roll length, friction rate 1 : 1) at 50°C. The fiber was added to the TPU as supplied or after oxidation. Although it can be assumed that all possible fiber orientation is achieved during the first mill pass,¹⁸ several additional passes were performed, rolling the film along the mill direction before each pass, to ensure homogeneity.

Characterization techniques

Scanning electronic microscopy (SEM)

The surface of the samples was analyzed with a Philips (The Netherlands) XL30 ESEM microscope. The samples did not need to be metallized and the pres-

TABLE II
Surface Composition (%) Obtained from the Carbon Fibers' Photoelectron Spectra

Carbon fiber	Nitric % used in the oxidation								
	0%			35%			70%		
	C	O	N	C	O	N	C	O	N
H	81.76	13.58	4.66	80.77	13.81	5.42	78.49	16.95	4.56
D	84.17	14.65	1.18	78.37	19.83	1.80	74.46	23.60	1.94
K	90.91	8.64	0.45	85.47	13.25	1.28	84.03	14.79	1.18

sure used in the microscope was 1.8 Torr. The images were taken from the failure surface resulting from the strain–stress test performed to study the composites' mechanical properties.

X-ray photoelectron spectroscopy (XPS)

The photoelectron spectra (XPS) were recorded in a Fisons Escalab 200R spectrometer equipped with a hemispherical energy analyzer and Mg- K_{α} X-ray source (h.v. = 1253.6 eV, $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$), which operates at a power of 120 W. Instrument monitoring, spectrum storage, and processing were done on a PDP 11/04 computer from Digital Equipment Co. (Maynard, MA), using software supplied by Fisons Co.

The samples were degassed in the pretreatment chamber until reaching a residual pressure of 2×10^{-5} Torr and were then transferred to the analysis chamber. Throughout the analysis base pressure was maintained below 3×10^{-9} Torr, achieved by means of a set of pumps sequenced in cascade: rotating, turbomolecular, and ion pump stations. For all sample runs, the analyzer energy throughput was set at 10 eV. The conditions described are generally considered optimum for operation at high resolution.

Dynamic mechanical thermal analysis (DMTA)

The rheological properties of the composites and TPU were measured in a Metravid RAC 815 viscoanalyzer. The samples were subjected to a compression-tension test, using a frequency of 1 Hz. The dimensions of the parallelepipedic samples were $5 \times 0.9 \times 3 \text{ mm}$; the temperature was varied between -100 and 100°C with a heating rate of $5^{\circ}\text{C}/\text{min}$. The applied deformation was $1 \mu\text{m}$.

Mechanical properties

Tensile strength and elongation at break were determined using a strain–stress test¹⁹ with an Instron (Canton, MA) 4301 test instrument. The stretching rate used was 500 mm/min and the values obtained were the average of at least five replicates with a standard deviation less than 10%.

RESULTS AND DISCUSSION

Surface and interface characterization

Among the results discussed below are found both improvement and worsening of the TPUs' properties after preparation of the composites. SEM was used to confirm whether those improvements were the result of a good interaction between TPU and carbon fibers. Figure 1(a)–(c) show, respectively, the SEM images of

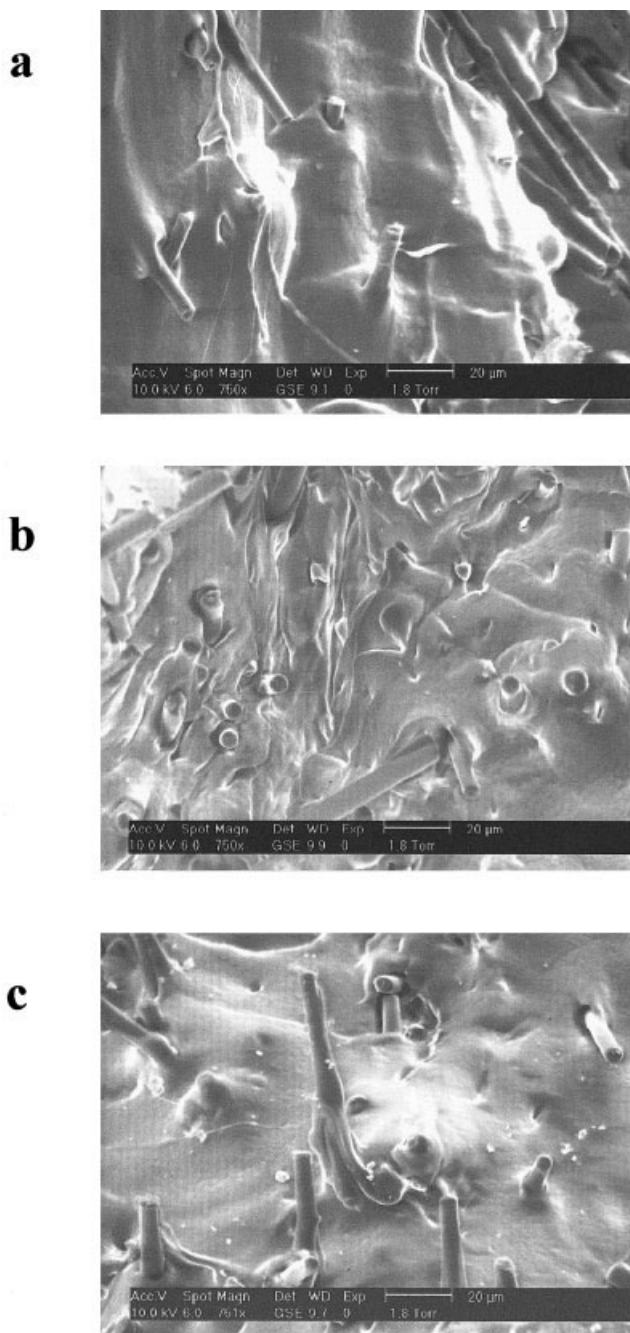


Figure 1 SEM image of the (a) H0N, (b) H35N, and (c) H70N composite failure surface chosen as representative.

the H0N, H35N, and H70N composites' failure surface chosen as representative of the improvement results. In every case, it may be observed that after the break of the composite sample (to determine its mechanical properties), the TPU matrix is attached to the carbon fiber. This provides evidence of a good TPU–carbon fiber interaction, which allows us to assert that, as expected, the improvement of the composite properties discussed below is influenced by the nature of the fiber and its consequent influence on the TPU–carbon fiber interaction.

TABLE III
O/C Atomic Ratios Obtained from the TPU and Carbon Fibers' Photoelectron Spectra

Sample	Nitric % used in the oxidation		
	0%	35%	70%
H	0.166	0.171	0.216
D	0.174	0.253	0.317
K	0.095	0.155	0.176
TPU	0.262/0.020 ^a	—	—

^a N/C atomic ratio for the TPU.

Table III presents the values of the O/C atomic ratio obtained from the fibers' photoelectron spectra (H35N photoelectron spectrum, chosen as representative, is shown in Fig. 2). On one hand, it shows an increase in the O/C ratio as the nitric acid concentration in the oxidation process increases. On the other hand, H and D carbon fibers show a higher polarity than that of K carbon fiber at any nitric acid concentration, of which the D carbon fiber is the most polar of the series. It should be expected that an increase in the polarity of the carbon fiber would result in an improvement of the CF-TPU matrix interaction, attributed to the polar nature of the TPU matrix, and thus the composites prepared with D and H carbon fibers should give better final properties. To study in more detail the influence of the carbon fiber's polarity on the composite properties, we calculated the O/C atomic ratio in the final composite attributed exclusively to the carbon fibers, at different degrees of oxidation and different contents of fibers (Table IV). These results are discussed later, together with the properties of the composites.

Mechanical properties of the composites

Figures 3, 4, and 5 show the variation of the tensile strength with the fiber content for the three fibers at 0, 35, and 70% nitric oxidation, respectively. For nonoxidized fibers (0% nitric, Fig. 3), D0N does not undergo any variation, whereas K0N decreases slightly and H0N increases with the fiber content (being the only one that improves the matrix properties). In light of these results, the mechanical properties of the CF do not seem to constitute a main factor in the reinforcement of the TPU matrix, given that the composite tensile strengths obtained are well below expected values, considering the properties of the CF (Table I), for fiber contents above the critical volume (even at 30 wt % CF content, and the composite mechanical properties yielded even worse results because of an excessive stiffness). Nevertheless, other polymeric matrices (SBS, epoxy, etc.) showed an improvement of their properties when mixed with CF.^{20,21} This difference in results seems to be related with the higher polarity of SBS and epoxy matrices related to the TPU used in the

present study. A higher polarity would allow a better and higher CF-polymeric matrix interaction and would result in an improvement of the mechanical properties in agreement with the characteristics of the CF used.

Because the mechanical properties of the CF have proved not to be related to those of the resulting composite, the remaining factors that differentiate the CF (length, diameter, and surface polarity) must thus be responsible for the improvement in the matrix properties. The effect of K0N [with low surface polarity (Table III), a length well above its critical length, and a high diameter (Table I)] can be explained as the CF acts more as a hindrance for the TPU structure than as a reinforcement. This is attributed to its low polarity and high diameter (which increases its volume, decreasing the possible CF-TPU matrix interactions resulting from a poor distribution of the CF polar sites in relation to the TPU matrix). That would minimize the interactions of the CF-TPU matrix and cause a decline in the original matrix properties arising from the hindrance of the CF to the organization of the TPU matrix structure. The relatively high CF length does not help to prevent the hindrance.

Regarding D0N [with a medial surface polarity (Table III), a length below its critical length, and a high diameter (Table I)], on one hand, its high diameter (that increases the CF volume, worsening the distribution of the CF polar sites in relation to the TPU matrix) would hinder the CF-TPU matrix interaction. On the other hand, its short length would prevent a possible hindrance to the TPU structure. Both features counteract each other and result in unmodified TPU matrix properties. Whether an increase in the CF polarity is able to improve the TPU-CF interaction, thus improving the matrix properties, is discussed below.

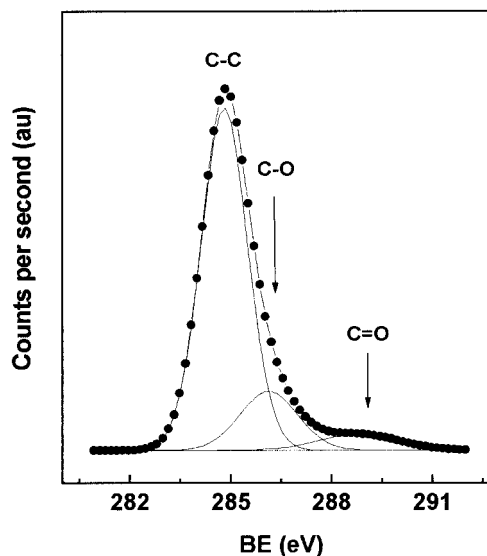


Figure 2 H35N photoelectron spectrum (XPS).

TABLE IV
O/C Atomic Ratios in the Composites, Exclusively Attributed to the Carbon Fibers,
Considering the Different Contents and Oxidation Treatments

Fiber content (wt %)	Nitric % used in the oxidation/carbon fiber								
	0%			35%			70%		
	H	D	K	H	D	K	H	D	K
7	0.011	0.012	0.007	0.012	0.018	0.010	0.015	0.022	0.012
15	0.024	0.026	0.014	0.026	0.038	0.023	0.033	0.047	0.026

This time, the short length of the fiber helps to prevent steric hindrance, contrarily to the behavior of K0N.

Finally, for H0N [medial surface polarity (Table III), a length well above its critical length, and a low diameter (Table I)], it seems that if the CF-TPU matrix has minimal and compatible polarity that would guarantee a good interaction, CF would improve the matrix properties even without the need to improve the matrix-CF interaction (i.e., nonoxidized CF). In addition, the small diameter of the CF ensures a small volume, helping to maximize the possible CF-matrix interactions attributed to a better distribution of the CF polar sites in relation to the TPU matrix.

When the oxidation degree of the CF increases (35 wt % nitric acid, Fig. 4), the trend followed by the composite prepared with K carbon fiber (K35N) remains constant. It seems that the increase in the CF polarity is not enough to exceed the negative effect of its high diameter that together with its length create, as explained earlier, a hindrance to the TPU structure, worsening the matrix properties. For the composites prepared with H and D carbon fibers (H35N and D35N) a higher increase was found in the tensile strength in relation to the nonoxidized fibers, attributed to an improvement in the CF-TPU matrix interaction, which results in a higher reinforcing effect to the TPU matrix. The fact that D35N shows the same trend as that of H35N in spite of the different CF length and diameter is ascribed to the significant increase in the surface polarity of the first in relation to the second (Table III), which makes the reinforcing effect of both CFs comparable.

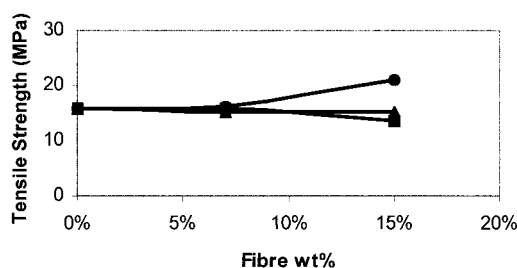


Figure 3 Variation of the tensile strength with the fiber content in the TPU-CF composites prepared with the three CF not oxidized (●, H0N; ▲, D0N; ■, K0N).

Finally, at the maximum CF oxidation degree (70 wt % nitric acid, Fig. 5), the composite prepared with K carbon fiber (K70N) does not change its behavior, providing evidence that even at maximum oxidation degree its polarity is not enough to prevent its hindering effect to the TPU structure. The composites prepared with D and H carbon fibers (D70N and H70N, respectively) show a smaller reinforcing effect than at 35 wt % nitric acid, although their polarity is higher (Table III). Moreover, H70N shows a decrease in its properties after 7 wt % CF content. This is probably attributable to the high oxidation degree of the CF surface that would saturate the urethane groups in the TPU matrix.

In fact, both untreated and 35 wt % nitric acid oxidized H CFs have a polarity that at 7 wt % (O/C = 0.011 and O/C = 0.012 respectively, Table IV) or 15 wt % (O/C = 0.024 and O/C = 0.026, respectively, Table IV) the fiber content would be able to interact with the polar urethane groups (see the N/C atomic ratio in Table III) of the matrix. Nevertheless, the high polarity of the CF oxidized at 70 wt % nitric acid would give at 15 wt % fiber content an amount of polar groups (O/C = 0.033, Table IV) higher than those available in the TPU matrix (N/C = 0.020, Table III). Therefore, whereas H0N and H35N reinforce the TPU matrix interacting with it, H70N would only be able to interact correctly at a 7 wt % fiber content, thus further decreasing the mechanical properties of the composite because of excessive stiffness.

For D CF the explanation is similar, but its behavior is less evident than that of H70N because of its smaller

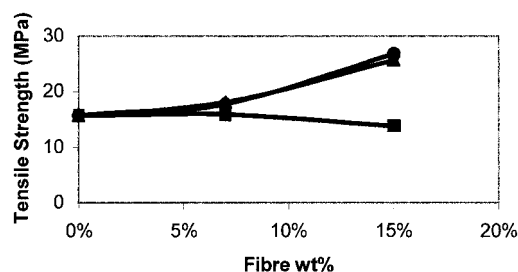


Figure 4 Variation of the tensile strength with the fiber content in the TPU-CF composites prepared with the three CF oxidized at 35% nitric (●, H35N; ▲, D35N; ■, K35N).

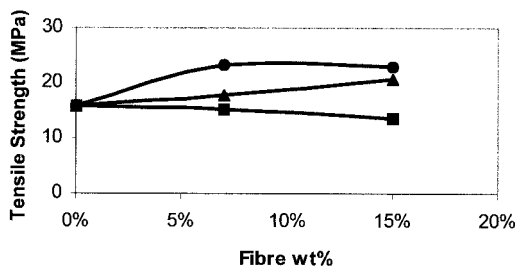


Figure 5 Variation of the tensile strength with the fiber content in the TPU-CF composites prepared with the three CF oxidized at 70% nitric (●, H70N; ▲, D70N; ■, K70N).

length and higher diameter (i.e., higher volume), which allows fewer interactions with the matrix even at higher polarity in its surface.

The elongation at break of the composites was also determined (Figs. 6–8), which substantially agree with the tensile strength results. D0N shows an almost constant trend, which corresponds to its constant tensile strength value. H0N decreases its elongation at break beyond 7 wt % fiber content, corresponding to an increase in the matrix stiffness resulting from the fiber-reinforcing effect. Finally, K0N decreases beyond 7 wt % fiber content because of its hindering effect to the organization of the structure explained above.

As the CF oxidation increases (35 wt % nitric acid, Fig. 7), the composite prepared with K carbon fiber (K35N) maintains the same trend, in accordance with its tensile strength results. Regarding D35N and H35N, as their reinforcing effect to the matrix increases (Fig. 4), their elongation at break decreases because of an increase in the matrix stiffness.

Finally, at the CF maximum oxidation degree (70 wt % nitric acid, Fig. 8), the three composites show a decreasing tendency. K70N decreases its elongation at break because, even at the maximum oxidation degree, its polarity is not sufficient to prevent its hindering effect to the TPU structure, as explained above. H70N and D70N also show a decreasing tendency because of the increase in the matrix stiffness for the fiber-reinforcing effect (Fig. 8).

Regarding the dynamic mechanical properties, the results obtained are presented in Figures 9 to 11. For

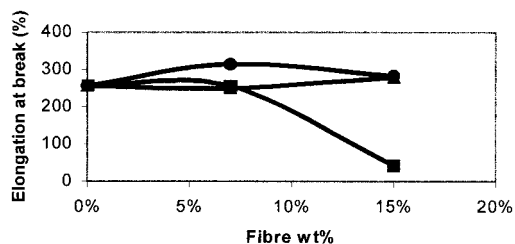


Figure 6 Variation of the elongation at break with the fiber content in the TPU-CF composites prepared with the three CF not oxidized (●, H0N; ▲, D0N; ■, K0N).

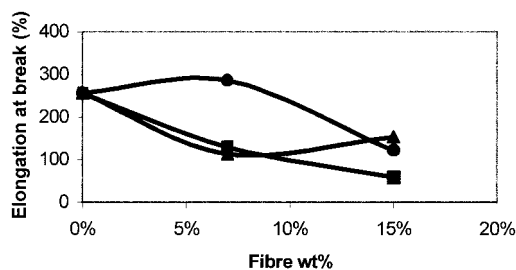


Figure 7 Variation of the elongation at break with the fiber content in the TPU-CF composites prepared with the three CF oxidized at 35% nitric (●, H35N; ▲, D35N; ■, K35N).

the H CF, the variation of the storage modulus (E') as a function of the temperature for the composites (prepared at different CF contents and different oxidation degrees) and the original TPU matrix is represented in Figure 9. At both 7 and 15 wt % fiber content [Fig. 9(a) and (b), respectively], H0N shows the higher modulus followed by H35N and the TPU matrix, of which the composite with H70N has the lowest E' of the series. This result is in complete agreement with the results obtained from the elongation at break, confirming the increase of the stiffness of the composite as the oxidation of the fiber increases.

For the D CF, the variation of E' as a function of the temperature for the composites (prepared at different CF contents and different oxidation degrees) and the original TPU matrix is represented in Figure 10. All the curves follow the same trend at both 7 and 15 wt % fiber content [Fig. 10(a) and (b), respectively], although their modulus value is different, being higher for TPU and D0N, followed by D70N and D35N, which is in agreement with the results obtained from the elongation at break, confirming the unmodified properties of D0N in relation to the TPU matrix.

Figure 11(a) and (b) represent, respectively, the variation of the storage modulus of the three composites prepared with K CF and the original TPU matrix at 7 and 15% CF content. For the four samples, at 7% fiber content the modulus experiences a slow and continuous decrease as the temperature increases (which is higher than its value for TPU), followed by K0N with

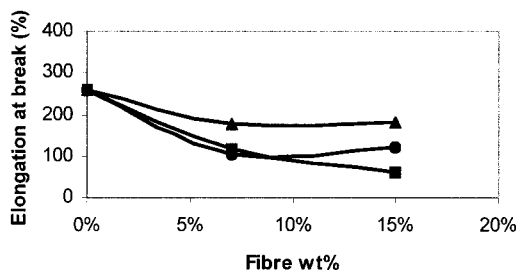


Figure 8 Variation of the elongation at break with the fiber content in the TPU-CF composites prepared with the three CF oxidized at 70% nitric (●, H70N; ▲, D70N; ■, K70N).

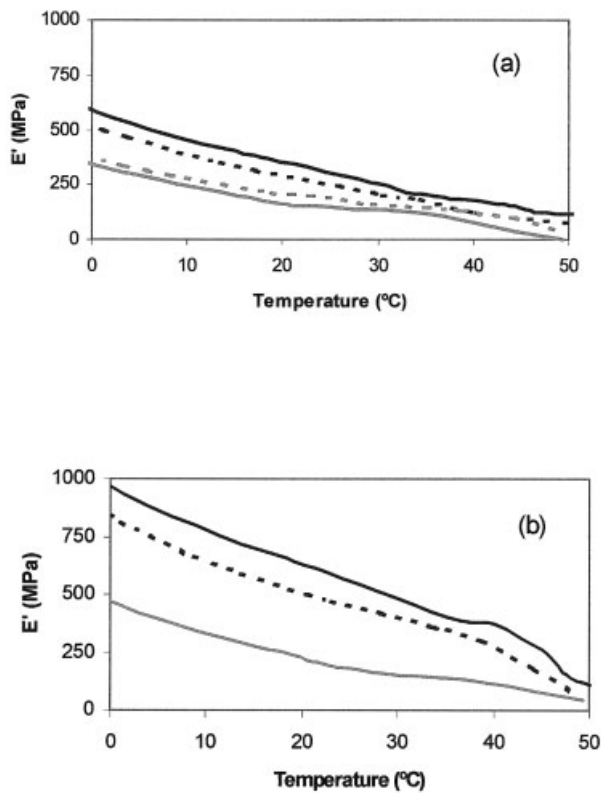


Figure 9 Variation of the storage modulus (E') as a function of the temperature for the TPU-H CF composites after different oxidation treatments and the original TPU matrix (—, H0N; ····, H35N; — —, H70N; - · - ·, TPU): at (a) 7% CF content and (b) 15% CF content.

a quite similar value to that of K35N and K70N. This result, in agreement with the above statements, provides further evidence of the negligible CF-TPU interaction and the consequent worsening of the TPU matrix properties as the CF is added. As the amount of CF increases [Fig. 11(b)], the moduli of K0N, K35N, and K70N decrease and the behavior of the three composites becomes virtually identical, providing evidence of a worsening of the TPU matrix properties.

All the tendencies discussed above are in perfect agreement with those followed by the moduli obtained from the tensile test, although the values are significantly different because of the different conditions of both tests (e.g., DMTA: $E'_{7H35N} = 300$ MPa; tensile test: $G_{7H35N} = 53$ MPa; DMTA: $E'_{7D35N} = 170$ MPa; tensile test: $G_{7D35N} = 21$ MPa).

In summary, the dynamic mechanical properties of the composites show trends that are in agreement with those followed by their elongation at break, tensile results, and surface characteristics.

CONCLUSIONS

The mechanical properties of CF do not seem to have a significant influence on the mechanical properties of

the composites prepared with the medial polar TPU matrix, given that neither GPCF nor HPCF improves the matrix properties at the expected level.

On the other hand, the surface polarity, length, and diameter of the CF influenced the composite mechanical properties. For a CF, a minimal and compatible polarity in both its surface and TPU matrix would guarantee an improvement of the TPU matrix properties. This fact confirms that GPCF may improve the TPU matrix the same as HPCF, if the polarity of GPCF (i.e., ability to interact with the TPU matrix) is similar to the polarity of HPCF.

Finally, the reinforcing effect of CF on the matrix will be enhanced for short and thin fibers. A small diameter will decrease the CF volume, increasing the possible CF-TPU matrix interactions because of a better distribution of the CF polar sites in relation to the TPU matrix. On the other hand, short fibers provide an attractive solution because longer fibers interfere with the TPU structure, worsening the matrix properties.

In summary, a composite with better properties than those of the original TPU matrix may be obtained by combining polar, thin, and short CFs with a medial polar TPU matrix, independently of the original CF mechanical properties.

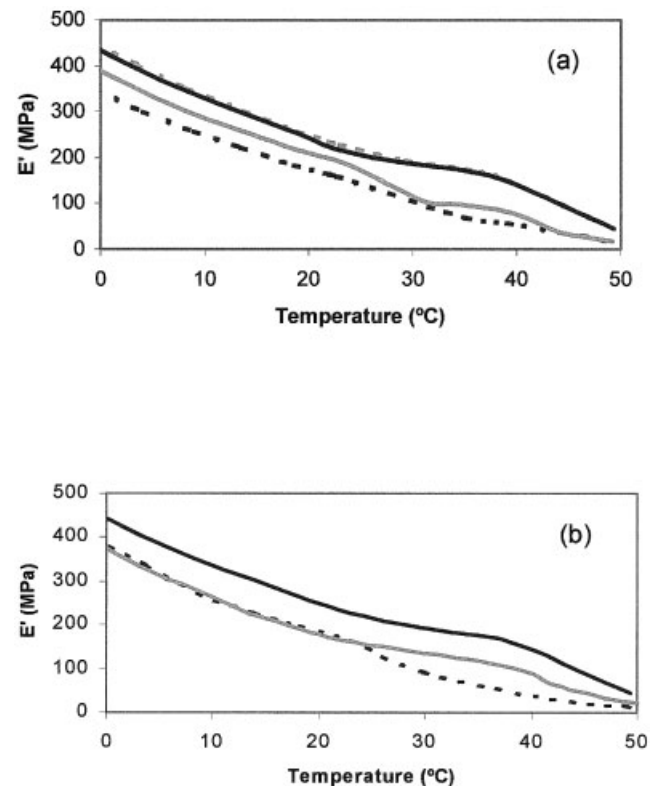


Figure 10 Variation of the storage modulus (E') as a function of the temperature for the TPU-D CF composites after different oxidation treatments and the original TPU matrix (—, D0N; ····, D35N; — —, D70N; - · - ·, TPU): at (a) 7% CF content and (b) 15% CF content.

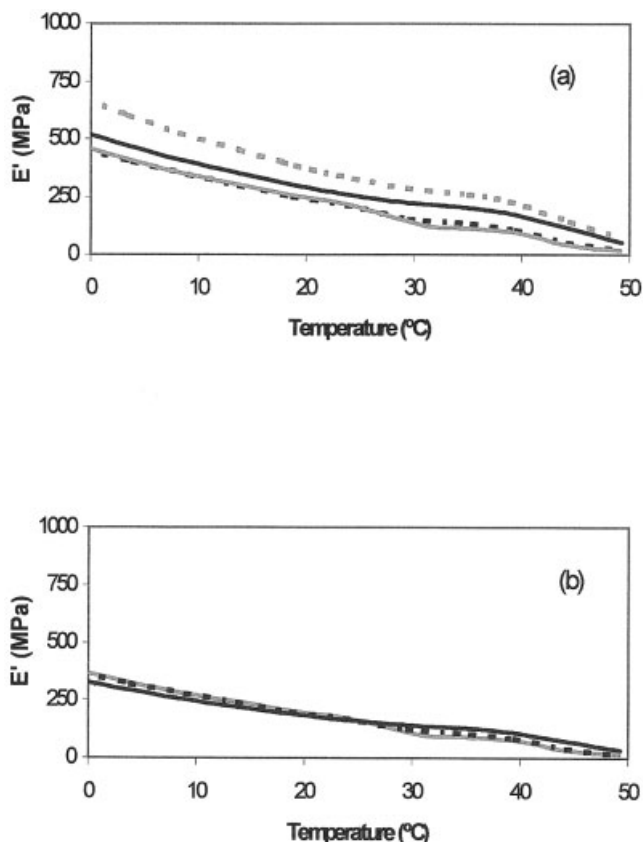


Figure 11 Variation of the storage modulus (E') as a function of the temperature for the TPU-K CF composites after different oxidation treatments and the original TPU matrix (—, K0N; ····, K35N; — —, K70N; - · - ·, PU): at (a) 7% CF content and (b) 15% CF content.

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