

# Processability and Mechanical Performance of Hybrid Composites Based on Poly(ether sulfone) Modified with a Glass Fiber-Reinforced Liquid Crystalline Polymer

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**ABSTRACT:** Hybrid composites, based on poly(ether sulfone) (PES) and glass fiber-reinforced copolyester liquid crystalline polymer (gLCP) up to 40% gLCP, were obtained by injection molding: these polymers were immiscible. Despite its higher viscosity, the gLCP acted as a processing aid for PES. The Young's modulus of the composites increased linearly with gLCP content, attributed to the opposing effects of increasing skin thickness and decreasing orientation of the fibrillated LCP in the skin. The break properties decreased with increasing gLCP content, mainly because of the lack of adhesion between the phases. The notched im-

pact strength increased substantially on addition of 10% gLCP, suggesting that the dispersed rigid particles changed the fracture behavior of PES. The composite with 10% gLCP appeared to be the most attractive because it showed an increase in stiffness of 18%, 6.5-fold impact strength, and a tensile strength similar to that of PES. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 854–860, 2004

**Key words:** composites; fibers; liquid-crystalline polymers (LCP); poly(ether sulfone); structure-property relations

## INTRODUCTION

The use of liquid crystalline polymers (LCPs) to modify the rheological, physical, and mechanical properties of thermoplastics is a way to develop "in situ" composite materials with outstanding properties.<sup>1</sup> This is because LCPs usually show good mechanical properties, working temperatures, and chemical resistance, and low viscosity and shrinkage values. However, they have some disadvantages,<sup>2</sup> such as poor weld strength, weak surface (creating fibrils by rubbing), and strong anisotropy in mechanical properties. The use of fillers in LCPs increases the viscosity<sup>3,4</sup> and decreases the tensile strength.<sup>2,5,6</sup> However, the filled LCPs show increases in the flexural and tensile modulus, and in thermal endurance associated with incorporation of inorganic fillers, and the required properties of the LCP materials can be promoted while minimizing the unwanted ones.<sup>2,3</sup>

Poly(ether sulfone) (PES) is a rigid and tough high-performance thermoplastic, which also shows high

hydrolytic and thermooxidative stability at high temperatures. However, it is sensitive to organic solvents. PES has been blended with several LCPs.<sup>7–21</sup> The blends were shown to be practically immiscible<sup>8–11</sup> and were characterized by low interfacial adhesion.<sup>9,13,15</sup> Although additive behavior<sup>9</sup> has also been observed, the elastic modulus of injected blends showed slight negative deviations with respect to the rule of mixtures.<sup>7,8,13</sup> The tensile strength usually increased less than the stiffness,<sup>9,14</sup> and the flexural properties followed the behavior of the tensile properties.<sup>9,12,13</sup>

On filling LCPs, a more homogeneous orientation within the sample cross section,<sup>6</sup> and a loss of coarse structure in the moldings<sup>5</sup> without substantial loss in molecular orientation, were reported. Their behavior did not depend on the nature of the filler, and the reinforcement was better with fibers than with particulates because of the higher aspect ratio of the former.<sup>3</sup> No significant differences were obtained between the properties of LCPs filled with glass or carbon fibers.<sup>4,22</sup>

Fillers have also been used to reinforce thermoplastic/LCP blends. In most studies, the inorganic reinforcement was added as a third component,<sup>23–32</sup> but fiber-reinforced matrices, such as glass fiber-reinforced poly(ether imide) (PEI)<sup>33</sup> or PES,<sup>34</sup> have also been used. There are many studies of filled LCPs<sup>2–6,22,35–37</sup> and filled thermoplastic/LCP blends<sup>23–33</sup>; however, to

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**TABLE I**  
Main Properties of the Neat Materials

Property	Unit	PES	gLCP
Density	g/cm <sup>3</sup>	1.37	1.67
Vicat softening point	°C	220	—
Heat distortion temperature at 1.8 MPa	°C	—	265
Tensile modulus	MPa	2690	11,700
Tensile strength	MPa	89.6	130
Notched Izod impact strength	J/m	59.8	120

our knowledge there is no study of thermoplastic/filled LCP composites.

The aim of this study was to evaluate the effects of using a glass fiber-filled LCP (gLCP) to reinforce PES. Hence, the phase behavior, processability, and morphology of PES/gLCP composites up to 40% gLCP, processed by injection molding, were investigated by means of dynamic mechanical thermal analysis (DMTA), melt flow index (MFI) measurements, scanning electron microscopy (SEM), and quantitative measurements of the orientation by the orientation parameter. The mechanical properties were studied by means of tensile and impact tests.

## EXPERIMENTAL

The polymers used in this work were commercial products. PES was Ultrason E2010 (viscosity number: 56 cm<sup>3</sup>/g) from BASF AG (Ludwigshafen, Germany). The LCP was Zenite 6130 L (gLCP) from DuPont (Boston, MA), which is an aromatic copolyester based on hydroxybenzoic acid and terephthalate units, containing 35% glass fiber. The main properties of both materials are summarized in Table I.

After drying PES at 135°C for 15 h and gLCP at 120°C for 12 h, injection molding of the neat PES and gLCP and of the composites was carried out in a Battenfeld BA 230E reciprocating screw injection-molding machine (Kottingbrunn, Austria). The screw had a diameter of 18 mm,  $L/D$  ratio of 17.8, compression ratio of 4, and helix angle of 17.8°. The barrel temperature was 330°C and the mold temperature 30°C. An injection pressure of 1920 bar and an injection rate of 7.4 cm<sup>3</sup>/s were used. MFI measurements were carried out using a Ceast extrusion plastometer (Torino, Italy) at 315°C, with a 5.0-kg load (ASTM D-1238).

The phase behavior of the composites was analyzed by dynamic-mechanical tests carried out in a DMA Q800 apparatus (TA Instruments, New Castle, DE) from 30 to 250°C in the flexural mode, at a frequency of 1 Hz and at a heating rate of 4°C/min. The specimens had approximate dimensions of 40 × 10 × 1.1 mm<sup>3</sup>.

The polarized ATR spectra were obtained at a 45° angle of incidence using a Nicolet Magna-IR 560 spectrophotometer (Nicolet Analytical Instruments, Madison, WI), equipped with an ATR accessory (Spectra-Tech, Shelton, CT). The resolution was 8 cm<sup>-1</sup> and four measurements were carried out for each reported value. The calculation of the orientation parameter ( $f$ ), which is related to the dichroic ratio, is explained elsewhere.<sup>38</sup> The average orientation is expressed as the orientation parameter.

Tensile testing was carried out on 3.3-mm-thick tensile specimens (ASTM D-638, type IV) using an Instron 4301 tester (Canton, MA) at 23 ± 2°C with a crosshead speed of 10 mm/min. The Young's modulus ( $E$ ), break stress ( $\sigma_b$ ), and ductility, measured as the break strain ( $\epsilon_b$ ), were obtained from the force-displacement curves. Notched Izod impact tests were carried out on a Ceast 6548/000 pendulum. The ASTM D-256 impact specimens were 3.3 mm thick and their notches (depth = 2.54 mm; radius = 0.25 mm) were machined after injection molding. A minimum of eight specimens were tested for each reported value in both the tensile and impact tests. The composite morphology was analyzed by scanning electron microscopy (SEM; Hitachi S-2700, Ibaraki, Japan) after gold coating (JEOL Ion Sputter JFC-1100, Tokyo, Japan). The accelerating voltage was 15 kV.

To calculate the glass fiber length distribution and the average length, samples of approximately 6 g were cut from the central section of the tensile specimens across the full thickness and were burned at 650°C. The residue was dispersed in acetone and, after drying, was observed by SEM. The lengths of 200 fibers were measured manually and the weight-average ( $l_w$ ) and number-average lengths ( $l_n$ ) were calculated, respectively, by means of the following expressions:

$$l_w = \frac{\sum n_i l_i^2}{\sum n_i l_i} \quad (1)$$

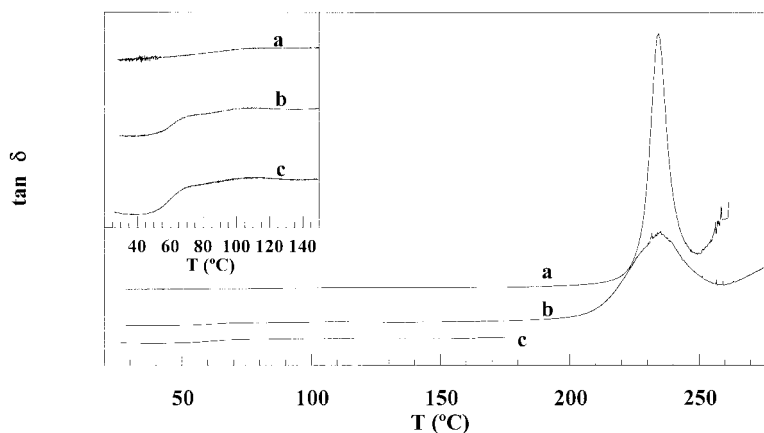
$$l_n = \frac{\sum n_i l_i}{\sum n_i} \quad (2)$$

where  $n$  is the number of fibers and  $l$  is the fiber length.

The critical fiber length was calculated by the expression<sup>39</sup>

$$l_c = 4/3 \bar{l} \quad (3)$$

where  $\bar{l}$  is double the weight-average fiber length of at least 100 debonded fibers on transversal sections of fractured tensile specimens.



**Figure 1** DMTA plots of the pure PES (a) and gLCP (c) and of the 60/40 composite (b). The insert shows the glass-transition region of the gLCP.

## RESULTS AND DISCUSSION

### Phase behavior and processability

The thermal transitions of pure gLCP were almost undetectable by DSC, probably because of the small heat capacity increase of the glass-transition temperature  $T_g$  and the low melting heat. Thus, the phase behavior of the composites was studied by DMTA. Figure 1 shows the  $\tan \delta$  curve of the 60/40 PES/gLCP composite and those of the pure components. The insert shows a magnification of the glass-transition region of the gLCP. The rest of the composites gave similar results. As can be seen, the  $\tan \delta$  peaks remained at the same temperature both in the pure components and in the composite (234°C for PES and 109°C for gLCP). This indicated, as in other PES/LCP blends,<sup>8–11</sup> that the two polymers were immiscible, and that the composites were composed of two pure amorphous phases.

It is known that inorganic reinforcements increase the viscosity of thermoplastics.<sup>3,25,26</sup> This adverse effect can be overcome by the addition of an LCP, which in hybrid composites may decrease viscosity to values even lower than that of the pure thermoplastic.<sup>25–28</sup> This possibility was investigated by means of MFI measurements of both the pure components and two compositions of the composites. The data are collected in Table II. As may be seen, the addition of 10% gLCP to PES increased the MFI

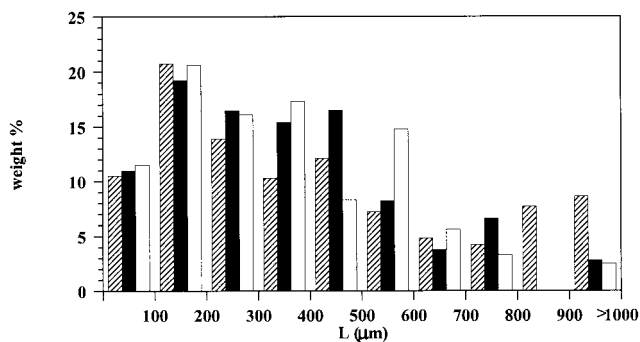
by 30%, despite the lower MFI of gLCP compared with that of PES. Thus, the viscosity increase attributed to the presence of glass fiber is important at large glass fiber contents, but becomes much less relevant at lower levels, as in the PES/gLCP composites. However, 20% gLCP did not give rise to an additional MFI increase. This agrees with the stated negative influence on the viscosity of higher glass fiber levels. Thus, despite the lower MFI of pure gLCP compared with that of PES, gLCP acts as a processing aid for PES. This could be a consequence of both the high incompatibility between the polymeric phases and also of a slipping effect of the migration of the LCP on the wall.

### Morphology

The cryogenically fractured surfaces of the tensile specimens were observed by SEM. The glass fiber was homogeneously distributed across the specimens. The fibers were predominantly oriented in the flow direction, although orientation in the center of the specimens was less general. The orientation of the fibers in the gLCP and in the blends was very similar. The fiber length weight distributions of the processed gLCP and the 70/30 and 90/10 composites are shown in Figure 2. The weight-average fiber length was 484  $\mu\text{m}$  in the gLCP, and 407 and 396  $\mu\text{m}$  in the 70/30 and 90/10 composites, respectively (number-average lengths: 290, 272, and 270  $\mu\text{m}$ , respectively). Thus, only slight fiber breaking took place during mixing. Given the viscosity decrease observed in the hybrid composites, breaking probably occurred at the first mixing stages in the injection machine (i.e., before a homogeneous blend was obtained). The critical fiber length, measured as stated in the experimental section, was 244  $\mu\text{m}$ . Thus, the fraction of fibers of length less than  $l_c$  was high because, as seen in Figure 2, roughly 40% of

**TABLE II**  
Melt Flow Index (MFI) of PES and the Composites as a Function of the gLCP Content

Percentage gLCP	MFI (g/10 min)
0	6.1 ± 0.2
10	8.1 ± 0.3
20	8.0 ± 0.3
100	2.3 ± 0.1

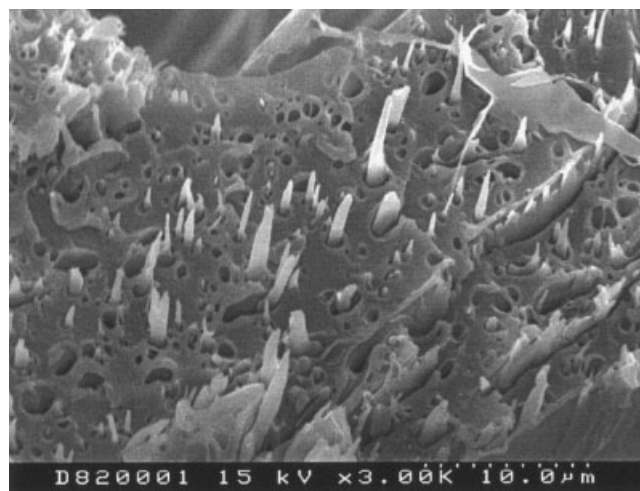


**Figure 2** Glass fiber length weight distributions of the gLCP (▨), 70/30 (■), and 90/10 composites (□).

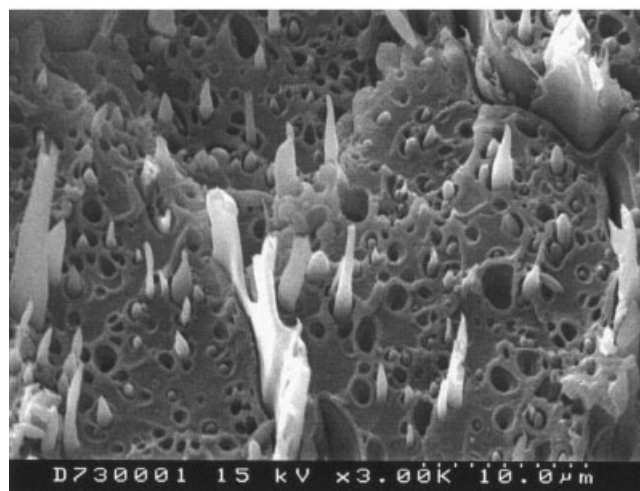
the fibers of both gLCP and the blends were below the critical fiber length.

With respect to the morphology of the LCP, the cryogenically fractured tensile specimens showed, as is usual in thermoplastic/LCP blends, both skin and core zones. The morphology of the skin of the composites with 20, 30, and 40% gLCP is shown in Figure 3(a)–(c), respectively. The morphology of the composite with 10% gLCP was similar to that of Figure 3(a), although the LCP fibrils were smaller. As may be seen, the fibrillation of the LCP was high because of the high shear and some elongational flows. In the 80/20 composite [Fig. 3(a)], thin LCP fibrils appeared. In the composite with 30% gLCP [Fig. 3(b)], the fibrils were thicker and some large structures appeared. In the 60/40 composite of Figure 3(c), the bundles of fibers and the overwhelming presence of LCP prevented observation of the morphology. PES/R5 blends<sup>7</sup> showed very similar morphology at all compositions. Sheetlike-shape particles in the skin were also seen in both injected PES/VA<sup>8</sup> and PES/copolyester and copolyesteramide LCP<sup>13</sup> blends, across the composition range and with 30% LCP, respectively.

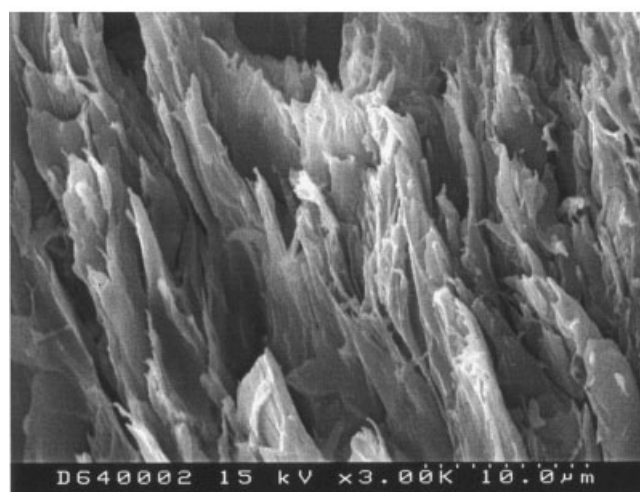
The morphology of the core of the 90/10 and 80/20 composites was spherical, with an average particle size of 1–3 and 3 μm, respectively. That of the composites with 30% gLCP showed two morphologies, shown in Figure 4(a) and (b), respectively. The morphology of Figure 4(a), which was similar to that of the 90/10 and 80/20 composites, appeared roughly in 25% of the core. The large LCP structures of Figure 4(b) were more often seen in the 60/40 composite. In PES/R5<sup>7</sup> and PES/VA<sup>12</sup> blends, the heterogeneity of the blend, mainly in the core, was also high and irregular large particles also appeared. In the core of injected PES/LCP blends,<sup>8,13</sup> some thin fibrils appeared. Their presence was attributed to the slight shear flow characteristic of the core. In poly(ether imide) (PEI)/glass fiber/copolyester LCP composites,<sup>33</sup> LCP microfibrils were seen in the skin and undeformed LCP droplets in the core. A few glass fibers of the core were



(a)

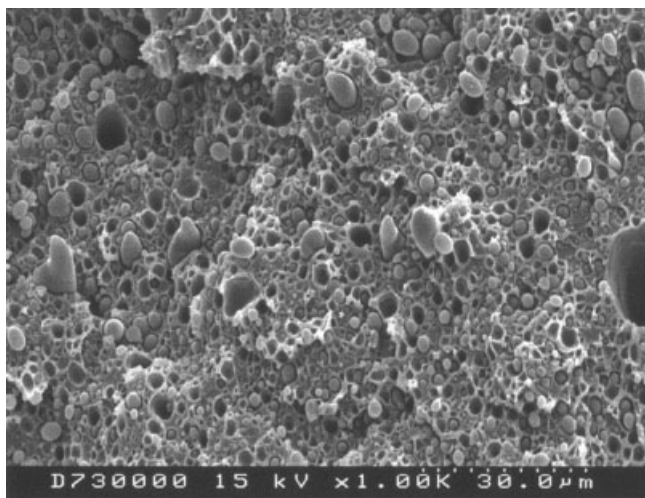


(b)



(c)

**Figure 3** SEM photomicrographs of the skin section of cryogenically fractured tensile specimens of PES/gLCP composites at gLCP contents of (a) 20%, (b) 30%, and (c) 40%.



(a)



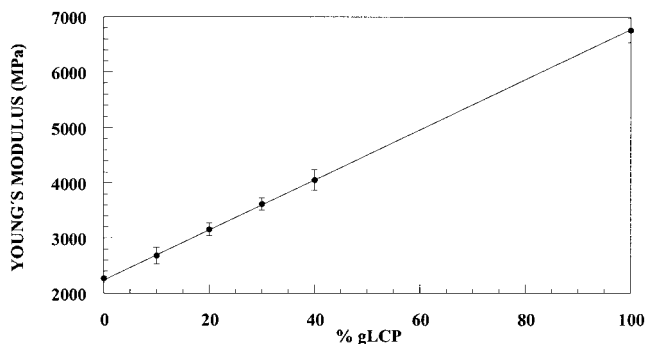
(b)

**Figure 4** SEM photomicrographs of the core section of cryogenically fractured tensile specimens of PES/gLCP composites at 30% gLCP content.

oriented in the transverse direction, reducing the anisotropy in mechanical properties of the blends.

### Mechanical properties

Figure 5 shows the Young's modulus of the composites as a function of the gLCP content: the modulus values followed very closely the linear rule of mixtures, leading to increases in the modulus of PES of 20% with only 10% gLCP. Both negative deviations<sup>8,12</sup> from linearity, and linear behavior<sup>13,14</sup> were previously observed in PES/LCP blends. In hybrid composites, linear,<sup>33</sup> positive<sup>23–26,32,33</sup> and negative<sup>29,32</sup> deviations from linearity have been seen.



**Figure 5** Young's modulus of the composites versus gLCP content.

Considering the reasons for this modulus behavior, the orientation of the glass fibers was similar both in the blends and in gLCP; therefore it does not account for deviations in the modulus. The fiber length decreased upon blending but, although it clearly influences properties such as the tensile strength, it does not influence the modulus because of the very small strain at which it is measured. Thus, taking into account the mostly globular LCP morphology of the core, the main parameter controlling the modulus behavior should be the orientation of the LCP fibers in the skin. For this reason, it was measured by the orientation parameter, the data of which measurements are collected in Table III. As may be seen, at low gLCP contents (10 and 20%), the orientation parameters were high, indicating that the fine fibrils reinforced the blend better than the thick fibrils and large LCP structures. This does not agree with the linear behavior of the modulus, which could be interpreted as a lack of change in morphology. However, the skin thickness is another parameter that influences the modulus; thus it was measured as a function of the gLCP content, and the results are given in Table IV. The thickness of the skin was small in low gLCP content composites, and higher at large gLCP levels. This should counteract the change in orientation, and give rise to the observed linear modulus behavior.

The ductility values of the composites are presented in Table V. The addition of the brittle gLCP to PES led

**TABLE III**  
Orientation Parameters in the Skin of the Blends Monitored at  $1715 \text{ cm}^{-1}$

Percentage gLCP	$f$
10	$0.27 \pm 0.04$
20	$0.24 \pm 0.03$
30	$0.19 \pm 0.02$
40	$0.19 \pm 0.02$
100	$0.15 \pm 0.01$

**TABLE IV**  
Mean Skin Thickness of the Blends  
Versus gLCP Content

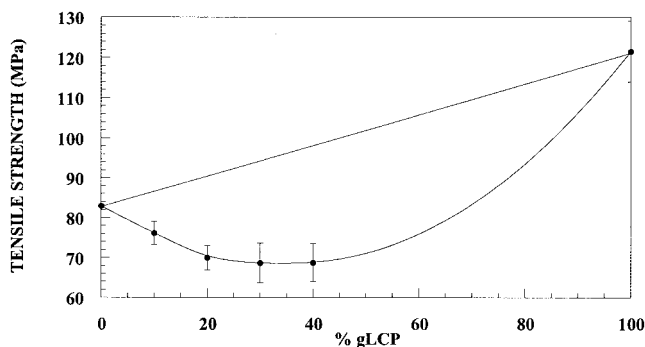
Percentage gLCP	Skin thickness ( $\mu\text{m}$ )
10	$365 \pm 21$
20	$462 \pm 83$
30	$541 \pm 25$
40	$628 \pm 37$

to a strong decrease in ductility. The decrease in ductility upon addition of 10% gLCP is usually seen in hybrid composites,<sup>31,33</sup> and is attributed to the brittle nature of the second component and the corresponding change in the shape of the stress-strain curve.

Figure 6 shows the tensile strength of the composites as a function of gLCP content: it decreased upon gLCP addition. This behavior is not unusual in hybrid composites because the tensile strength has been seen to increase,<sup>27-29</sup> decrease,<sup>32,33</sup> or remain constant<sup>24</sup> with the LCP content. Considering the reasons for this tensile strength behavior, the decrease on addition of 10% gLCP must be partially influenced by the fast breaking, which should overcome the increase in the modulus. Another factor that influences the tensile strength is the shorter fiber length in the blends. This should lead to a less-effective contribution of the glass fibers to the tensile strength because of the larger presence of fiber tips, where the contribution of the fibers to strength is less. This effect is in addition to that of the ductility decrease. In the rest of the compositions, the tensile strength initially decreased and then was mainly constant. The fiber length had no effect, given that it was generally constant in the blends. This tensile strength behavior does not agree with the expected positive influence of the modulus, which leads to higher initial slopes in the stress-strain curve and thus should lead to larger tensile strength at increasing gLCP contents. However, as seen in Table V, ductility clearly decreased when the gLCP content was increased from 10 to 20%. This must have counteracted the positive influence of the modulus, leading to the observed tensile strength behavior. The slight decreases in tensile strength, when the gLCP content

**TABLE V**  
Ductility of the Blends Versus gLCP Content

Percentage gLCP	$\epsilon_b$ (%)
0	$74 \pm 8$
10	$5.0 \pm 0.6$
20	$3.1 \pm 0.2$
30	$2.7 \pm 0.6$
40	$2.2 \pm 0.3$
100	$2.7 \pm 0.2$



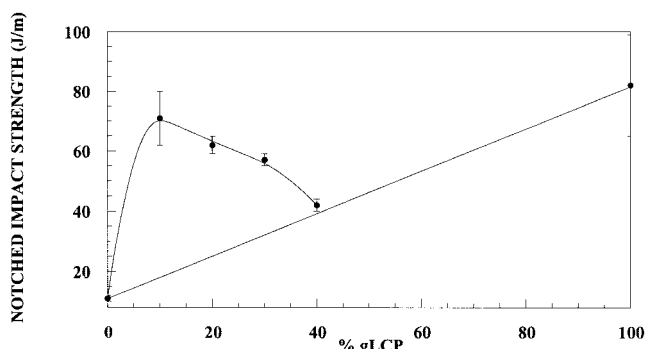
**Figure 6** Tensile strength of the composites versus gLCP content.

increased to both 30 and 40%, agreed with the also slight decreases in ductility.

The notched impact strength of the composites is shown in Figure 7. The notched impact strength of PES increased sharply (6.5-fold) with only 10% gLCP. This is surprising because this behavior, although typical of rubber-toughened blends, is unexpected here because of the brittle behavior of gLCP. This suggested that dispersed hard and brittle particles may also be able to change the fracture characteristics of the matrix, concentrating stress and leading to larger fracture surface upon breaking. This behavior was previously seen in "in situ" composites, such as PES/R5<sup>7</sup> or PSF/R5,<sup>40</sup> and indicates that, although the glass fibers also contribute,<sup>32</sup> the decrease in the notch sensitivity of PES was mainly attributed to the LCP.

## CONCLUSIONS

PES/gLCP composites were composed of two pure amorphous phases. The processability of the PES/gLCP composites was greater than that of PES, despite the lower MFI of gLCP compared to that of PES. The glass fibers were predominantly oriented in the flow direction, and very few broke upon mixing. The mor-



**Figure 7** Notched impact strength of the composites versus gLCP content.

phology of the LCP in the core was mainly spherical. The fibrillation in the skin was higher at low gLCP contents, indicating that the thin LCP fibrils reinforced more than the thick fibrils and large structures.

The Young's modulus very closely followed the linear rule of mixtures because of the combined effects of increasing skin thickness and decreasing LCP orientation in the skin at increasing gLCP contents. The tensile strength decreased at increasing gLCP content, as a consequence mainly of the decrease of ductility in the composites. This is typical of blends and composites with lack of adhesion between the phases. The notched impact strength increased upon the addition of gLCP, especially at low gLCP contents. This unexpected high impact strength suggested that the dispersed hard and brittle LCP particles may change the fracture behavior of the matrix and decrease the notch sensitivity of PES.

The composite with 10% gLCP content showed the best mechanical performance. This is because, besides easier processability, the Young's modulus and notched impact strength increased 18% and 6.5-fold, respectively, with respect to those of pure PES, without significant loss of tensile strength.

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