

# Influence of Type of Compatibilizer on the Rheological and Mechanical Behavior of LCP/TP Blends under Different Stationary and Nonstationary Shear Conditions

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**ABSTRACT:** The addition of small amounts of liquid-crystalline polymers to thermoplastics leads to the formation of *in situ*-reinforced materials, with improved processability and mechanical properties. Nevertheless, the lack of adhesion between the thermoplastic and the liquid-crystalline polymer often occurs, thus requiring the use of compatibilizers. In this case, the results of several previous works show that there is an improvement of strength, usually accompanied by a decrease of toughness and, thus, the interest of LCP/TP blends for industrial applications will certainly increase if both strength and toughness are obtained. Additionally, the emphasis of previous studies has been on the evaluation of the properties of the blend under stationary conditions and not under non-stationary ones, which are, in fact, those most relevant to processing sequences. Thus, the present work focuses on the influence of type of compatibilizer on the mechanical and rheological properties of polypropylene/LCP blends under nonstation-

ary conditions. In terms of mechanical properties, the traditional increase of tensile strength was obtained for all compatibilizers, which was essentially due to the formation, during processing, of thinner and longer fibrils of LCP dispersed in the matrix than those observed for the noncompatibilized blends. Additionally, an improvement of the impact strength and flexural modulus was also observed for the blend in which a compatibilizer with an elastomeric nature was used. Rheologically, the experiments most sensitive to the structure were those performed in transient shear, with an increase of the transient stress (in the form of an overshoot) of different magnitudes being observed for the different compatibilizers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 694–703, 2005

**Key words:** liquid-crystalline polymers (LCP); thermoplastics; compatibilization

## INTRODUCTION

New *in situ*-reinforced materials with improved mechanical properties and easier processability are obtained by the addition of liquid-crystalline polymers (LCPs) to thermoplastics, and their rheological, mechanical, and morphological properties have been widely studied during the last few years.<sup>1–17</sup> As a consequence of the morphology being largely retained after processing, a mechanical enhancement in the extrusion direction is obtained, *i.e.*, an improvement of both tensile modulus and tensile strength are achieved through the addition of LCPs to thermoplastics. The elongation at break, however, is usually drastically

reduced. Another problem is that, owing to their high aromatic content, LCPs typically exhibit high interfacial tension toward aliphatic polymers. Accordingly, a decrease of the impact strength is also usually obtained for TP/LCP blends.<sup>18,19</sup> Therefore, the industrial application of these *in situ*-reinforced materials is still limited.

The latter problem can be partially overcome through the addition of compatibilizers that promote a decrease of the interfacial tension between the two components and a better dispersion of the LCP in the matrix, as previously observed by a number of researchers.<sup>20–28</sup> The compatibilization is usually achieved by physical or chemical interactions between the components of the blend and the compatibilizer. Therefore, functionalized graft or block copolymers are often used for the compatibilization of LCP/thermoplastic blends.<sup>22,24–27</sup> Both graft and block compatibilizers should contain segments identical with those

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of the blend components, allowing them to migrate to the interface and reduce the tension between the matrix and the dispersed phase. As previously described, an extensive number of studies were performed with compatibilized LCP/TP blends. The literature review of this introduction, however, will be essentially focused in systems containing Rodrun LC3000,<sup>10,20,22,27</sup> since this is the liquid-crystalline polymer that is present in the LCP/TP systems in the study.

Datta and Baird<sup>22</sup> used maleic anhydride-grafted-PP (MAGPP) as a compatibilizer for Rodrun/PP blends and found that the addition of this compatibilizer leads to an increase of the Young's modulus for values higher than those predicted by the rule of mixtures. This increase was observed for blends with 20, 50, and 80 wt % LCP. Additionally, an increase of both tensile strength and toughness was observed. In this sense, the addition of MAGPP was revealed to be quite effective in terms of improvement of the tensile properties. Nevertheless, no information exists about the influence of the addition of MAGPP on the impact properties of the blends.

The addition of a compatibilizer to an LCP/thermoplastic blend may be detrimental for the formation of the typical fibrillar structure that is known to be responsible for the mechanical enhancement in the flow direction. O'Donnell and Baird<sup>27</sup> found that the addition of a considerable amount of compatibilizer gives rise to LCP droplets with small dimensions that make the formation of fibrillar structures difficult. Thus, it is fundamental to analyze properly the best chemical structure and also the correct amount of compatibilizer to improve the adhesion between the two components of the blend without compromising the typical fibrillar morphology.

Wanno *et al.*<sup>10</sup> studied the influence of the compatibilizer on the morphological properties of polypropylene and Rodrun LC3000. For this purpose, they used three compatibilizers: a tri-block copolymer of styrene (ethylene-butylene) styrene (SEBS), an ethylene-propylene diene monomer (EPDM), and an anhydride maleic-grafted-EPDM (MA-g-EPDM). They reported that the composites containing compatibilizers have a better dispersion of the LCP and that the LCP fibrils are thinner compared with those in the noncompatibilized blends. The compatibilizer that showed the best results was SEBS, which was attributed to its chemical structure (constituted by groups chemically compatible with both the dispersed and the continuous phase). With respect to the rheology, they observed an increase of the viscosity with the addition of compatibilizers, especially for the blends in which SEBS was used. This behavior was only observed for the lower shear rates and was attributed to an enhancement of the molecular entanglements at the interface. This study was only focused on the morphological and rheological properties, with no informa-

tion about the mechanical behavior of the compatibilized blends being provided.

Bualek-Limcharoen *et al.*<sup>20</sup> studied the effect of the addition of compatibilizers on the tensile and impact properties of films of PP/Rodrun LC3000 blends. The compatibilization was, in this case, performed by the use of three compatibilizers: a triblock thermoplastic elastomer of styrene-ethylene-butylene-styrene (SEBS), a maleic anhydride-grafted-SEBS (MA-SEBS), and a maleic anhydride-grafted-polypropylene (MA-PP) containing 1.8 and 0.1 wt % of maleic anhydride, respectively. Their aim was to study the influence of the addition of compatibilizers with elastomeric and thermoplastic natures (by comparing the properties of blends compatibilized with SEBS and MA-PP) and the influence of the presence or absence of anhydride maleic in compatibilizers with an elastomeric nature (by comparing the blends with SEBS and SEBS-MA). The main conclusions were that the elastomeric compatibilizers, SEBS and MA-SEBS, are more effective than MA-PP since they lead to the increase of viscosity and thus to the formation of thinner fibrils and to an improvement of the impact strength, and that the effectiveness of compatibilizers with elastomeric nature is reduced by the addition of maleic anhydride. A shortcoming of this study was the fact that it was carried out for films and not for injection-molded samples, and the applicability of LCP/TP compatibilized systems in industrial purposes requires an analysis in terms of injection-molded specimens, since the thermomechanical history imparted on the material in the latter is very different from that of the former.

To clarify the role of compatibilizers with different chemical natures on the mechanical performance of injection-molding specimens, namely in terms of their tensile and impact strengths, PP/Rodrun LC3000 blends were compatibilized through the addition of five different compatibilizers. Three of these were custom synthesized and are mostly linear structures, part of the backbone being compatible with the polyolefin (matrix) and the other part with a liquid crystal compatible polyester structure. By varying the size and composition of these two segments, it was possible to vary the compatibility with each one of the components of the blend and to establish the influence of the size and composition of both segments on the mechanical performance of the blends. The remaining two compatibilizers were commercial ones, one of a thermoplastic nature and the other of an elastomeric nature, in both cases grafted with maleic anhydride.

From the rheological point of view, the emphasis of the previous studies on compatibilized liquid-crystalline polymer and thermoplastic blends has been on the evaluation of their fundamental properties under stationary conditions<sup>17-29</sup> and not under transient ones, which are, in fact, those most relevant to processing sequences. One of the few exceptions is the work of

Lazkano *et al.*,<sup>5</sup> where the authors studied the transient response of two 30 wt % of LCP noncompatibilized blends of PP/Rodrun LC5000. The preparation of these blends was carried out in a different way, thus leading to two blends, differing in terms of the diameters of the LCP structures. In their work, some relationships were established between the evolution of both stress and first normal stress difference as a function of the strain and the diameters of the LCP structures. The transient results obtained for the LCP/TP blend revealed a shear stress overshoot for very low deformations, followed by a shallow undershoot at higher deformations and a normal stress overshoot located at approximately the same strain. They considered this behavior to be due to the orientation and deformation of the LCP structures. Iza *et al.*,<sup>23</sup> on the other hand, studied the influence of the addition of different compatibilizers in the rheological behavior of PS/PE blends and concluded that the interfacial effects can be described by the evolution of both shear stress and first normal stress difference with the applied strain, obtained for transient shear conditions.

Recently, the present authors<sup>30,31</sup> have resorted to the use of large amplitude oscillatory shear (LAOS) and Fourier transform rheology (FTR) to show that these measurements are more sensitive than both steady-state and linear oscillatory rheology to structure variations in extruded noncompatibilized LCP/TP blends differing in their LCP contents. For example, Filipe *et al.*,<sup>30</sup> reported that the transient shear measurements performed on blends with different LCP contents show an overshoot for the transient stress, the magnitude of which increases with increasing LCP content.

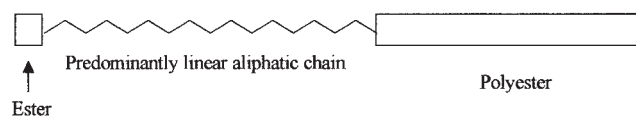
To help fill some of the gaps in knowledge identified above, the main aims of this work are to determine which rheometrical technique(s), oscillatory shear, FTR, or transient shear is/are more sensitive to the variations in blend morphology and under which conditions and, with this information, to assess the influence different compatibilizers have in the rheological and mechanical behavior of injection-molded samples of PP/Rodrun LC 3000 blends.

## EXPERIMENTAL

### Materials

The materials used for the preparation of the LCP/thermoplastic blends were polypropylene (Stamylan P 12E62) from DSM and Rodrun LC 3000 from Unitika. The liquid crystalline polymer is a copolyester constituted by 60 mol % of HBA and 40 mol % of PET. To improve the compatibility between the liquid-crystalline polymer and the thermoplastic, five different compatibilizers were used.

Of these, three compatibilizers (A, B, and C) were prepared in the framework of the present work. Since



**Figure 1** Schematic representation of the compatibilizer structure.

the composites that are being tested are based on blends of LCP (a *co*-polyester) with polypropylene (thermoplastic), the compatibilizers synthesized present an oligomeric aliphatic and linear structure as schematized in Figure 1. The reactants used in the synthesis of compatibilizer A were Dodecanol, a dimeric acid, and one polyester, Terol. The dodecanol and the dimeric acid due to their chain length present higher compatibility with polypropylene while Terol presents more compatibility with Rodrun LC3000. In the second compatibilizer, B, Terol has been substituted by PET, thus increasing the compatibility with the LCP. The third compatibilizer, C, is based on tall oil fatty acid (TOFA), and PET, which allowed for a decrease in the aliphatic chain length. More details pertaining the synthesis of these compatibilizers will be reported elsewhere.<sup>32</sup> The fourth compatibilizer, D, is a commercial material constituted by maleic anhydride-grafted-polypropylene (Epolene G-3003 Wax) and was supplied by Eastman. Compatibilizer E, the fifth compatibilizer, is an ethylene-propylene copolymer grafted with maleic anhydride (0.3 % by weight), with the commercial name Exxelor VA 18020 and was supplied by Exxon Mobil Chemical.

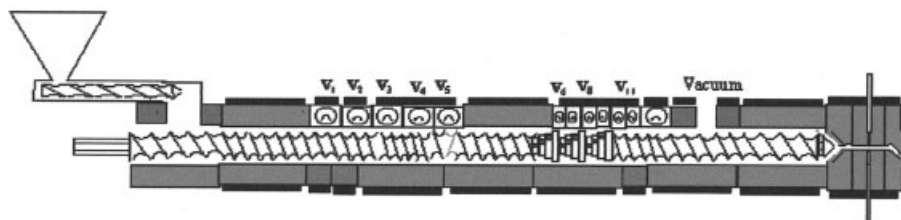
### Methods

#### Extrusion

All of the materials were dried in an oven at 90°C for 24 h before processing. A *co*-rotating twin-screw extruder from Leistritz (LSM 30.34) was used to prepare blends with 10 wt % LCP and 2 wt % compatibilizer A, B, C, D, and E. A length-to-diameter ratio (*L/D*) of 29 was employed. The processing temperature was set at 220°C, the screw speed employed was 150 rpm, and the output rate used was 4 kg/h. The cylinder and screw profiles used for the extrusion of these blends are presented in Figure 2. The final extrudates were immediately quenched in a water bath and subsequently pelletized.

#### Injection molding

Before injection molding all of the blends previously obtained by extrusion were dried in an oven at 90°C for 24 h. Tensile specimens (*dogbone-shaped*) of 60×4×2 mm (length × width × thickness), impact specimens of 55 × 40 × 2 mm thick, and flexural specimens of



**Figure 2** Screw and cylinder profile used for the preparation of blends.

40×12×2 mm were produced by injection molding using an injection-molding machine ENGEL model ES200/45 HL-V. The temperature profile used for this purpose was 170, 190, and 200°C, for the first, second and third zones of the barrel, respectively. The nozzle temperature was set at 210°C and the mold temperature used was 30°C.

#### Morphological characterization

The morphological characterization was performed by scanning electron microscopy (SEM) using a scanning electron microscope ZEISS DSM 962. All of the cryogenically fractured samples were previously coated using a POLARON SC502 and then examined by SEM at an accelerating voltage of 10 kV. These observations were performed for the longitudinal and transversal cuts of the final extrudates.

#### Rheological characterization

Rheological measurements were carried out in an ARES rotational rheometer from Rheometrics and included oscillatory shear, both in the linear and nonlinear regime, and transient shear flow measurements for all of the blends. The measurements in both oscillatory shear (linear regime) and transient shear were performed at 200°C, while the measurements in oscillatory shear under nonlinear conditions were carried out at 170°C. Two different geometries were used, a plate–plate geometry with 8 mm diameter and a gap of 0.25 mm (for the dynamic measurements) and a cone plate geometry with 25 mm diameter for the transient shear flow measurements (which allowed both transient shear stress and transient first normal stress difference to be studied). The dynamic experiments performed under linear conditions were carried out by applying a strain of 10%, for a frequency range between 1 and 300 rad.s<sup>−1</sup>. For the dynamic measurements under the nonlinear regime, time sweep measurements were performed at 6.28 rad.s<sup>−1</sup> and for different strains ranging from  $\gamma_0 = 1$  to  $\gamma_0 = 5$ . Fourier transformation was then performed to the resultant response and the nonlinearity was obtained from the relative intensity between the third harmonic and the fundamental frequency ( $I(3\omega_1)/I(\omega_1)$ ). It should be

mentioned that the temperature used for the later measurements (170°C) was the highest temperature for which reproducible results were obtained. However, considering previous rheo-optical measurements<sup>31</sup> we can assure that, at this temperature, the liquid-crystalline polymer structures inside the matrix are completely molten, even though for the pure LCP a biphasic structure would be most probably present, since its transition temperature is over 180°C. This technique has already been used to characterize the nonlinear character of LCP/TP blends and other materials.<sup>30,31,33–35</sup>

The transient measurements were performed applying a shear rate of 1 s<sup>−1</sup> during 600 s. A preshear of 0.3 s<sup>−1</sup> was applied to these samples during 600 s, to guarantee the same starting conditions for all of the samples.

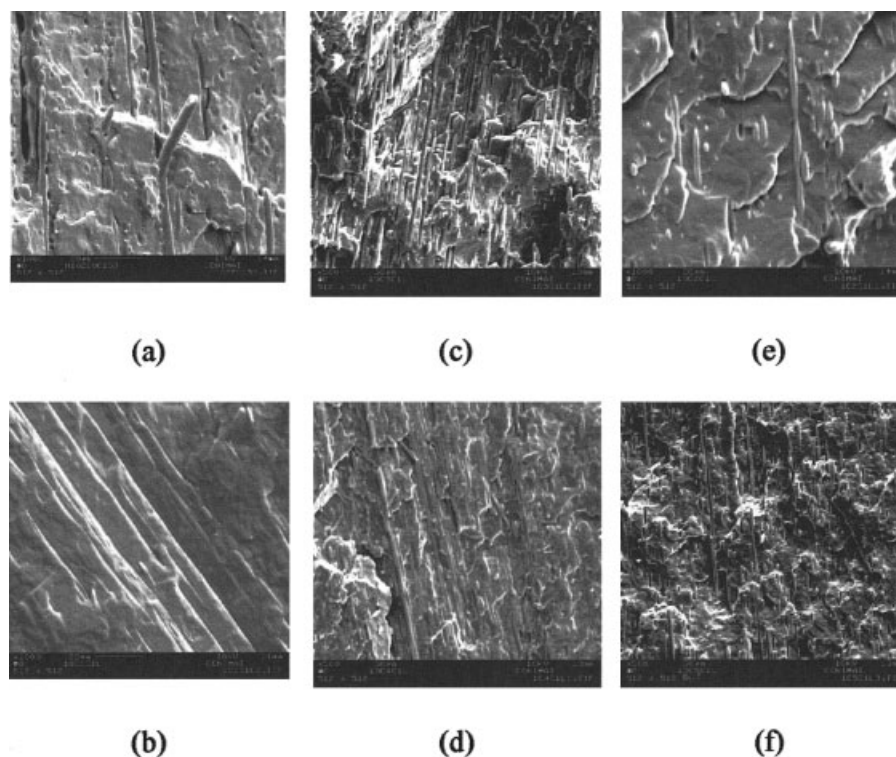
#### Mechanical characterization

Tensile, flexural, and impact measurements were carried out for injection-molded specimens. The equipment used for the impact measurements was a Rosand Instrumented Falling Weight Impact Tester, Type 5. The impact mass used was 25 kg and the impact velocity was set at 2 m/s. A set of five measurements was done and the final results from both the peak force and the peak energy were obtained by the mean value of the different measurements.

The tensile properties were tested using an Instron Universal Tester Machine model 1.16 at room temperature. A cross-head speed of 5 mm/min and a load cell of 50 kN were used. An extensometer (model Instron 2630-100) was used for these measurements. The mean and the standard deviation for the different tensile properties were calculated from five specimens.

The flexural properties were measured using an Instron Universal Tester Machine model 1.16 at room temperature. The cross-head speed was set at 2 mm/min. These measurements were carried out for specimens produced in the direction of the flow and in the direction perpendicular to the flow, and the results were obtained from the average of a set of five measurements.





**Figure 3** SEM images for the longitudinal cuts performed to the final extrudates of blends with 10 wt % LCP (a) without compatibilizer; (b) with compatibilizer A; (c) with compatibilizer B; (d) with compatibilizer C; (e) with compatibilizer D; (f) with compatibilizer E. Magnification  $\times 1,000$  (a, b, and e) and  $\times 500$  (c, d, and f).

## RESULTS AND DISCUSSION

### Morphological properties

To analyze the morphology of the different blends, scanning electron microscopy was performed for the extrudates. In addition to the typical transversal cuts, longitudinal cryogenic fracture was performed to better clarify the formation of LCP fibrils. The first observation that can be made is that the addition of compatibilizers leads to the formation of thinner and longer fibrils, with a more homogeneous distribution than that observed for the noncompatibilized blends. From the analysis performed for the longitudinal cuts, (Figure 3) it can be concluded that the addition of compatibilizers B, C, D, and E leads to the formation of LCP fibrillar structures with a good dispersion along the thermoplastic matrix. This is not as obvious for the blend with compatibilizer A, a fact that will be of great relevance to the tensile properties (see below).

The morphology obtained for these compatibilized blends reveals that the aspect ratio of the LCP fibrils seems to be higher and the distribution of the disperse phase is more uniform for the blends with compatibilizers B, C, and E than for the blend with compatibilizer D. In principle, this behavior is related to the rheological properties of the different compatibilized blends as will be discussed later.

The observation of the transversal cuts (Figure 4) showed that the addition of these compatibilizers is

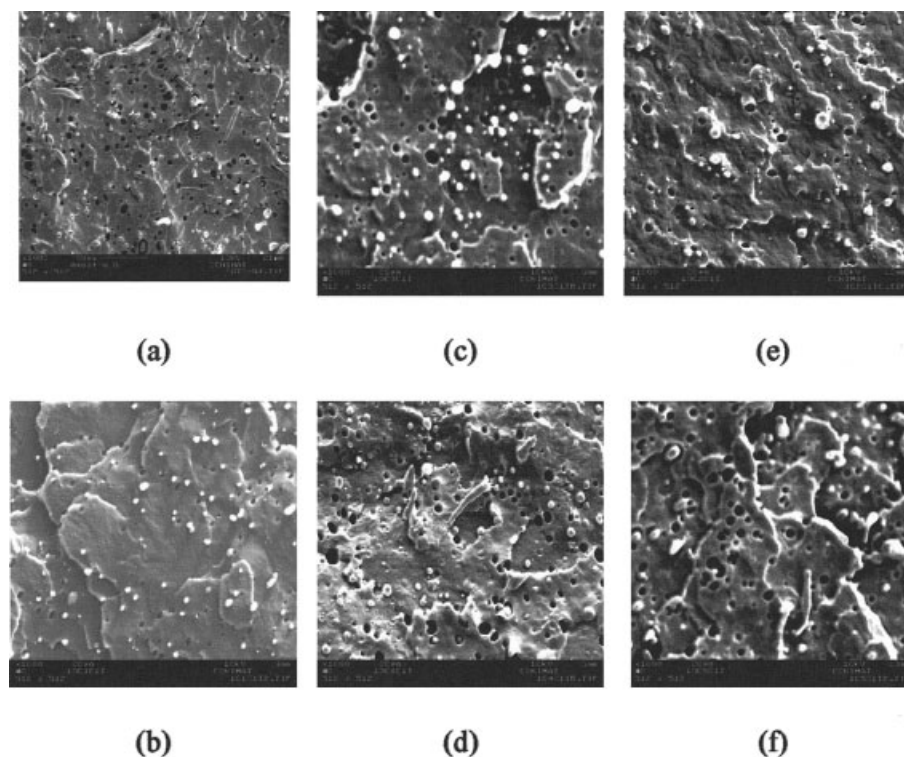
not enough to avoid the pullout of the LCP fibrils from the matrix that usually occurs during the cryogenic fracture and is due to the lack of adhesion between the disperse and the continuous phases. In this case, there were no significant differences between the different blends and, therefore, a similar behavior for the impact properties is to be expected.

In conclusion, the addition of compatibilizers to the blend with 10 wt % LCP leads to an enhancement of the fibrillar formation in the extrusion direction and to an improvement of fibril dispersion.

### Rheological properties

The rheological measurements performed in oscillatory shear revealed that there are no significant differences between the different compatibilized blends, as can be seen in Figures 5, 6, and 7, with the possible exception of the blend with compatibilizer E, which shows slightly higher complex viscosity and storage modulus than the remainder. These results are somewhat unexpected, especially for the noncompatibilized blend and that with compatibilizer A, since these showed larger morphological differences and are a clear indication that linear oscillatory shear is not sensitive enough to the changes in morphology induced by the presence of the compatibilizers.

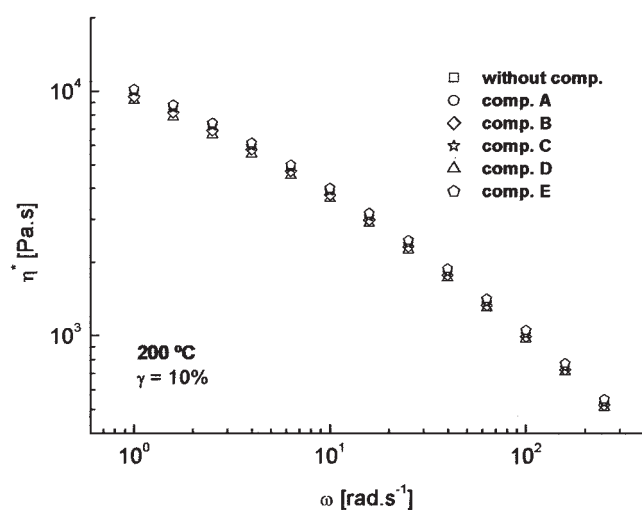
To do so, one must resort to large amplitude oscillatory shear LAOS as shown in Figure 8. This shows a



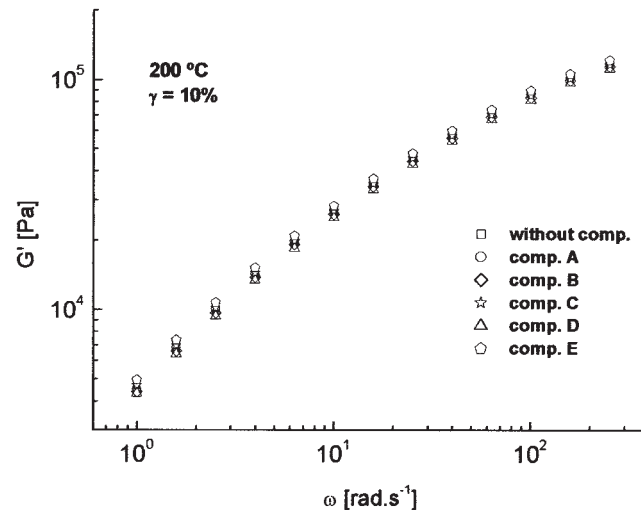
**Figure 4** SEM images for the transversal cuts performed to the final extrudates of blends with 10 wt % LCP (a) without compatibilizer; (b) with compatibilizer A; (c) with compatibilizer B; (d) with compatibilizer C; (e) with compatibilizer D; (f) with compatibilizer E. magnification  $\times 1000$  (a–e).

decrease of the nonlinear character of all of the blends in which the compatibilization was more effective (B, C, D, and E) and an increase for the blend with compatibilizer A relative to that of the noncompatibilized blend, as was expected from the observed differences in fibrillar structure. Thus, it seems that there is a relationship between the effectiveness of the compati-

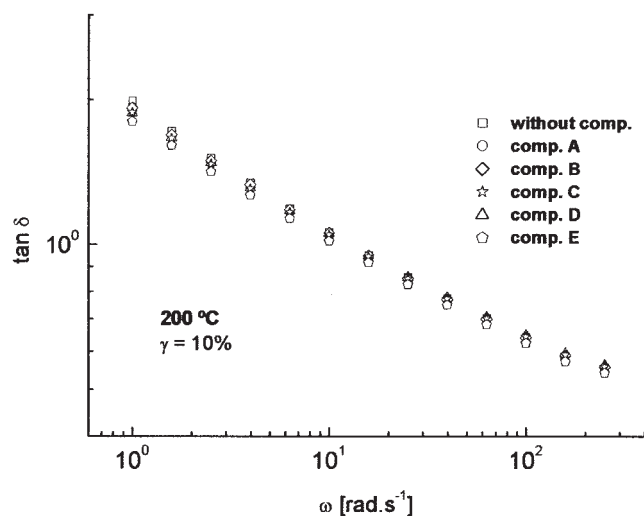
bilizer, *via* the observed fibrillar structure, and the nonlinear character, expressed by means of  $I(3\omega_1)/I(\omega_1)$ . Despite that, the use of FT rheology is not sensitive enough to clearly distinguish between blends in which the compatibilization was successful (blends with compatibilizers B, C, D, and E). To do so, another technique is needed to evaluate distinct interfacial



**Figure 5** Influence of the compatibilizer type on the complex viscosity of 10 wt % LCP blends at 200°C.



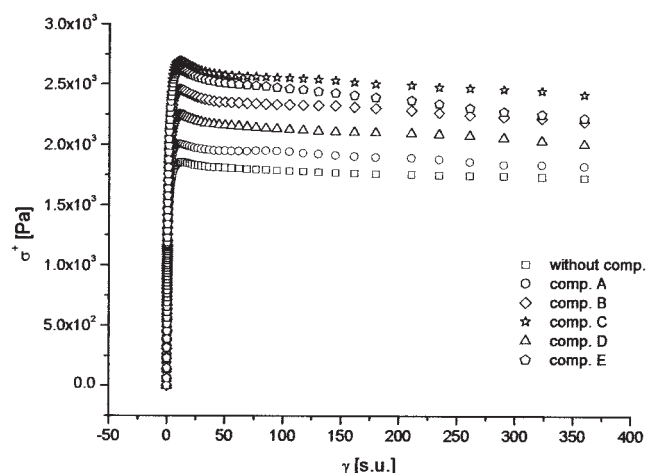
**Figure 6** Influence of the compatibilizer type on the storage modulus of 10 wt % LCP blends at 200°C.



**Figure 7** Influence of the compatibilizer type on the loss tangent of 10 wt % LCP blends at 200°C.

effects that arise from the addition of different compatibilizers.

Considering this need, transient shear measurements were performed at a shear rate of  $1 \text{ s}^{-1}$  during 600 s and after application of preshear of  $0.3 \text{ s}^{-1}$  for 600 s. The evolution of the transient stress as a function of the strain for the blends with compatibilizers A to E and also for the noncompatibilized blend is presented in Figure 9. The addition of the compatibilizer leads in all of the cases (for a similar strain of 11.1 strain units) to an increase of the transient stress, which is probably related to the interfacial modifications that occur by the addition of the compatibilizer. This overshoot is usually observed in liquid-crystalline polymer and thermoplastic blends and is associated with the rotation of the director of the LCP into

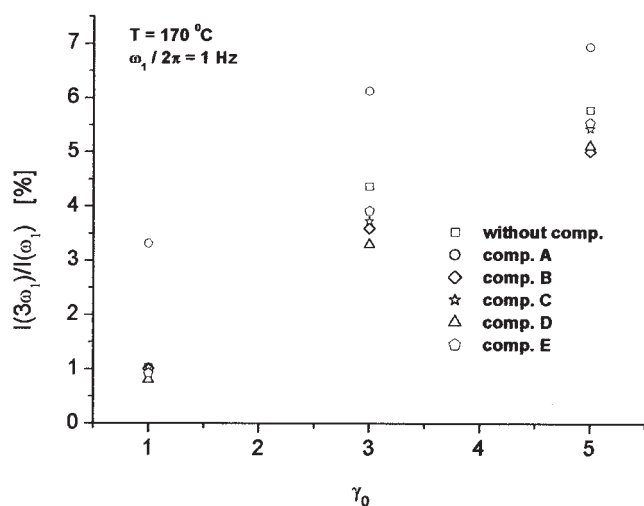


**Figure 9** Transient stress ( $\sigma^+$ ) for 10 wt % LCP blends with and without compatibilizer (start-up at  $1 \text{ s}^{-1}$ ,  $T = 200^\circ\text{C}$ ).

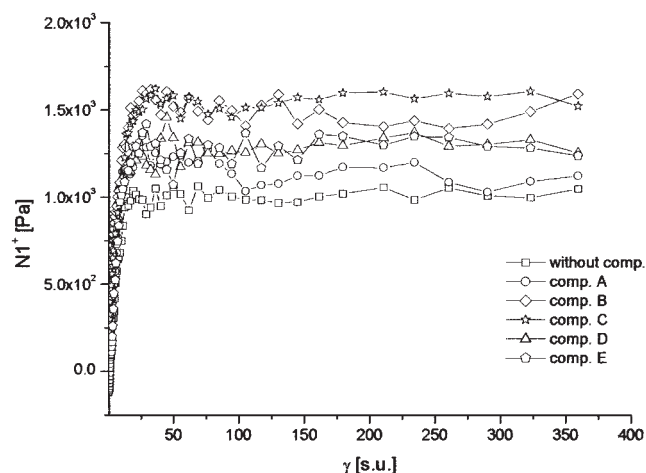
the flow direction.<sup>5</sup> The magnitude of this overshoot is different according to the compatibilizer used, being higher for the blends with compatibilizer C and E and lower for the noncompatibilized blend and that with compatibilizer A. After a strain of 11.1 strain units, a decay of the transient stress is observed for all of the blends until plateau values are reached.

Thus, the indications are that, while LAOS experiments are essentially sensitive to the fibrillar structure, transient measurements are more so to interfacial interactions between the two phases.

In the transient first normal stress difference,  $N1^+$ , despite a larger experimental scatter, differences for the different compatibilized blends were also observed (see Figure 10). Similarly to the transient stress, an increase of the transient first normal stress difference was observed for the compatibilized blends,



**Figure 8** Influence of the compatibilizer type on the evolution of  $I(3\omega_1)/I(\omega_1)$  with applied strain at  $170^\circ\text{C}$ .



**Figure 10** Transient first normal stress difference ( $N1^+$ ) for 10 wt % LCP blends with and without compatibilizer (start-up at  $1 \text{ s}^{-1}$ ,  $T = 200^\circ\text{C}$ ).

which must be once more attributed to changes in the interfacial tension between the LCP and thermoplastic. For the higher strains, the highest values of  $N1^+$  were observed for the blend with compatibilizer C. Despite this, these differences were not as pronounced as those observed for the transient stress. For example, the blends with compatibilizer C and B show very similar values of  $N1^+$  for low strains. It should be pointed out, however, that the chemical structure of these two compatibilizers is quite similar, the most important difference being the length of the aliphatic chain, which is longer in compatibilizer B. Additionally, it can be stated that compatibilizers D and E (with the same maleic anhydride content) present a similar behavior for the evolution of  $N1^+$  with the strain.

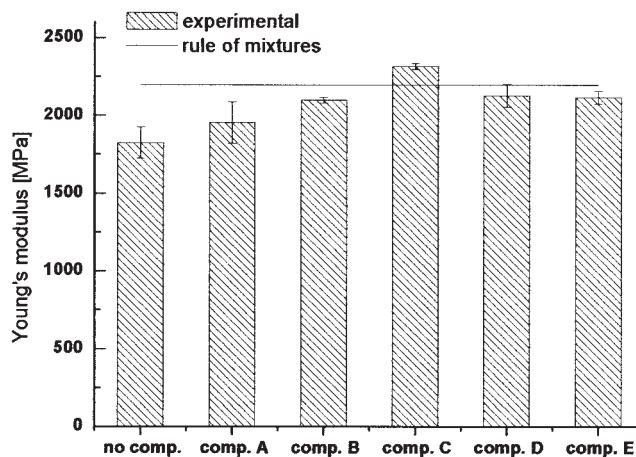
Contrary to what happened with the Lazkano *et al.*<sup>5</sup> work, we did not observe any shear stress undershoot. However, our blend has a much lower LCP content (10 wt %) compared with the 30 wt % LCP of their blends, which means, in our case, the droplets must be comparatively smaller, which may prevent the appearance of the shear stress undershoot.

### Mechanical properties

To understand the influence of the addition of different compatibilizers on the mechanical properties of liquid-crystalline polymer and thermoplastic blends, five blends with 10 wt % LCP and 2 wt % compatibilizer A to E were produced by extrusion and injection molding. Specimens of these blends were tested and compared with injection-molded specimens of blends with the same LCP content, without compatibilizer.

The tensile measurements revealed an improvement of the tensile properties for all the compatibilized blends compared with the noncompatibilized one, as shown in Figure 11, with the exception of the blend with compatibilizer A. In this case, it must be assumed that there is no influence, since the experimental error is larger than the observed differences in average Young's modulus. The reason for this behavior is probably related to the fact that compatibilizer A is highly compatible with one of the components of the blend (matrix) and tends to act as a plasticizer. For the blend with compatibilizer B, an improvement of 15% for the Young's modulus was obtained, which can be explained by its chemical structure. The LCP is a copolymer of PET with HBA and, thus, PET is expected to be more compatible with it than the terol used in compatibilizer A.

Analyzing the tensile properties shown for the blend with compatibilizer C, it can be concluded that this polymer is the more suitable among all the compatibilizers with a thermoplastic nature (from A to D) for the compatibilization of PP and Rodrun LC3000. The Young's modulus increased 27% against no increase, 15, and a 17% increase was obtained for com-



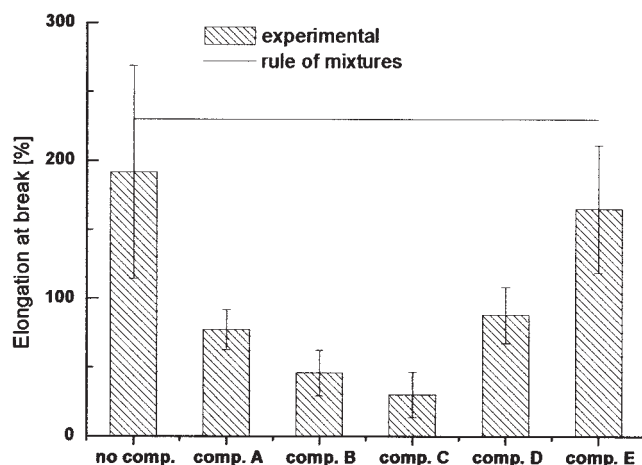
**Figure 11** Effect of the compatibilizer type on the Young's modulus for blends 10 wt % LCP.

patibilizers A, B, and D, respectively. It must be noted that compatibilizer B differs from compatibilizer C in the length of the aliphatic chain, which is much higher for compatibilizer B (C50) than for compatibilizer C (C20). Therefore, the reduction of the interfacial tension that is usually responsible by an increase of the tensile strength is dependent not only on the functional groups of the compatibilizer but also on the length of the aliphatic chain. In the present case, it seems that the longer alkyl chains in compatibilizer B cause a decrease in the electronic interactions at the interface due to the increase in the free volume. As far as the compatibilizer with an elastomeric nature is concerned, the results are similar to those of compatibilizer D.

Compatibilizer C was the only one that presented a Young's modulus with a positive deviation from the rule of mixtures (see Figure 11). Contrary to what was verified in the work of Datta and Baird,<sup>22</sup> the addition of PP grafted with anhydride maleic (compatibilizer D) did not show a positive deviation from the rule of mixtures (the value presented was 3.3% smaller than the one expected). In their work, however, they used higher LCP contents (20, 50, and 80 wt %) and observed that the improvement of the mechanical properties obtained by the addition of PP grafted with anhydride maleic is higher for blends with higher LCP content. The processing conditions used for the preparation of their blends were also quite different from those used in this work. Additionally, the amount of polypropylene grafted with maleic anhydride (MA-g-PP) used in their study was 10 wt % (with respect to the polypropylene matrix) while in our case it was only 2 wt %. All of these facts may be the explanation for the different results obtained in this work compared with those obtained by Datta and Baird.<sup>22</sup>

In terms of elongation at break, on the other hand, the elastomeric nature of the EPR-MA compatibilizer

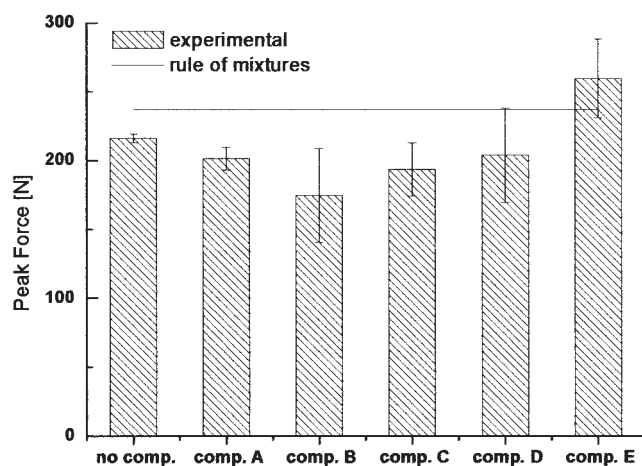




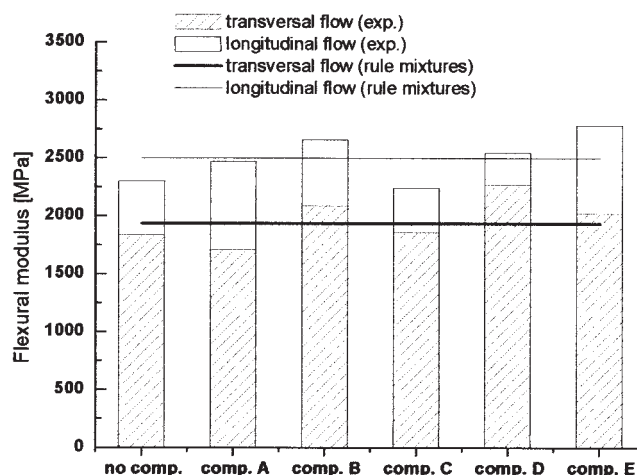
**Figure 12** Effect of the compatibilizer type on the elongation at break for blends with 10 wt % LCP.

(E) allows a significant increase of the elongation at break relative to the blends with compatibilizers having a thermoplastic nature (A to D), as would be expected. In fact, the elongation at break obtained for the blend compatibilized with EPR-MA (165%) was closer to that of the noncompatibilized blend (192%) than those obtained for the blends with compatibilizers A, B, C, and D (77, 46, 30, and 88 %, respectively), as shown in Figure 12.

In terms of the impact measurements, the energy absorption during the impact load is usually higher for blends with compatibilizers with an elastomeric nature, as shown in Figure 13. The highest impact strength was obtained for the blend with compatibilizer E (in fact, this was the only blend for which an improvement of the impact strength was obtained, within experimental error, relative to that observed for the noncompatibilized blend). The peak force presented by the blend with compatibilizer E is above



**Figure 13** Effect of the compatibilizer type on the impact force for blends with 10 wt % LCP.



**Figure 14** Effect of the compatibilizer type on the flexural modulus for blends with 10 wt % LCP.

that predicted by the rule of mixtures and in line with the findings of Bualek-Limcharoen *et al.*<sup>20</sup> for composite films containing PP and Rodrun LC3000. In fact, EPR-MA acts as impact modifier for the liquid crystalline and thermoplastic blend, improving the impact strength.

As expected, the values of the flexural modulus in the direction longitudinal to the flow were higher than those in the transversal direction, as shown in Figure 14, since the fibrils formed during injection molding are oriented in the direction of the flow. This behavior was verified for all the blends with and without compatibilizer. The only relatively unexpected finding is that the blend with the elastomeric compatibilizer (E) did not show a significant increase in flexural modulus relative to the others, as would be expected from its nature and the peak force results.

## CONCLUSIONS

During the last few years, significant attention has been focused on the mechanical improvement of LCP/TP blends by the addition of compatibilizers. However, the compatibilization often results in the improvement of tensile modulus at the expense of tensile elongation and toughness. In line with this need, five different compatibilizers differing in terms of chemical structure and nature were used to obtain the best mechanical enhancement in both strength and toughness.

Our results indicate that if this is to be accomplished, then compatibilizers with an elastomeric nature must be used. For example, in our case, this compatibilizer was the only one that was able to yield an improvement in both tensile modulus and impact resistance, which can be attributed to the increase in energy absorption during impact compared with the

other blends where compatibilizers with a thermoplastic nature were used, without a significant decrease in elongation at break. This result is essential for applications in which both high tensile strength and high elongation at break are needed. Thus, the blend compatibilized with EP-g-MA (compatibilizer E) is the one that can be used for a wider range of applications. However, for applications in which the tensile strength is the determinant factor (as in cables, for instance), compatibilizer C is the one that leads to better properties, due to the higher values of tensile modulus.

In terms of the morphology/rheology/properties relationships, the indications are that LAOS experiments are mostly sensitive to the existence (or otherwise) of the desired fibrillar structure present under processing, while transient measurements are more sensitive to interfacial interactions between the two phases. The results also seem to indicate that transient shear stress growth is the type of rheological experiment that correlates better with final blend properties, since the blends that show better mechanical properties are also those that show higher initial stress overshoots and equilibrium values.

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## References

- Choi, G. D.; Jo, W. H.; Kim, H. G. *J Appl Polym Sci* 1996, 59, 443.
- Choi, G. D.; Kim, S. H.; Jo, W. H. *Polym J* 1996, 28, 527.
- Filipe, S.; Maia, J. M.; Cidade, M. T. *Adv Mater Forum* 2004, 456, 476.
- Gao, P.; Lu, X. H.; Chai, C. K. *Polym Eng Sci* 1996, 36, 2771.
- Lazkano, J. M.; Peña, J. J.; Muñoz, M. E.; Santamaria, A. *J Rheol* 2002, 46, 959.
- Qin, Y.; Brydon, D. L.; Mather, R. R.; Wardman, R. H. *Polymer* 1993, 34, 3597.
- Qin, Y.; Brydon, D. L.; Mather, R. R.; Wardman, R. H. *Polymer* 1993, 34, 1197.
- Seppälä, J. V.; Heino, M. T.; Kapanen, C. *J Appl Polym Sci* 1992, 44, 1051.
- Viswanathan, R.; Isayev, A. *J Appl Polym Sci* 1995, 55, 1117.
- Wanno, B.; Samran, J.; Bualek-Limcharoen, S. *Rheol Acta* 2000, 39, 311.
- Whitehouse, C.; Lu, X. H.; Gao, P.; Chai, C. K. *Polym Eng Sci* 1997, 37, 1944.
- Mandal, P. K.; Bandyopadhyay, D.; Chakrabarty, D. *J Appl Polym Sci* 2003, 88, 767.
- Sukananta, P.; Bualek-Limcharoen, S. *J Appl Polym Sci* 2003, 90, 1337.
- Postema, A. R.; Fennis, P. J. *Polymer* 1997, 38, 5557.
- Scaffaro, R.; La Mantia, F. P.; Pentchev, I. T.; Hu, G. H. *Mol Cryst Liq Cryst* 1999, 336, 169.
- Farasoglou, P.; Kontou, E.; Spathis, G.; Gomez Ribelles, J. L.; Gallego Ferrer, G. *Polym Compo* 2000, 21, 84.
- Liang, Y. C.; Isayev, A. I. *Polym Eng Sci* 2002, 42, 994.
- Tjong, S. C. *Mater Sci Eng* 2003, R41, 1.
- Tjong, S. C.; Liu, S. L.; Li, R. K. Y. *J Mater Sci* 1996, 31, 479.
- Bualek-Limcharoen, S.; Samran, J.; Amornsakchai, T.; Meesiri, W. *Polym Eng Sci* 1999, 39, 312.
- Brostow, W.; Sterzynski, T.; Triouleyre, S. *Polymer* 1996, 37, 1561.
- Datta, A.; Baird, D. G. *Polymer* 1995, 36, 505.
- Iza, M.; Bousmina, M.; Jérôme, R. *Rheol Acta* 2001, 40, 10.
- Magagnini, P. L.; Pracella, M.; Minkova, L. I.; Miteva, T. S.; Sek, D.; Grobelny, J.; La Mantia, F. P.; Scaffaro, R. *J Appl Polym Sci* 1998, 69, 391.
- Miller, M. M.; Cowie, J. M. G.; Tait, J. G.; Brydon, D. L.; Mather, R. R. *Polymer* 1995, 36, 3107.
- Miller, M. M.; Cowie, J. M. G.; Brydon, D. L.; Mather, R. R. *Polymer* 1997, 38, 1565.
- O'Donnell, H. G.; Baird, D. G. *Polymer* 1995, 36, 3113.
- Lee, M. W.; Hu, X.; Yue, C. Y.; Li, L.; Tam, K. C. *Compos Sci Technol* 2003, 63, 339.
- Lee, M. W.; Hu, X.; Lin, L.; Yue, C. Y.; Tam, K. C.; Cheong, L. Y. *Compos Sci Technol* 2003, 63, 1921.
- Filipe, S.; Maia, J. M.; Leal, C. R.; Cidade, M. T.; *J Polym Eng*, to appear.
- Filipe, S.; Cidade, M. T.; Wilhelm, M.; Maia, J. M. *Polymer* 2004, 45, 2367.
- Duarte, A.; Cidade, M. T.; Filipe, S.; Correia, C. B.; Clarke, J.; Bordado, J. C. M., Personal Communication, June 2003.
- Wilhelm, M. *Macromol Mater Eng* 2002, 287, 83.
- Neidhöfer, T.; Wilhelm, M. *J Rheol* 2003, 47, 1351.
- Wilhelm, M.; Reinheimer, P.; Ortseifer, M. *Rheol Acta* 1999, 38, 349.