

Evolution of the Morphological and Rheological Properties along the Extruder Length for Compatibilized Blends of a Commercial Liquid-Crystalline Polymer and Polypropylene

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ABSTRACT: In a previous article, we reported on the evolution of the morphological and rheological properties along the length extruder for blends of a liquid-crystalline polymer (LCP), Rodrun LC3000, and polypropylene (PP). In this work, we extended this study to compatibilized PP/Rodrun LC3000 blends, containing 10 wt % LCP and different compatibilizers, to determine the influence of the addition of a compatibilizer during the processing and, consequently, on the final properties of such systems. The results revealed that the addition of compatibilizers led to a decrease in the mean diameters of the LCP structures, in comparison with those presented by the noncompatibilized

blend containing the same LCP content. This phenomenon occurred more quickly for those blends in which compatibilization was carried out in an efficient way. Linear oscillatory shear was mainly sensitive to the type of morphology present in the blends, whereas nonlinear oscillatory shear was more sensitive to the evolution in the droplet/fibril size and along the extruder length. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 347–359, 2006

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

INTRODUCTION

Liquid-crystalline polymer (LCP) and olefinic thermoplastic (TP) blends have been investigated during the last years as promising systems because of their improved mechanical properties, easier processability, and cost efficiency.^{1–20} The main problem in blending LCPs is that because of their chemical structure, with a frequently high aromatic content, they often exhibit low adhesion toward the TP polymer. This problem can be overcome through the addition of compatibilizers, the use of which will improve even more the mechanical properties of these blends.^{21–30} The compatibilizer activity can be basically described by a reduction of the interfacial tension between the TP and the LCP, which causes an emulsifying effect that leads to an improvement of the dispersion of the LCP in the TP. Several attempts have been carried out to achieve

high mechanical improvements by the addition of compatibilizers (i.e., the works of Datta and Baird,⁶ Wanno et al.,²² Bualek-Limcharoen et al.,¹⁹ and Miller et al.,¹⁶ among others). All these studies have concluded that the addition of compatibilizers to polypropylene (PP)/LCP blends leads to an improvement of the dispersion of the LCP fibrils in the PP matrix and to the formation of thinner LCP fibrils than those observed for noncompatibilized blends.

None of the aforementioned studies was focused on the evolution of the morphological and rheological properties of LCP and TP blends during the processing itself. Quite a few studies have been done on this subject for other kinds of noncompatibilized, immiscible blends, such as the works of Potente et al.³¹ and Bordereau et al.,³² who studied blends of PP and polyamide and of polystyrene and high-density polyethylene, respectively. Boersma and Van Turnhout³³ used dielectric spectroscopy to study the evolution of the morphology during extrusion for TP/LCP blends. With respect to the influence of the use of different screw elements on the morphology, the use of kneading-block elements leads to a high decrease in the dispersed-phase structures; this arises from the high pressures and shear rates developed, in comparison with those present in conveying and reverse-conveying elements. The importance of the capillary number for the modeling of both the deformation and breakup

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of the dispersed-phase structures has been additionally established.^{1,23}

In a previous work with noncompatibilized PP/Rodrun LC3000,¹ the evolution of the rheological properties during extrusion was related to the morphology obtained along the extruder length. The main conclusions of that work were that a decrease in the viscosity was verified along the length of the extruder. This first conclusion was associated with the progressive elongation and breakup of the LCP structures during the extrusion process. At the beginning of the extruder, the LCP structures present a dropletlike structure, whereas at the die exit, they have the form of fibrils, oriented along the flow direction (with a consequent reduction of the viscosity). A subdivision of the mixing processes that occur inside the extruder can be performed. In the beginning of the mixing process, dispersed structures with high diameters are dominant, and this means that high capillary numbers (capillary number \gg critical capillary number) are present. Under these conditions, the interfacial forces (which tend to keep the shape of the droplets) are overwhelmed by the viscous forces (which tend to deform and elongate the droplets), and distributive mixing is the dominant process. As it proceeds downstream, the interfacial stress becomes of the same order of magnitude as that of the shear stress (capillary number \propto critical capillary number), and the elongated structures developed in a previous stage start to break, generating smaller droplets. At this point, dispersive mixing starts to have greater importance. Nevertheless, the final morphology is not completely defined, being continuously dependent on the competition between deformation, breakup, and coalescence processes.

The main aim of this study is to extend the work already performed with noncompatibilized PP/Rodrun LC3000 blends¹ to blends in which compatibilization was carried out. Because the final properties of immiscible blends are strongly dependent on the morphology developed during extrusion, the study of the evolution of both the morphology and rheology for compatibilized blends is essential for controlling and optimizing the performance of LCP/TP blends. This study was carried out during several stages of the extrusion process by the morphological and rheological measurement of samples collected along the extruder length.

EXPERIMENTAL

Materials

Liquid-crystalline and TP blends were prepared with Rodrun LC3000 from Unitika (Japan) and PP (Stamylan P 12E62) from DSM (The Netherlands). The TP used for the preparation of the blends had a molecular

weight of 1,194,406 g/mol obtained by gel permeation chromatography and a melt flow index of 0.8 g/10 min (at 230°C and for 21.6 N). Stamylan P is an isotactic PP with a melting temperature of 165°C.

Rodrun LC3000 is a copolymer consisting of 60 mol % *p*-hydroxybenzoic acid and 40 mol % poly(ethylene terephthalate) (PET). The transition temperature obtained by differential scanning calorimetry for the LCP was 189°C (peak value). The molecular weight for the LCP was not obtainable because no solvent was found to be soluble with Rodrun LC3000.

To improve the adhesion between the two pure components, several different compatibilizers were used; three were synthesized in the framework of this work, and the other two were commercial grades. More details about these compatibilizers and the mechanical, rheological, and morphological properties of the final compatibilized LCP/PP blends are available elsewhere.³⁴

The first compatibilizer (A) was obtained by the reaction between dodecanol, a dimeric acid, and Terol. The dodecanol and the dimeric acid, because of their chain length, presented greater compatibility with PP, whereas Terol presented more compatibility with Rodrun LC3000. In the second compatibilizer, B, Terol was substituted by PET, and this increased the compatibility with the LCP; finally, compatibilizer C was based on a tall oil fatty acid and PET, and this allowed for a decrease in the aliphatic chain length. The fourth compatibilizer (D) was a commercial material consisting of maleic anhydride grafted PP (Epolene G-3003 Wax) and was supplied by Eastman. Compatibilizer E, the fifth compatibilizer, was an ethylene-propylene copolymer grafted with maleic anhydride (0.3 wt %), with the commercial name Exxelor VA 18020, and was supplied by ExxonMobil Chemical.

The concentration of LCP present in these blends was 10 wt %. The blends were compatibilized with 2 wt % compatibilizer (with respect to the TP weight).

Processing

All the materials were previously dried in an oven at 90°C for 24 h before processing. An LSM 30.34 corotating twin-screw extruder from Leistritz (Germany) with a length-to-diameter ratio of 29 was used to prepare the blends. The screw and cylinder profiles are presented in Figure 1. The screw used and depicted in Figure 1 consisted of a region of conveying elements, followed by a reverse-conveying element, which was located near valve 5. After this, the screw consisted of a conveying region, which was followed by 11 staggering kneading blocks (with a staggering angle of -60°) and by another group of conveying elements. The cylinder and screw configurations were defined in such a way that the zones of the screw in which the highest positive pressures existed (left-handed elements and kneading blocks) co-

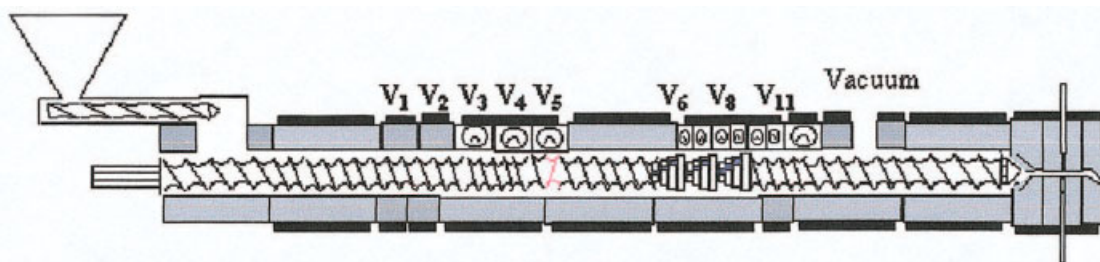


Figure 1 Screw and cylinder profile used for the processing of the blends with and without a compatibilizer (v_i is the i th valve that allows the removal of samples along the extruder length). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

incided with the zones in which the valves were placed. In such a way, it was possible to collect samples in those locations in which the highest morphological changes were expected to occur.

The processing temperature was 220°C, and the screw speed and the throughput used were 150 rpm and 4 kg/h, respectively. The final extrudates were immediately quenched in a water bath and subsequently pelletized. To study the rheological and morphological evolution during extrusion, samples were removed by means of a home-built collecting device system, which consisted of several collecting devices located at different positions along the extruder length, as mentioned above. This special extruder was previously used to study the morphological evolution in other systems (Covas et al.,³⁵ Machado et al.,³⁶ Van Duin et al.,³⁷ and Filipe et al.¹). When these collecting devices are used, only a few seconds (usually no more than 3) are needed to remove the samples, which are then immediately quenched in liquid nitrogen. Thus, it was expected that the original morphology developed inside the extruder would be retained.

Rheological characterization

All the samples collected along the extruder length and the final extrudates were used to produce 8-mm-diameter discs by compression molding, which afterwards were analyzed rheologically. The rheological characterization was carried out with an ARES rotational rheometer from Rheometrics (Germany). These measurements were performed both in the linear regime and in the nonlinear regime. The dynamic experiments in the linear regime were performed in oscillatory shear with a strain amplitude (γ_0) of 0.1 and at a temperature of 170°C. A frequency range of 0.99–158 rad/s was applied, and the gap was set at 0.25 mm.

Large-amplitude oscillatory shear (LAOS) was applied to the different samples collected at different locations along the extruder to generate a nonlinear response. A sinusoidal strain varying between $\gamma_0 = 1$ and $\gamma_0 = 5$ was applied for a temperature equal to 170°C and for a constant frequency of 6.28 rad/s [the

fundamental frequency (ω_1)]. The time data were Fourier-transformed, and this generated a Fourier spectrum consisting of several peaks located at the third harmonic ($3\omega_1$), the fifth harmonic ($5\omega_1$), the seventh harmonic ($7\omega_1$), and so forth and also at ω_1 . Each one of these peaks was described by means of an amplitude, a_n , and a phase, ϕ_n , where n is the multiple of ω_1 . The nonlinear character was obtained from the relative intensity between $3\omega_1$ and ω_1 and was represented by the normalized quantity $I(3\omega_1)/I(\omega_1)$.

This technique was extended recently by Wilhelm³⁸ and has been used to characterize several different kinds of systems (e.g., Wilhelm and coworkers,^{38–40} Filipe et al.,¹ and Neidhöfer et al.⁴¹).

Morphological characterization

The evolution of the morphology along the extruder length was studied by means of scanning electron microscopy (SEM). This characterization was performed for samples collected at different locations along the extruder. The equipment used for this purpose was a Zeiss DSM 962 scanning electron microscope (Switzerland). The samples were cryogenically fractured in the flow direction, coated with a Polaron SC502, and then examined by SEM at an accelerating voltage of 10 kV.

RESULTS AND DISCUSSION

Morphological properties

Because the aim of this study was to evaluate the influence of the presence of different compatibilizers on the rheological and morphological evolution during extrusion, a comparison was continuously carried out between the different compatibilized blends and the noncompatibilized blend at similar stages during the extrusion process.

The processing parameters, such as the screw and cylinder profiles, temperature, screw speed, and throughput were the same for all the blends, with and without a compatibilizer. The study of the morphol-

TABLE I
Temperature Profiles Measured Along the Extruder Length and Pressure at Die for the Blends With and Without Compatibilizers

Material	Temperature (°C)				Pressure at die (bar)
	Valve 4	Valve 6	Valve 8	Extrudate	
Uncompatibilized	226.2	227.6	229.6	236.1	30
Compatibilizer A	225.1	226.1	228.4	231.1	34
Compatibilizer B	226.8	228.5	230.2	237.0	38
Compatibilizer C	227.1	228.9	231.9	237.4	36
Compatibilizer D	227.2	230.1	231.4	237.1	39
Compatibilizer E	228.2	231.4	233.2	238.2	46

ogy and temperature profiles that developed during extrusion was carried out with a home-built collecting device system mentioned previously (Polymer Engineering Department, University of Minho). With this system, it was possible to collect samples in less than 3 s, which were immediately quenched in liquid nitrogen and thus retained their original morphology. Additionally, the use of this collecting device system allowed the evolution of the true melt temperature to be measured with a quick-response thermocouple. The analysis of the temperature profiles revealed that

an increase in the temperature occurred along the extruder and that the addition of different compatibilizers led to slight differences in the temperature profiles, as shown in Table I, which, in principle, would not affect considerably the morphology evolution of the different compatibilized blends.

The temperatures at the reverse-conveying element (near valve 5) are always lower than those at the region of the kneading blocks (located between valves 6 and 8), and this is mainly due to the higher shear rates and pressures that are present in the latter.

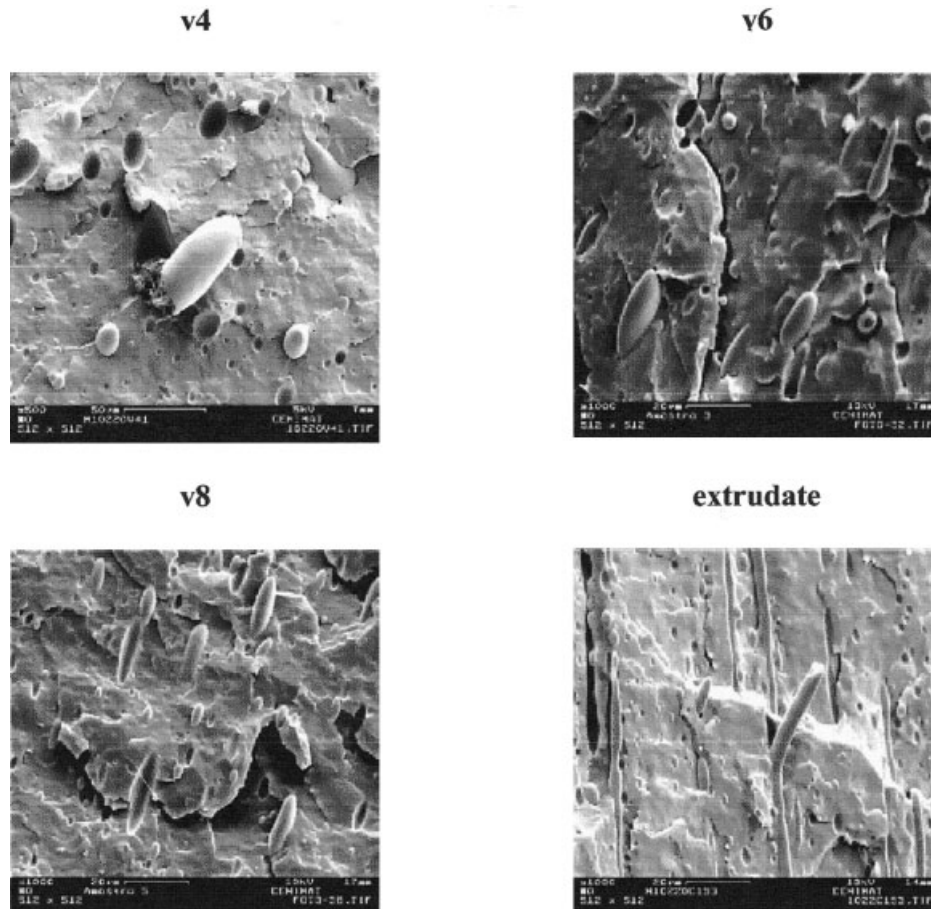


Figure 2 Morphological evolution along the extruder length for the noncompatibilized blend (SEM).

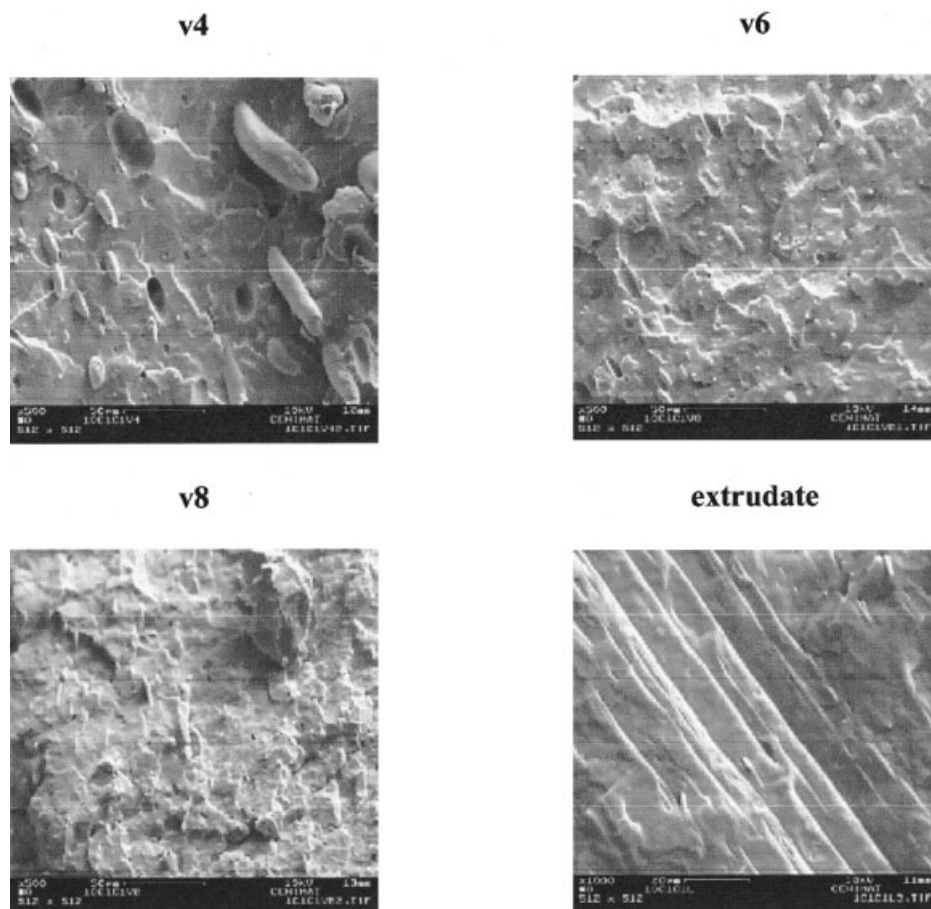


Figure 3 Morphological evolution along the extruder length for the blend with compatibilizer A (SEM).

The first blend to be analyzed and taken as the reference is the one without compatibilizer, which was already studied in a previous work with PP/Rodrun LC3000 blends.¹ In the beginning of the extrusion process, the morphology can be essentially described by large, dispersed drops of LCP, which by the action of increasing shear stress will progressively deform and elongate (valve 6 and valve 8). At the die, the droplets are subjected to the highest deformation, which leads to the formation of some fibrils (Fig. 2), which are jointly present with the droplets.

The addition of compatibilizer A does not have a significant effect on the morphology at the beginning of the process (cf. valve 4, Figs. 2 and 3); this means that the LCP droplets present diameters similar to those verified at the same position for the noncompatibilized blend (Fig. 3). The reason for this behavior is probably related to the fact that, because of its chemical nature, compatibilizer A is highly compatible with one of the components of the blend, most precisely, the matrix. Additionally, the part of the compatibilizer that is supposed to be compatible with the LCP is based on an oligomeric polyester (with the commercial name Terol) and not on PET (as in the case of compatibilizers B and C, which are discussed later),

which is in principle less efficient in terms of chemical interactions. Therefore, this chemical structure results in a material that tends to act as a plasticizer and not as a compatibilizer because the compatibilizer seems to be much more compatible with the matrix than with the LCP. Furthermore, the viscosity of the blend with compatibilizer A is lower than that of the noncompatibilized blend, and this results at the end of the process in a decrease in the pressure at the die (as shown in Table I).

At this point (valve 4), similarly to what has been observed for the noncompatibilized blend, a considerably wide range of diameters is present. Distributive mixing is dominant at this stage because the capillary numbers present at this point are higher than the critical capillary number. Therefore, the interfacial stress is overruled by the shear stress, and the deformation mechanisms are the dominant process. It seems that from valve 4 to valve 6, an improvement of the dispersion of the LCP structures along the matrix is verified. At this stage, a decrease in the diameters of the LCP structures is seen, and a more homogeneous distribution of these droplets along the matrix is obtained. Nevertheless, elongated structures are still present at valve 6, but in lower numbers and with

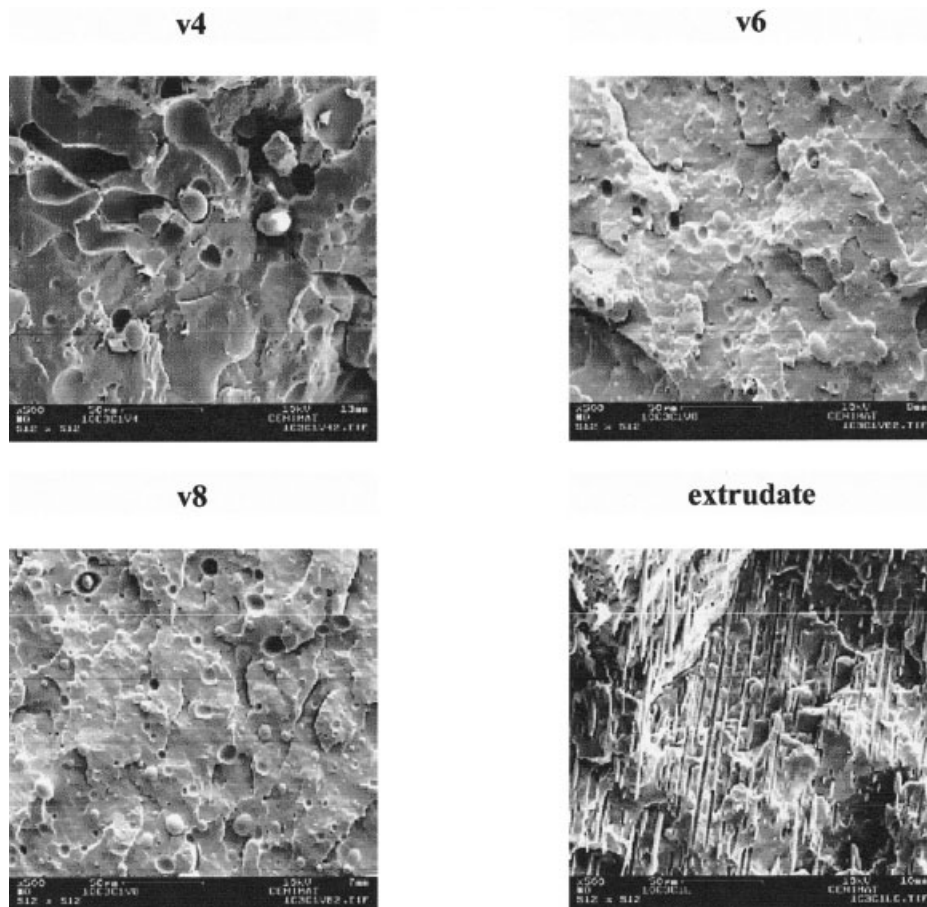


Figure 4 Morphological evolution along the extruder length for the blend with compatibilizer B (SEM).

lower aspect ratios than those present at valve 4. There are no significant differences between the samples collected at valve 6 and valve 8 for the blend containing compatibilizer A. Finally, the material is subjected to the highest elongational forces and the maximum deformation is achieved when it crosses the die, and the final morphology shows the presence of elongated structures, similar in aspect but thicker than the fibrils present in the noncompatibilized blend.

The different chemical structure presented by compatibilizer B prefigures a different morphological evolution along the extruder. In this case, the part of the chemical structure that is supposed to be compatible with the LCP consists of PET, instead of the oligomeric polyester (Terol) present in the chemical structure of compatibilizer A. This new arrangement is supposed to be more compatible with the LCP, which also contains PET, and thus lead to a more efficient compatibilization via similar van der Waals and π - π interactions.³⁴ The morphological analysis at valve 4 revealed a slight decrease in the LCP droplet size, in comparison with those of the noncompatibilized blend and the blend with compatibilizer A, at the same point (Fig. 4).

The presence of compatibilizer B leads to an increase in the overall pressure at the die in comparison

with those of both the noncompatibilized blend and the blend with compatibilizer A (see Table I). This might be the reason that the addition of compatibilizer B is more effective in terms of distributive mixing than compatibilizer A. The higher pressures might be derived from an increase in the viscosity, with respect to that of the blends with compatibilizer A and without a compatibilizer, which is later shown to exist. An increase in the viscosity produces an increase in the capillary number, which leads to more efficient and faster elongation and breakup of the LCP structures. As the local length scale decreases, the interfacial stress becomes of the same order of magnitude as that of the shear stress, and the dispersive mixing is dominant. The LCP structures previously elongated then start to break into droplets with smaller diameters, and the distribution of these structures along the matrix occurs in a more efficient way. For the blend with compatibilizer B, this process seems to occur quite quickly because no significant differences were observed between the samples collected at valve 6 and valve 8 (Fig. 4). Valve 6 is at the beginning of a kneading-block region, whereas valve 8 is at the end of this region (see Fig. 1). Also, the dispersion of the LCP structures is almost completely accomplished at

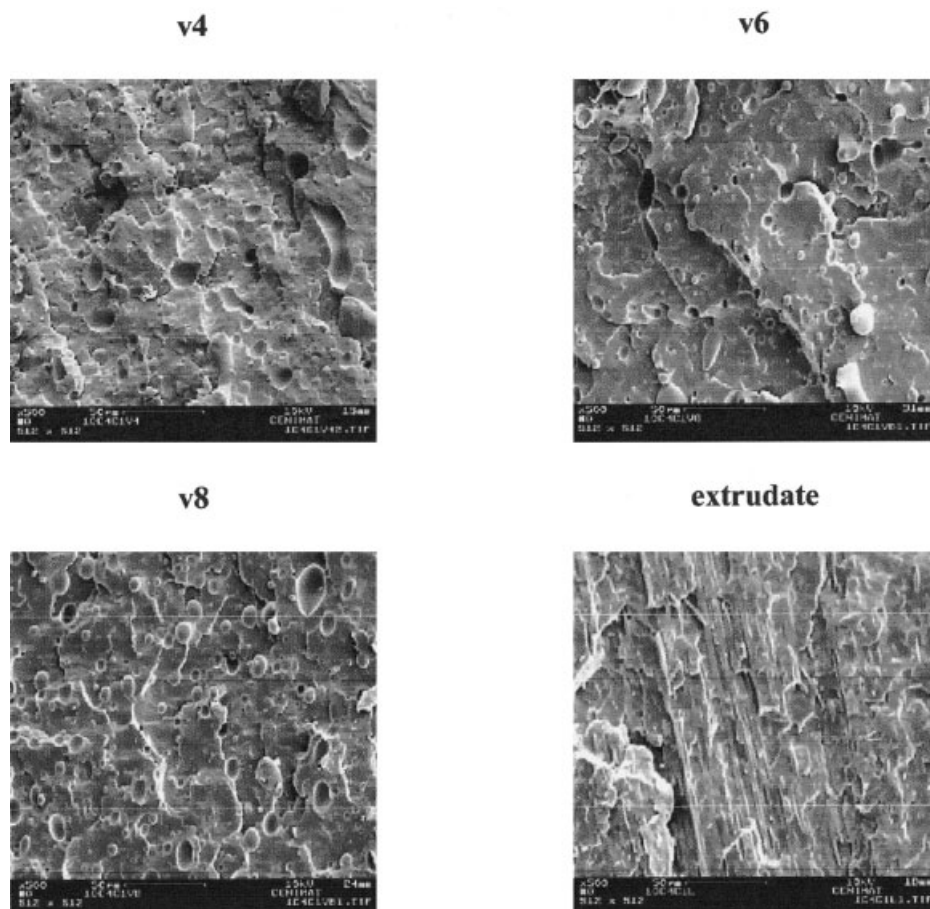


Figure 5 Morphological evolution along the extruder length for the blend with compatibilizer C (SEM).

valve 6. This means that the shear stress provided before the kneading blocks is already enough for the breakup of the LCP structures into droplets with smaller diameters. The formation of LCP fibrils with high aspect ratios was clearly seen; this confirmed the previous comments concerning the higher effectiveness of compatibilizer B in comparison with compatibilizer A (Figs. 3 and 4, respectively).

In conclusion, the addition of a compatibilizer to an LCP/TP blend should be performed in such a way that the degree of compatibility and reactivity of the compatibilizer with both dispersed and continuous phases are similar. Comparing the results obtained by the use of compatibilizers A and B, we can state that the degree of miscibility and reactivity between the aliphatic part of the compatibilizer and matrix and the nonaliphatic part of the compatibilizer and LCP must be of the same order of magnitude as that observed by the use of compatibilizer B because, in principle, this leads to a more efficient compatibilization. By this procedure, a higher degree of interaction between the compatibilizer and the pure components occurs, and this leads to an increase in the viscosity and thus higher fibrillar formation (as seen for compatibilizer B in comparison with compatibilizer A). As a result of

the higher degree of interaction and consequent increase in the viscosity, a higher pressure at the die occurs for the blend with compatibilizer B, with respect to that for the blend with compatibilizer A.

The addition of compatibilizer C seems to generate a blend in which a further reduction of the LCP diameters occurs, especially in comparison with compatibilizer A. The chemical structure of this compatibilizer is expected to be more compatible with both the LCP and TP because (1) the part of the backbone that is supposed to be compatible with the LCP consists of PET and (2) the backbone part that is compatible with the TP possesses a smaller length. The smaller length of the compatibilizer C backbone in comparison with that of compatibilizer B seems to be more efficient in the compatibilization process. This is expected because with a decrease in the alkyl chain one expects a decrease in the free volume of the compatibilizer chains, which, in principle, makes the interactions between the compatibilizer and the components of the blend, LCP, and TP easier. In conclusion, the shorter the alkyl chain of the compatibilizer is, the easier its interaction is with the LCP and matrix. Once more, the higher degree of interaction introduced into the LCP/TP system by the use of compatibilizer C antic-

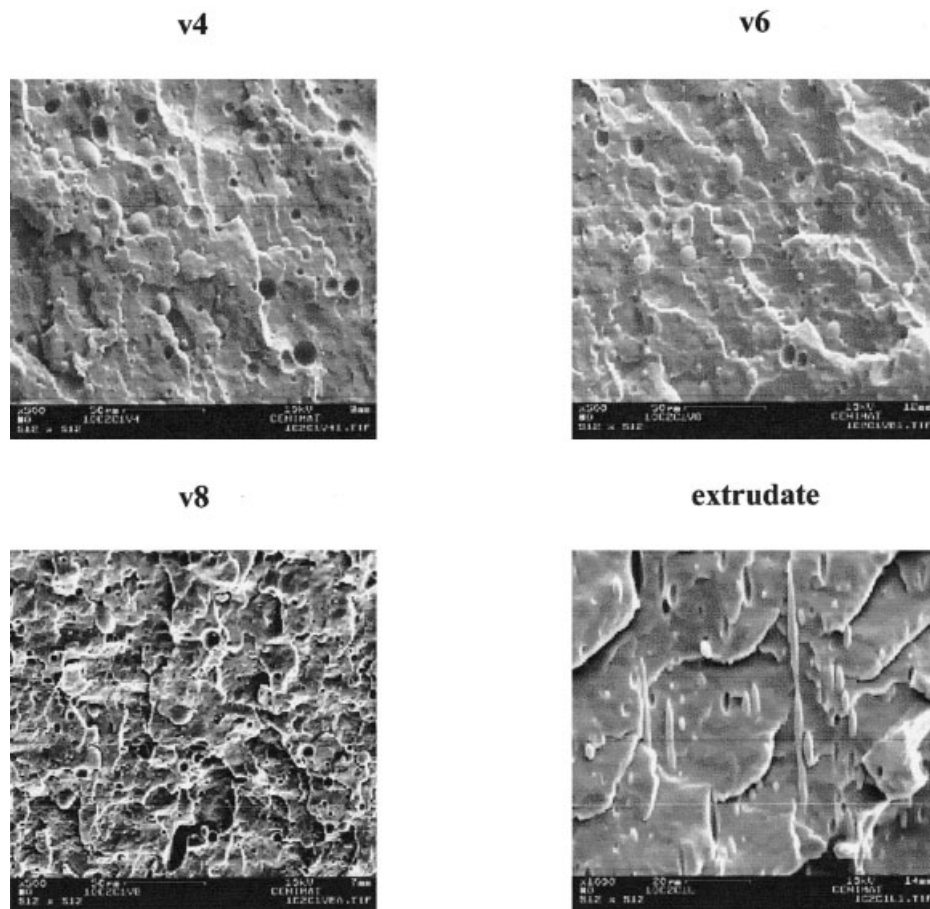


Figure 6 Morphological evolution along the extruder length for the blend with compatibilizer D (SEM).

ipates an increase in the pressure at the die in comparison with the blend in which the compatibilization is less effective, that is, the blend with compatibilizer A, as confirmed in Table I. Quite surprisingly, we did not observe an increase in the pressure at the die exit of the blend with compatibilizer C in comparison with the blend with compatibilizer B.

The morphologies presented at valve 4 and valve 6 are visually indistinguishable, as confirmed by linear rheology (shown later in Fig. 11). A better dispersion of the LCP along the matrix seems to occur between valves 6 and 8; however, the diameters seem to be almost unchanged from what is seen at valve 4 (Fig. 5). The morphology presented by the final extrudate is, as expected, composed of fibrils with high aspect ratios. The morphological similarities between the final extrudates of the blends with compatibilizer C and compatibilizer B are evident. The mechanical analysis previously performed, however, showed marked differences between the two compatibilized blends³⁴ (the blend with compatibilizer C possesses a higher tensile strength). Again, only slight differences between valve 4 and valve 8 are present in the blend with compatibilizer D, as shown in Figure 6.

The degree of dispersion is improved for all compatibilizers along the extruder length. However, the resulting fibrils for the blend with compatibilizer D have lower aspect ratios than those observed for the blends with compatibilizers B and C. By the addition of a compatibilizer such as compatibilizer D, which is a PP functionalized with maleic anhydride, a chemical interaction such as acidolysis is expected to occur between this group and the ester moieties of the LCP. However, the occurrence of this reaction requires the presence of catalysts. Therefore, because in principle a reaction between compatibilizer D and the LCP is difficult (because no catalyst is added), one might suggest that an interaction such as hydrogen bonding is responsible for the compatibilization. Because there is no chemical reaction and, therefore, there is no evidence of the formation of graft copolymers at the interface, we do not expect a significant increase in the overall viscosity and pressure, with respect to those of compatibilizers B and C.

The morphology shown for the blend in which compatibilizer E is used is significantly different, as depicted in Figure 7.

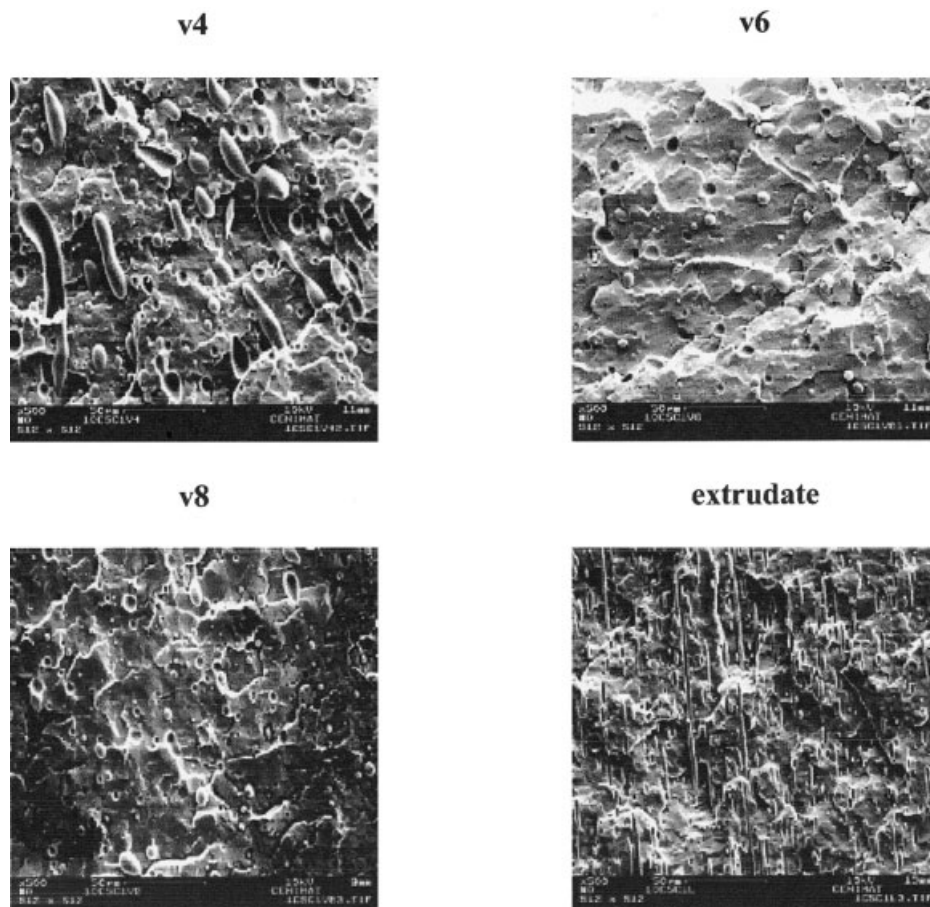


Figure 7 Morphological evolution along the extruder length for the blend with compatibilizer E (SEM).

First, the addition of this compatibilizer does not lead to a significant decrease in the diameters of the LCP structures at valve 4, as occurs for the blends with compatibilizers B, C, and D. The shape of the LCP structures is clearly different from what is seen for other compatibilized blends (Figs. 3–6). A high degree of elongation is, however, observed, and this means that at this point the distributive mixing is still the dominant process, contrary to what occurs for the blends containing compatibilizers B, C, and D (Figs. 4–6, respectively). A clear decrease in the diameters of the LCP structures occurs between valves 4 and 6, contrary to what occurs for the other compatibilized blends. The breakup processes for the blends with compatibilizers B, C, and D seem to occur faster than those for the blend with compatibilizer E. By the action of the shear stress developed inside the extruder, these structures then break, giving rise to the formation of LCP droplets with considerably lower diameters, at valve 6. From valve 6 to valve 8, the observed improvement is not in terms of a decrease in the diameters (which seems to be already accomplished at valve 6) but in terms of distribution. Finally, after the die, the LCP structures attain the maximum elongation, and fibrillar formation occurs. The breakup of the

LCP structures seems to occur to a larger extent in this blend, this being the reason that the LCP fibrils present lower aspect ratios than those observed for the blends in which compatibilizers C and B are used (Fig. 7).

In the case of compatibilizer E, the significant increase in the pressure at the die might be attributed to its chemical nature. The higher elasticity of the material would in principle result in increased resistance to deformation at increased shear rates, such as those present at the die. Additionally, the lower degree of fibrillar formation along with the presence of droplets at the final extrudates may explain the higher viscosities and thus the higher pressures at the die exit.

Rheological properties

As described previously, a study of the evolution along the extruder length was carried out by the use of oscillatory shear within the linear and nonlinear regimes. The first part of this analysis is devoted to the evolution of the storage modulus and complex viscosity along the extruder (Figs. 8–13). In the second part, a quantification of the nonlinear character is per-

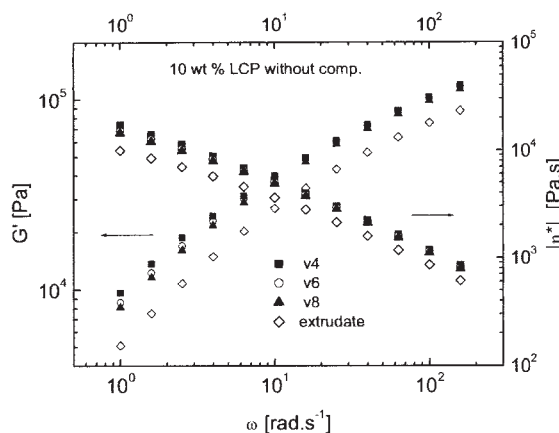


Figure 8 Evolution of the storage modulus (G') and complex viscosity ($|\eta^*|$) along the extruder length for the non-compatibilized blend at 170°C.

formed to estimate how the progression of the nonlinearity occurs during processing (Figs. 14–19).

Because of the improved efficiency in terms of the dispersive and distributive mixing that occur when compatibilizers are added to the blend, smaller differences between samples collected at different locations along the extruder are expected in comparison with the case without a compatibilizer. A comparison of the rheological behaviors along the extruder length for compatibilized and noncompatibilized blends is thus unavoidable in this discussion.

In light of the results in linear oscillatory shear, for all the blends (Figs. 8–13) it is apparent that both the storage modulus and the complex viscosity remain relatively constant along the extruder, and only at the die are significant changes observed. In this case, a decrease in both the viscosity and storage modulus

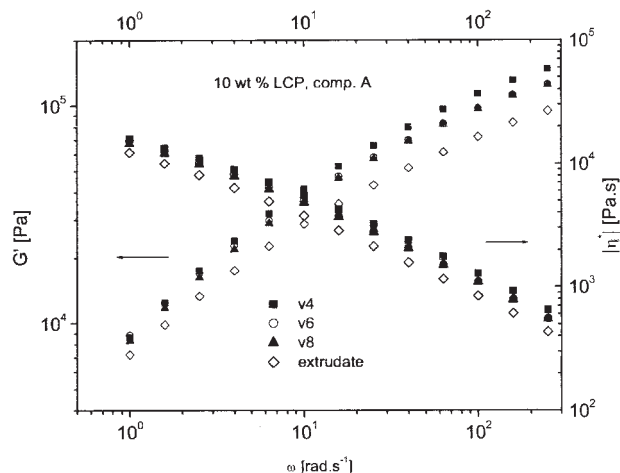


Figure 9 Evolution of the storage modulus (G') and complex viscosity ($|\eta^*|$) along the extruder length for the blend with compatibilizer A at 170°C.

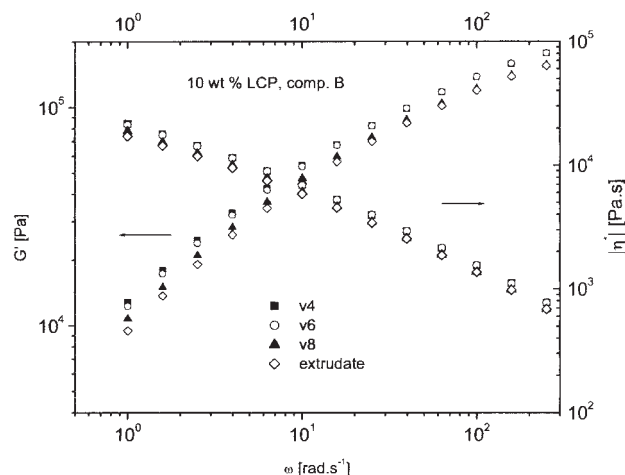


Figure 10 Evolution of the storage modulus (G') and complex viscosity ($|\eta^*|$) along the extruder length for the blend with compatibilizer B at 170°C.

can be observed between samples collected before and after the die, and it might be associated with the different morphologies present (inside the extruder, the LCP has the form of droplets, whereas for the extrudates, it presents a fibrillar morphology).

This effect is particularly relevant for the noncompatibilized blend and the blend with compatibilizer A. In principle, nonspherical particles yield higher apparent volume fractions than spherical particles, and so an increase in the viscosity is expected for the final extrudates. However, when no compatibilization is carried out or ineffective compatibilization occurs, a lack of adhesion at the interface occurs, and the orientation of the LCP structures may become the dominant factor; this leads to a decrease in the viscosity for the final extrudates (Figs. 8 and 9).

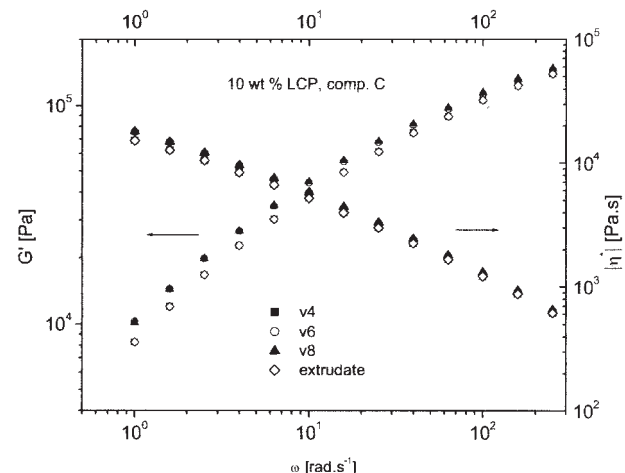


Figure 11 Evolution of the storage modulus (G') and complex viscosity ($|\eta^*|$) along the extruder length for the blend with compatibilizer C at 170°C.

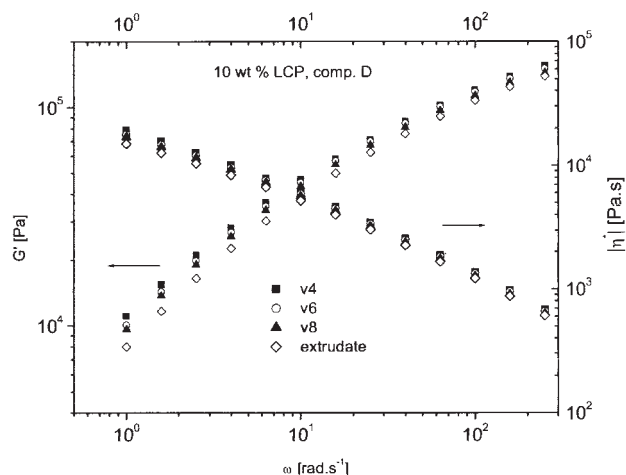


Figure 12 Evolution of the storage modulus (G') and complex viscosity ($|\eta^*|$) along the extruder length for the blend with compatibilizer D at 170°C.

When the compatibilization is carried out with compatibilizers B–E, changes in the rheological behavior of the PP/LCP system along and at the exit of the extruder still occur (Figs. 10–13), but with a much lower order of magnitude. In fact, the viscosities between the samples collected before (valves 4, 6, and 8) and after the die are now almost indistinguishable, and although a slight decrease in both the viscosity and storage modulus can be observed at the die exit, the effect is much smaller than it was previously.

In conclusion, for our materials, linear oscillatory shear is able to distinguish between the types of structures present but is not sensitive enough to detect finer differences between droplet dimensions as the material progresses inside the extruder. In addition to this drawback, the majority of industrial processes occur

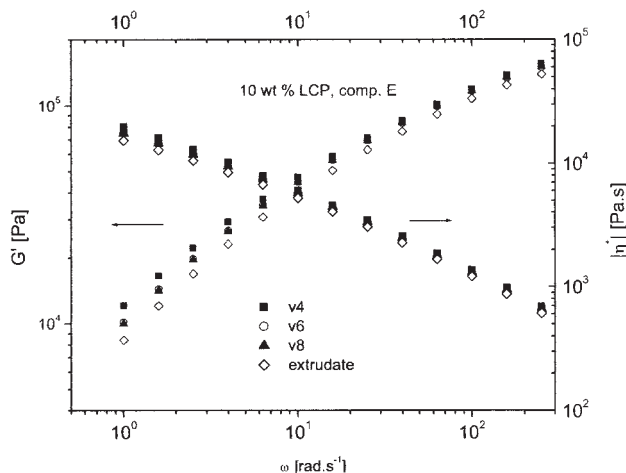


Figure 13 Evolution of the storage modulus (G') and complex viscosity ($|\eta^*|$) along the extruder length for the blend with compatibilizer E at 170°C.

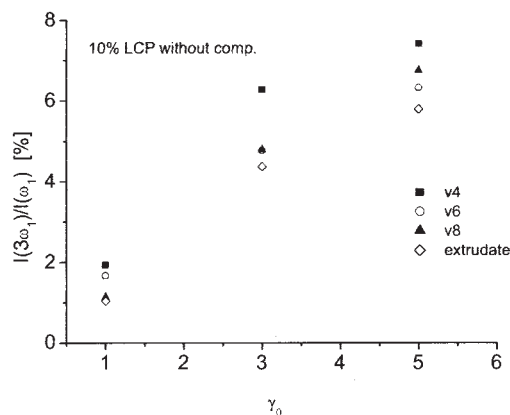


Figure 14 Increase in $I(3\omega_1)/I(\omega_1)$ with the applied γ_0 values for the different samples collected along the extruder length (blend without a compatibilizer at 170°C).

in a nonlinear regime, and so it is of great interest to study the rheological behavior under these conditions and not under linear ones.

A prime candidate for this study, because of its ease of use and large potential for this type of system,¹ is LAOS. In this case, we have followed the method outlined for noncompatibilized blends containing different LCP contents:¹ a sinusoidal strain excitation was applied at a constant frequency and temperature, and the resultant torque response was Fourier-transformed. The Fourier transformation generated a spectrum with peaks located at the fundamental frequency ($\omega_1/2\pi$) and at odd multiples ($3\omega_1, 5\omega_1, 7\omega_1$, etc.).^{38,39} Each peak was characterized by means of an amplitude, a_n , and a phase, ϕ_n , where n is an odd multiple of the fundamental excitation frequency. The evaluation of the nonlinear character was obtained from $I(3\omega_1/2\pi)/I(\omega_1/2\pi)$, which represents the relative intensity between the third harmonic ($3\omega_1/2\pi$) and the fundamental excitation frequency ($\omega_1/2\pi$). The evolu-

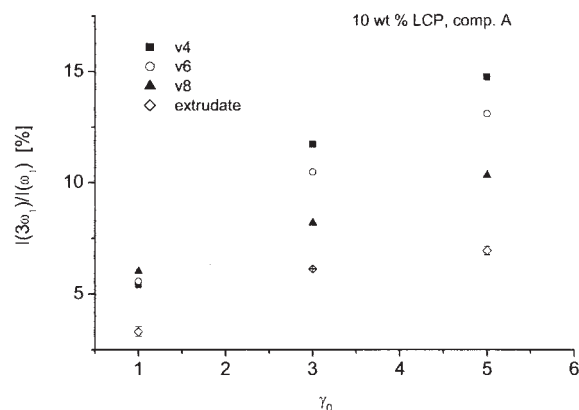


Figure 15 Increase in $I(3\omega_1)/I(\omega_1)$ with the applied γ_0 values for the different samples collected along the extruder length (blend with compatibilizer A at 170°C).

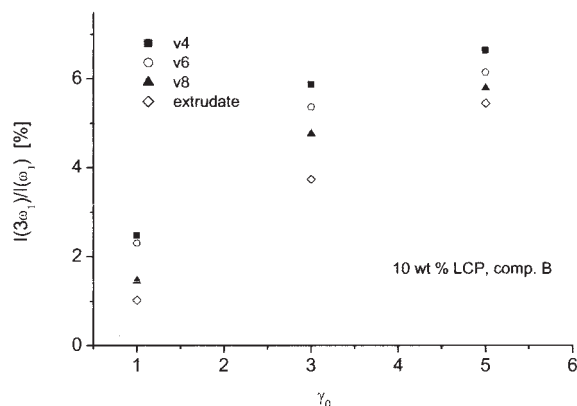


Figure 16 Increase in $I(3\omega_1)/I(\omega_1)$ with the applied γ_0 values for the different samples collected along the extruder length (blend with compatibilizer B at 170°C).

tion of $I(3\omega_1/2\pi)/I(\omega_1/2\pi)$ with the applied strain was studied for all the samples collected along the extruder length (from valve 4 to the final extrudate).

Because of the rheological response under nonlinear conditions and in contrast to the linear data, a clear distinction between samples collected at different locations along the extruder can be made. The nonlinear character, expressed by means of the evolution of $I(3\omega_1)/I(\omega_1)$ as a function of γ_0 , differs according to the location in the extruder. As verified previously for noncompatibilized systems,¹ the degree of nonlinearity decreases progressively and in a very clear way along the extruder for all the blends (Figs. 14–19); this can be directly related to the progressive decrease in the dispersed-phase diameters.

The differences in terms of the nonlinear character are especially pronounced for the blend with compatibilizer A, as shown in Figure 15. This is in agreement with the morphological analysis, which shows that this is the blend for which the LCP droplets present

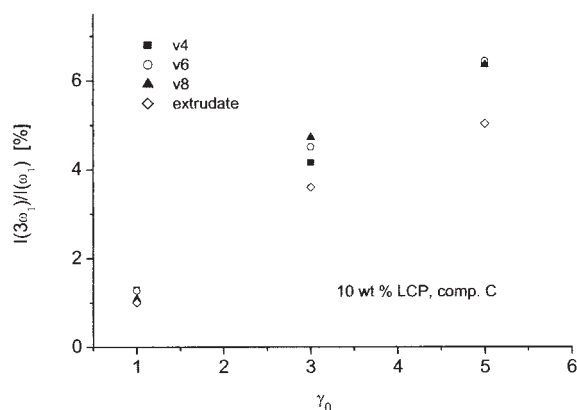


Figure 17 Increase in $I(3\omega_1)/I(\omega_1)$ with the applied γ_0 values for the different samples collected along the extruder length (blend with compatibilizer C at 170°C).

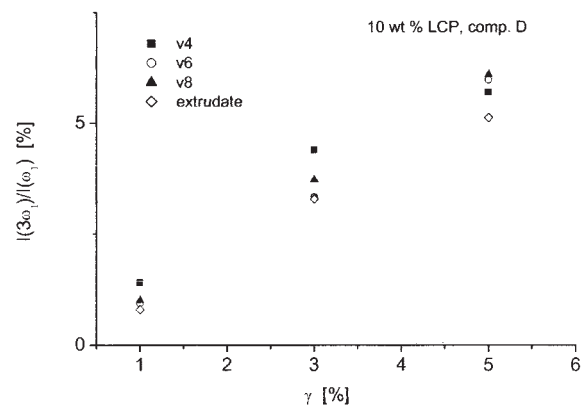


Figure 18 Increase in $I(3\omega_1)/I(\omega_1)$ with the applied γ_0 values for the different samples collected along the extruder length (blend with compatibilizer D at 170°C).

the highest dimensions (Fig. 3). However, at valve 4, the morphology presented for the blend with compatibilizer A is quite similar to the one observed for the noncompatibilized blend (Figs. 14 and 15). Thus, the nonlinear character must not depend exclusively on the diameters of the dispersed phase; the action of the compatibilizer at the interface must have an additional and important contribution.

The blend with compatibilizer C, on the other hand, is the one for which the smallest differences have been verified between samples collected at different valves (Fig. 17); this is an indication of a more homogeneous structure and is also compatible with the improved mechanical properties that this blend possesses.³⁴ Again, a decrease in $I(3\omega_1)/I(\omega_1)$ occurs for the final extrudates, in comparison with those of the samples collected at the valves.

In terms of the final extrudates, it can be considered that the addition of a compatibilizer leads to a decrease in the nonlinear character for all the compatibilized blends, except for the blend with compatibi-

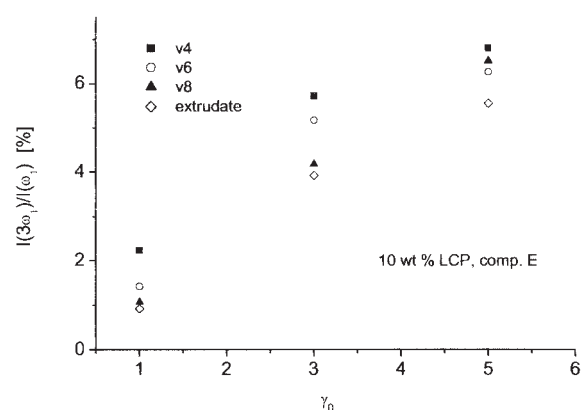


Figure 19 Increase in $I(3\omega_1)/I(\omega_1)$ with the applied γ_0 values for the different samples collected along the extruder length (blend with compatibilizer E at 170°C).

lizer A, for which considerably higher nonlinearities have been observed.

In conclusion, LAOS is a very powerful tool for the indirect analysis of the evolution of the morphology of these blends along the extruder, being sensitive not only to the type of structure present but also to the average disperse-phase dimensions.

CONCLUSIONS

Most of the fundamental research on the mixing of immiscible polymers has been focused on ideal systems, with typical Newtonian behaviors and well-defined flow conditions. The study of the mixing processes that occur during the extrusion of LCP and TP blends clearly involves a much higher degree of complexity, thus requiring improved knowledge and intense study and the use of several complementary methods.

To take advantage of the high mechanical strength of LCPs, the use of compatibilizers is required for the preparation of LCP/TP blends. According to the chemical structure of the latter, a different degree of compatibilization may occur, and this basically means that a different morphology will be obtained during the extrusion process. Taking this work as a basis, we can state that the way in which the morphology evolves along the extruder length differs according to the compatibilizer used because different compatibilizer molecular structures induce different degrees of efficiency of both distributive and dispersive mixing; that is, the decrease in the LCP structure diameters occurs more quickly and the LCP fibrils of the final extrudate become thinner and longer than those presented by the blends in which the compatibilization is not so effective.

From a rheological point of view, the use of linear oscillatory shear is useful to distinguish between the types of microstructures present, but it is not sensitive enough to study in depth the evolution along the extruder length. For this, LAOS and Fourier transform rheology analysis have been used. This analysis establishes that the degree of nonlinearity decreases clearly along the extruder as a result of the progressive decrease in the LCP structure diameters; thus, the nonlinear character seems to be strongly correlated to the efficiency of the compatibilizer. For example, the use of the least effective compatibilizer (compatibilizer A) led to an increase in the nonlinear character, in contrast with what was verified for the blends in which compatibilization was effective (compatibilizers B–E).

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