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Evolution of morphological and rheological properties along the extruder length for blends of a commercial liquid crystalline polymer and polypropylene

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Abstract

The main aim of this work is to study the morphological and rheological evolution during extrusion of blends of polypropylene and a commercial liquid crystalline polymer, Rodrun LC3000. This study was performed for blends with 10, 20 and 40 wt% LCP, processed at 220 and 240 °C. For this purpose, a special collecting device was used that allows the removal of samples at different locations along the extruder length. The results of the morphological study revealed that the mean diameter of the LCP structures decrease as they proceed along the extruder axis. The rheological properties were also studied ex situ both in the linear and in the non-linear regime. From the results obtained in oscillatory shear it was observed that the elastic modulus and the complex viscosity decreases from the beginning to the end of the extrusion process, reaching a minimum for the final extrudate. FT rheology was used to study the non-linear viscoelastic behavior and the results also show marked difference between samples collected at various stages of the process, the ratio $I(3\omega_1)/I(\omega_1)$ decreasing along the extruder.

Keywords: Liquid crystalline polymer and thermoplastic blends; Morphological and rheological evolution; Fourier transform rheology

1. Introduction

Polymer blending is an important attempt to obtain new reinforced materials, in which improved processability and properties are achieved by combining the individual properties of each pure component. The study of the evolution of polymer blend morphology during processing receives more and more attention and different techniques have been used in order to obtain an improved knowledge on this subject (see, for example, the works of Shi and Utracki [1], Tyagi and Ghosh [2], Potente et al. [3,4] and Scott and Macosko [5]). During compounding, several factors influence the final morphology, including shear, elongational and hydrodynamic forces involved during compounding and also the rheological properties of the components of the blend. The deformation of the LCP droplets into fibrillar structures or the coalescence of the LCP structures depends on the ratio between the viscous force and the interfacial force. This ratio is frequently described by the Capillary number, *Ca*, which is defined by:

$$Ca = \frac{\eta_m \cdot \gamma \cdot r}{\sigma} \tag{1}$$

where, η_m is the viscosity of the matrix, γ is the shear rate, r is the radius of the LCP droplets and σ is the interfacial tension between the two pure components. The influence of the capillary number on the stability of the LCP structures has already been studied in liquid crystalline polymer and thermoplastic blends by Lazkano et al. [6]. Postema and Fennis [7], Chan and co-workers [8]. Kernick and Wagner [9] studied the influence of both viscous and interfacial forces in the final morphology, confirming the importance of the capillary number.

The morphology obtained during extrusion of immiscible blends varies along the different regions within the extruder. At the beginning of the compounding process the pure components are added at room temperature in the form of pellets or powder, then subsequently heated and melted, giving rise to a heterogeneous blend containing a disperse

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and a continuous phase. At the beginning of the extruder, specifically in the feed zone, the shear forces are the dominant ones in the process [2]. Furthermore, at this stage the blend is not completely melted and the disperse phase is usually constituted by spherical or ribbon-like structures, which will start to be stretched afterwards, as a result of the combination of shear and elongational forces. This deformation processes usually starts upon melting, where the formation of droplets and/or elongated structures is expected [2]. Nevertheless, break-up processes or coalescence processes will also start and the ratio between the interfacial forces (that tend to keep the drop spherical) and the viscous forces (that tend to elongate the droplets) will define which of these will dominate [1,4]. In the mixing zones of the extruder, the shear forces are increased relatively to the previous stages, and, therefore, the breaking processes of the elongated structures will be dominant. At this region of the extruder, spherical structures, with a decreased domain size and a narrower distribution, than those observed at the beginning of the process are observed [2]. The final dimensions of these structures depend on the mechanical history and also on the ratio between the viscosity of the two components of the blend [1]. Finally, due to the high shear rates and extensional forces developed in the extruder die, a fibrillar morphology will be produced, as a result of the elongation suffered by the spherical LCP structures formed previously, at the metering zone.

The final morphology, which depends largely on the morphological evolution during polymer blending, is directly related to the ultimate mechanical properties, research on this subject being reported, for example, by Gi Dae Choi and co-workers [10] and by Sangmook Lee et al. [11]. The processing conditions employed, like temperature profile, screw speed, throughput and also the configuration of the screw, control the several stages of the extrusion process. Therefore, they will define the morphology obtained at the end of the process. For example, the use of kneading blocks in the screw configuration will promote mixing and will lead to the reduction of the droplet's diameters. This effect is more pronounced for high screw speeds and also for high throughputs [12]. Some theoretical derivations were also made by Shi and Utracki [13] and by Huneault et al. [14], regarding the evolution of the morphology during compounding in a twin-screw extruder. In these studies different mechanisms were used to explain droplet's break-up and dispersion. They considered two different mechanisms for the break-up: one where the stable filaments are formed and that describes the behavior of the large droplets and another, where break-up occurs during flow and is responsible for the generation of relatively small droplets. They stated that, according to the capillary number involved, one of these break-up mechanisms will occur. Relatively to the influence of the processing conditions, they noticed that the morphology is very sensitive to the screw configuration used during extrusion.

The interest in studying liquid crystalline polymer and thermoplastic blends has increased significantly in the last few years and can be attributed to the mechanical and processability improvement potential of these blends. In fact, mechanical improvements were found for these kind of blends in different studies performed by Yoshikai et al. [15] and Datta and Baird [16], among others. The formation of high aspect ratio LCP fibrils inside the thermoplastic matrix leads to the creation of reinforced composites in situ.

Viswanathan and Isayev [17] and Yoshikai et al. [15] studied the influence of the LCP content on the final morphology and noticed that the increase in the LCP content leads to the increase in the fibrils and that the formation of fibrils is easier for the blends with the highest LCP contents. Additionally, they found out that the fibrils are thicker, longer and with a better packing for the blends with the higher LCP content, which can explain the mechanical improvement obtained in these cases.

Other researchers studied the influence of the most important parameters on the final morphology. Wano and co-workers [18] studied the effect of the thermoplastic viscosity on the LCP structure formed in blends of polypropylene and Rodrun LC3000. They found that the high aspect ratio LCP fibers are achieved only for blends in which the matrix has the higher viscosity. Boersma and Van Turnhout [19], on the other hand, used dielectric spectroscopy for on-line monitoring of the morphological evolution of liquid crystalline and thermoplastic blends. In their study they concluded that the fibrillar structures are achieved in the mixing elements, which is explained by the higher shear rates observed in that region. Additionally, they found out that the mean particle size decreases with increasing shear rate. Finally, Potente et al. [4] investigated the morphology development in polypropylene and polyamide blends during processing in a co-rotating twin-screw extruder. They used a special technique to remove samples along the extruder. This technique needed less than 1 min, in order to minimize the morphological changes due to the relaxation of the structure. They pointed out that only a small change in the number average diameter of the disperse phase was observed along the extruder length. They concluded on the existence of an inverse correlation between the viscosity of the matrix, and the average diameter observed for the disperse phase.

As seen above, several studies were conducted in order to understand how the morphological evolution occurs during the compounding of immiscible blends. However, the rheological evolution along the extruder length, and the relation between the morphology and the rheology developed during the compounding of liquid crystalline and thermoplastic blends was not studied yet. In this work, a rheological study is carried out, both in the linear and in the non-linear regime, in order to attain an improved knowledge on this subject.

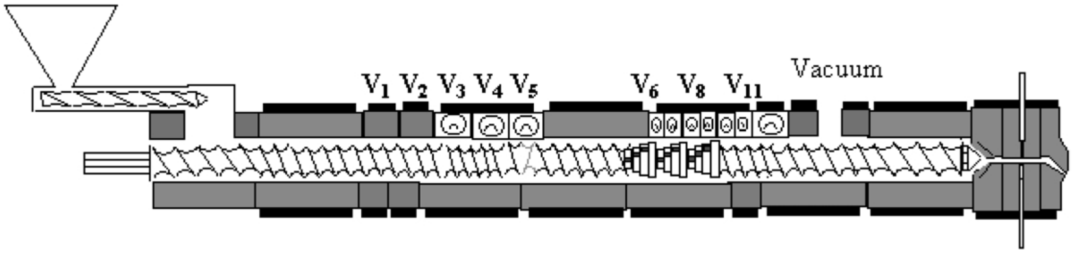


Fig. 1. Screw and cylinder profile used for the processing of the blends with 10, 20 and 40 wt% LCP (v_i is the i-th valve that allows the removal of samples along the extruder length).

2. Experimental

2.1. Materials

Liquid crystalline polymer and thermoplastic blends were produced using polypropylene (Stamylan P 12E62 from DSM) and a liquid crystalline polymer (Rodrun LC3000 from Unitika). The thermoplastic used for the preparation of the blends is an isotatic polymer with a weight-average molecular weight ($\overline{M_w}$) of 1,200,000 g/mol (obtained by GPC) and a melt flow index of 0.8 g/10 min (at 230 °C and for 21.6 N). The liquid crystalline polymer is an aleatory copolyester of 60 mol% of *p*-hydroxybenzoic acid (HBA) and 40 mol% of polyethylene terephthalate (PET). The molecular weight for the LCP was not obtainable, since no solvent was found to dissolve Rodrun LC 3000.

2.2. Processing

All the materials were dried in an oven at 90 °C for 24 h, before processing.

Blends with 10, 20 and 40 wt% LCP were produced using a Leistritz LSM 30.34 co-rotating intermeshing twin-screw extruder with a screw diameter of 33.7 mm and a length to diameter ratio (*L*/*D*) of 29. The cylinder and screw configuration used for the preparation of these blends is presented in Fig. 1. The screw speed was set at 150 rpm, the output rate used was 4 kg/h and the processing temperatures, set constant along the extruder profile, were 220 and 240 °C. After processing, the blends were immediately quenched in a water bath and subsequently pelletized. During processing samples were removed in different locations along the extruder length, using a home built collecting device system (DEP-University of Minho, Machado et al. [20]). With this system, 1–3 g samples can be collected in less than 3 s and without disturbing the flow, which are then immediately quenched in liquid nitrogen. Thus, the original morphology developed inside the extruder was almost completely retained. This system was previously used to study the morphological evolution in different kinds of blends (see, for example, Covas et al. [21], Machado et al. [22] and Van Duin et al. [23]).

2.3. Rheological characterization

The samples collected along the extruder (for blends with 10, 20 and 40 wt% LCP, processed at 220 °C) and the final extrudates were compression moulded in discs of 8 mm diameter and then characterized using a ARES rotational rheometer from Rheometrics. Although this compression induces an extra thermal cycle on the samples, this has been found before [24] to alter the morphology only slightly (and in the same way for all samples), since shear is virtually absent and compression molding is carried out at relatively low temperatures. Thus, any differences in the original morphology between the different samples will, by and large, be retained after compression moulding. Rheological measurements were carried out both in the linear and the non-linear regime in order to establish differences between the different samples removed at different locations in the extruder. The dynamic experiments in the linear regime were performed in oscillatory shear, with $\gamma_0 = 0.1$ strain amplitude at 170 °C. A frequency range from 0.99 to 158 rad/s was applied and the gap was set at 0.25 mm. For the dynamic measurements performed in the non-linear regime, time sweep measurements were carried out for different strains ranging from $\gamma_0 = 0.1$ to $\gamma_0 = 7$. For these measurements the frequency was set at 6.28 rad/s and the temperature used was 170 °C. The time data was Fourier transformed giving rise to frequency data. More details about this technique are available elsewhere (Wilhelm et al. [25], Wilhelm et al. [26], Wilhelm [27]).

In order to study the possibility of polypropylene degrading during the experiments, shear was applied during 30 min to it at both 220 and 240 °C. Both viscosity and storage modulus remained constant, which indicates no degradation of the material. Additionally, Postema and Fennis [7] have found that below 260 °C no thermal degradation occurs for a polypropylene with MFI ranging from 0.7 to 20 g/10 min, whereas the MFI of the PP used in this work is 0.8 g/10 min. Considering that the processing temperatures were 220 and 240 °C and that the material was always below 260 °C (as can be observed in the temperature profiles measured in both cases), in Table 1 no degradation was expected to occur.

Table 1
Temperature profiles measured along the extruder length for the blends with 10, 20 and 40 wt% LCP, processed at 220 and 240 °C

Processing temperature (°C)	LCP content (wt%)	Temperature (°C)							
		Valve 4	Valve 5	Valve 6	Valve 7	Valve 8	Valve 9	Valve 10	Extrudate
220	10	226.2	228.4	227.9	229.4	229.6	231.7	232.2	236.1
	20	225.6	224.7	225.3	228.4	229.2	230.9	231.8	233.7
	40	222.6	224.3	224.7	225.2	227.3	228.9	231.0	231.5
240	10	242.5	243.2	243.4	244.8	244.1	244.9	245.2	245.4
	20	241.6	243.1	243.1	244.4	244.2	244.3	244.8	245.1
	40	241.2	242.7	241.7	241.2	243.3	243.9	241.0	243.9

2.4. 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 of the blends with 10, 20 and 40 wt% LCP processed at 220 °C. The equipment used for this purpose was a Scanning Electron Microscope ZEISS DSM962. The samples were cryogenically fractured, and coated using a POLARON SC502 and then examined by SEM at an accelerating voltage of

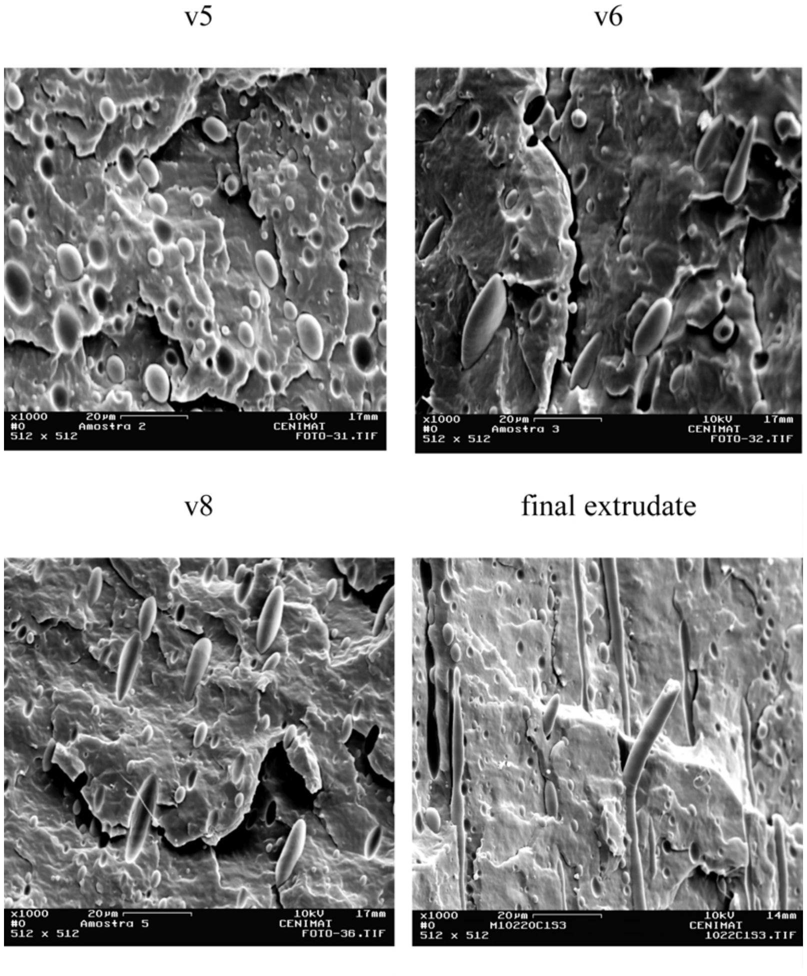
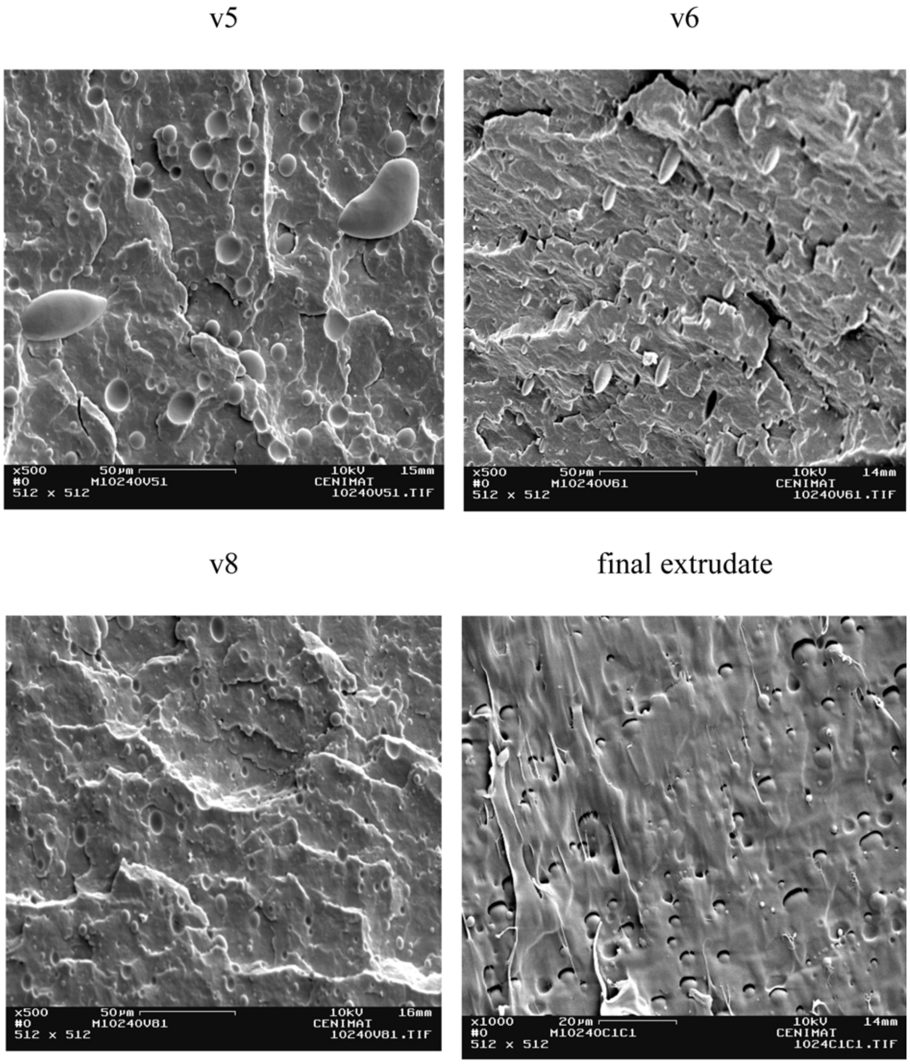


Fig. 2. (a) Morphological evolution along the extruder length for the blend with 10 wt% LCP processed at 220 °C (SEM). (b) Morphological evolution along the extruder length for the blend with 10 wt% LCP processed at 240 °C (SEM).


v5

v6

v8

final extrudate

(b)

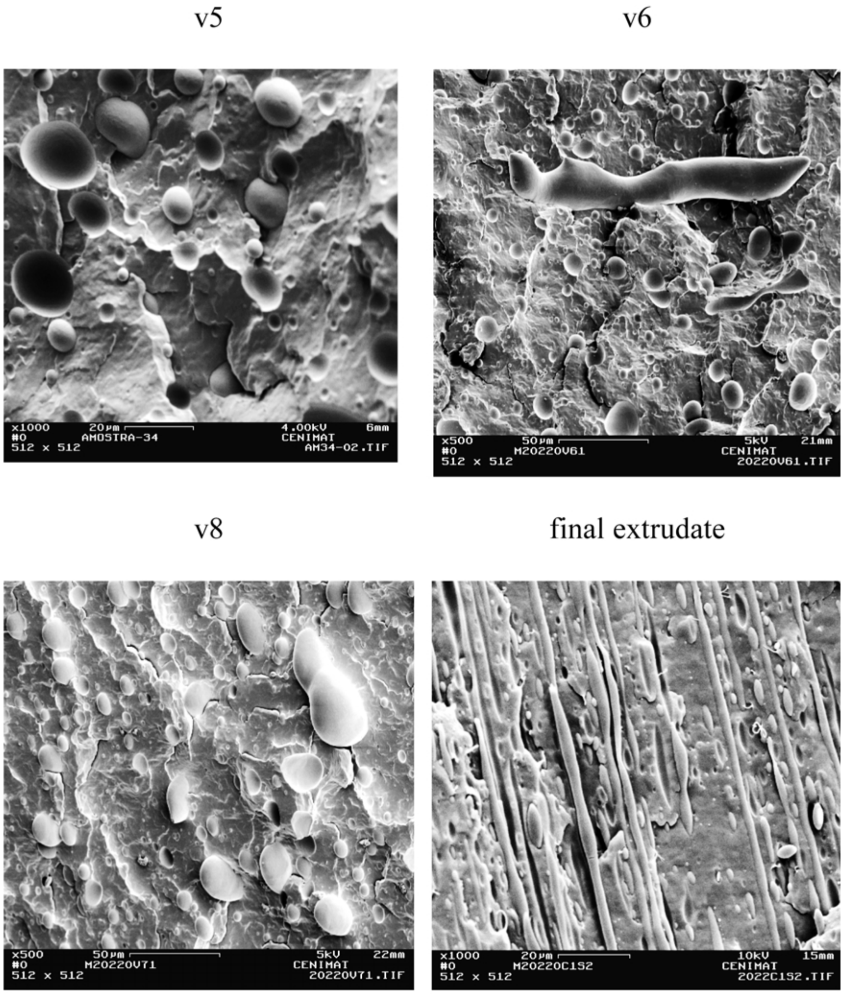
Fig. 2 (*continued*)

10 kV. The morphology of the samples (in the form of compression moulded discs) used in the rheological measurements (both in the linear and non-linear regime) was also characterized by light microscopy, using a Linkam shearing system CSS 450. This procedure was used in addition to SEM because the shear cell allows the observation of the morphology before, during and after shearing, which is not possible to be done using solely SEM. In order to check the morphology of the disperse phase structures during shear at the same conditions used for the rheological measurements, morphological observations were performed over compression moulded discs with 8 mm diameter subjected to oscillatory shear at 170 °C, 6.28 rad/s and for different strains, ranging from $\gamma_0 = 0.1$ to $\gamma_0 = 7$ (Figs. 7 and 8 were obtained from measurements performed with an amplitude strain equal to 0.3).

3. Results and discussion

3.1. Morphology

During extrusion the developed morphology depends on several different parameters such as processing temperature, screw speed, throughput and screw elements. Taking these facts into account, different morphologies are to be found at different locations along the extruder length, according to the specific conditions in each zone. Even in the current case, where the same temperature was set for the different heating zones along the extruder, thermal differences were observed along the cylinder length, as can be seen in Table 1. For example, the temperature at the conveying elements was lower than the observed at the kneading elements, which is essentially due to the lower shear rates and pressures in the former.



v5

v6

v8

final extrudate

(a)

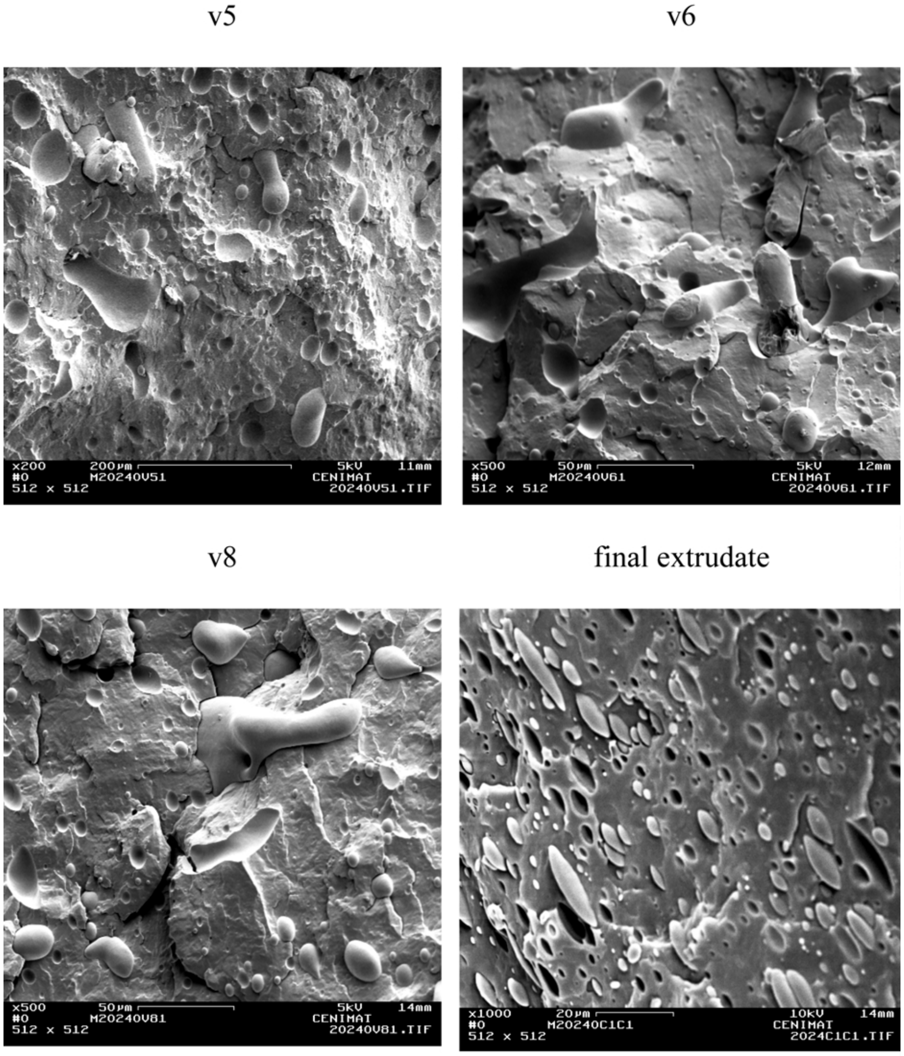
Fig. 3. (a) Morphological evolution along the extruder length for the blend with 20 wt% LCP processed at 220 °C (SEM). (b) Morphological evolution along the extruder length for the blend with 20 wt% LCP processed at 240 °C (SEM).

The morphological measurements carried out for the blends with 10, 20 and 40 wt% LCP (see Figs. 2–4) show that, at the beginning of the extruder, the LCP structures are essentially droplets distributed along the thermoplastic matrix. These LCP structures are progressively elongated along the extruder length, giving rise to fibrillar structures at the exit of the die. During processing, the material is subjected to shear and elongational forces that are responsible for the deformation and eventual break-up of the LCP structures.

Looking at the SEM images (Fig. 2(a)) obtained for the blend with 10 wt% LCP (processed at 220 °C) it can be concluded that the LCP structures in the samples collected in valve 5 are less elongated than the samples removed at valve 6. This was expected, since the first sample was collected near a reverse-conveying element (located near valve 5), while the second sample was removed at valve 6, situated at the beginning of the mixing elements. The larger dimensions observed for the samples collected at the reverse-conveying zone can be explained as a consequence of the increase in the residence time that occurs in this region of the screw. On the other hand, at the mixing zones, i.e. the kneading blocks, the shear rate is increased and as a consequence the shear stress is high enough to guarantee the elongation of the LCP droplets, as can be observed for the samples collected at valve 6. Finally, the material crosses the die, where it experiences the highest shear rates and elongations. Consequently, a maximum deformation will occur, giving rise to a morphology where the LCP structures have the form of fibrils with the highest aspect ratio.

It is important to point out that in Figs. 2–4, the microphotography presented for the extrudate was obtained with samples cryogenically fractured in the longitudinal direction, instead of the usual transverse direction, since this allowed for a better definition of the fibrils.

When comparing the SEM images obtained for the blends with different LCP contents, processed at the same



(b)

Fig. 3 (*continued*)

temperature (220 °C), it is possible to extract some conclusions about the influence of the LCP content on the morphology along the extruder length.

Comparing Figs. 2(a), 3(a) and 4(a) it can be concluded that an increase in the disperse phase content leads to an increase in the mean particle size at a given location along the extruder, as expected (Fig. 5). This increase was not observed for the final extrudates, in which no significant differences were observed between the different blends, except that the density of the LCP fibrils increases clearly with the LCP concentration.

In order to establish the influence of the temperature on the morphology, two different processing temperatures were used (220 and 240 °C). The first consideration, and the most important one, is that high processing temperatures lead to a lower viscosity of both components, which promotes the coalescence of the disperse phase. Moreover, the relative viscosity ratio between the two components was higher at 220 °C comparing with the one observed at 240 °C (see Fig. 6). As already stated [1] the formation of fibrillar structures will be easier for a viscosity ratio close to 1. Furthermore, the viscosity ratio slightly increases as a function of the shear rate, since at high shear rates, the polypropylene matrix shows more pronounced shear-thinning than the LCP.

Therefore, the formation of fibrillar structures was significantly improved for the blends with 10 and 20 wt% LCP processed at 220 °C, (Figs. 2(a) and 3(a)), whereas for the 40 wt% LCP blend, the incorporation content of the latter is so high that no significant differences can be seen, long fibrils being present in large numbers for both processing temperatures. For a lower processing temperature, the higher viscosity of the matrix disfavors the flow of the disperse phase inside the continuous phase. Due to the higher viscosity of the matrix, the stress to which the LCP structures are subjected is significantly higher than the stress

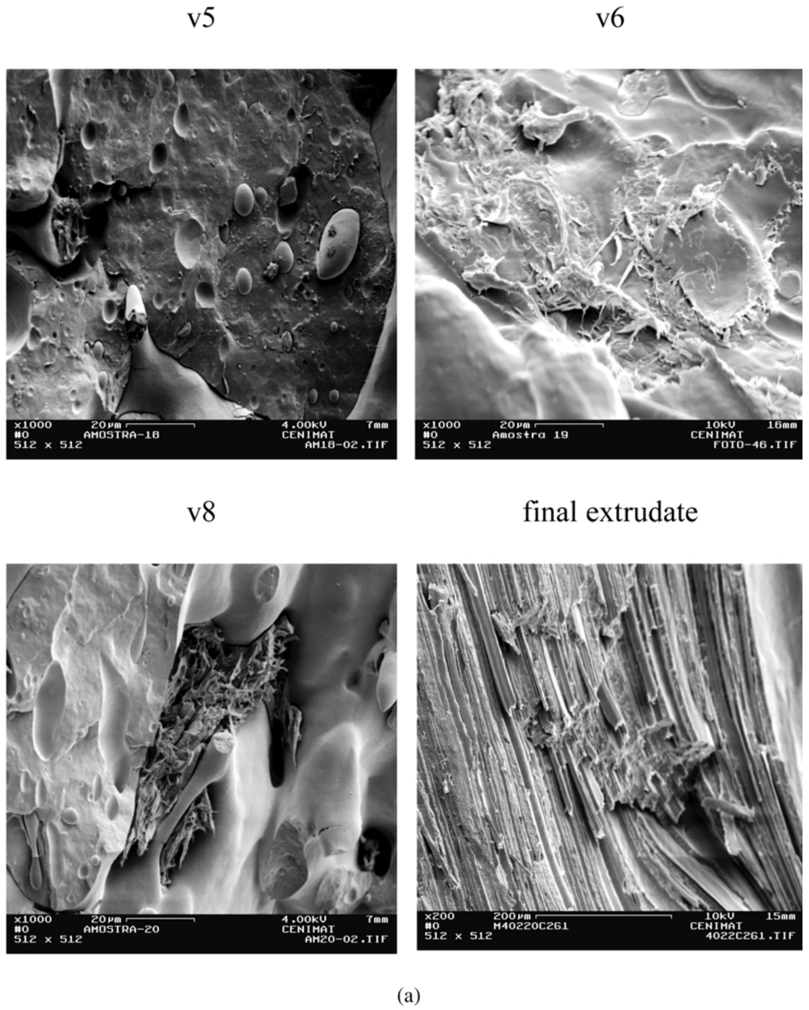


Fig. 4. (a) Morphological evolution along the extruder length for the blend with 40 wt% LCP processed at 220 °C (SEM). (b) Morphological evolution along the extruder length for the blend with 40 wt% LCP processed at 240 °C (SEM).

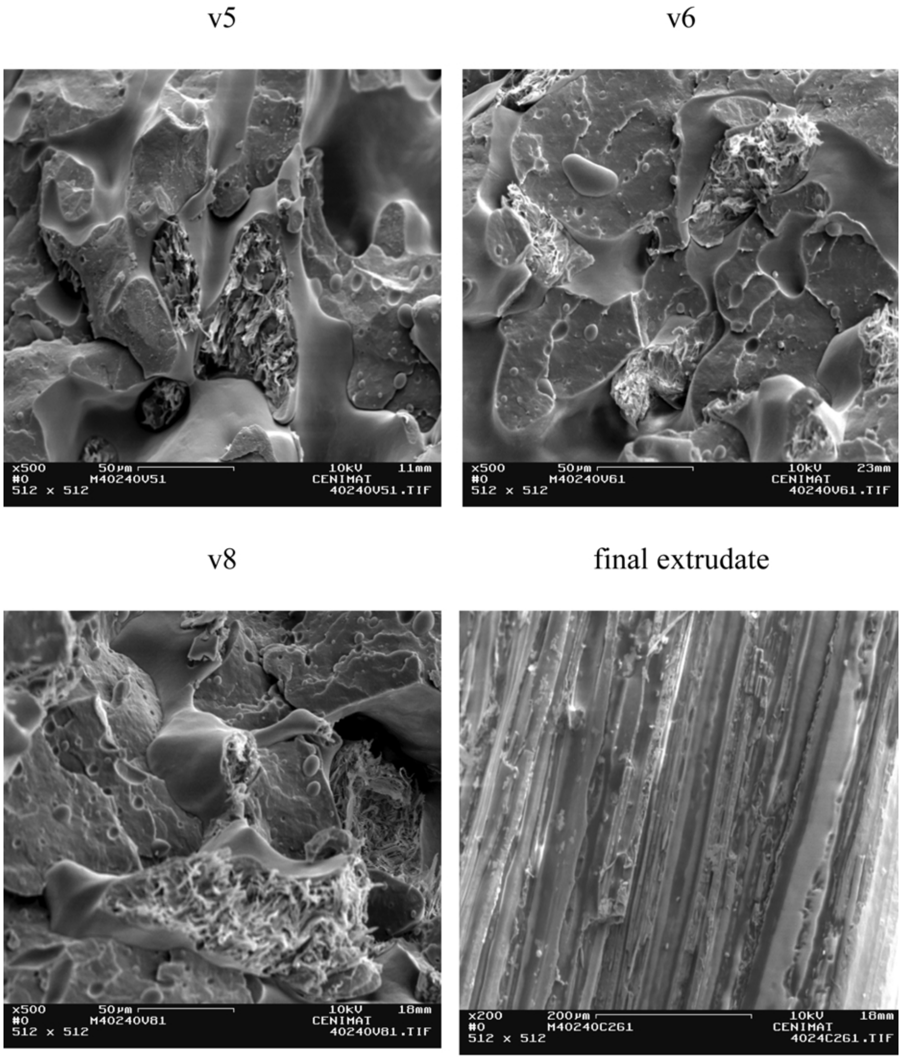
observed at higher processing temperatures, leading to an easier deformation and thus to a more homogeneous morphology.

As already described, moulded discs were produced from the samples collected along the extruder and in the extrudate, in order to study the evolution of the rheological properties along its length. In order to confirm the morphological changes observed by SEM inside the extruder, optical measurements under shear were also performed for samples collected along its length, at 170 °C, using a Linkam Shearing System CSS450 coupled with an optical microscope (Fig. 7).

The images obtained for the discs corresponding to 10 wt% LCP (processed at 220 °C) allow several conclusions to be drawn: the moulded discs that correspond to the samples collected at valve 5 show LCP structures with droplet shapes, while for the moulded discs corresponding to the samples removed at valves 6 and 8, elongated LCP structures were observed. These observations are in agreement with the morphological results obtained for the samples directly collected from the extruder valves (Fig. 2(a)). Similar conclusions can be drawn for the blend with 20 wt% LCP (Fig. 8). It was not possible to use the Linkam System for the morphological analysis of the blend with 40 wt% LCP, due to the opacity of this material.

3.2. Linear oscillatory rheology

The study of the linear rheological properties of the pure components and blends is essential to understand the morphology developed for LCP/TP blends. As already discussed, a fibrillar morphology or a disperse droplet morphology will develop depending on the viscosity ratio and on the capillary number. For a viscosity ratio lower than 1, a finer and a more uniform distribution of the LCP phase is obtained, while for viscosity ratios higher than 1, the LCP structures became larger and the dispersion will be less uniform than for lower viscosity ratios. The formation of fibrillar structures is easier for viscosity ratios near unity [28,29]. Since, for these blends the viscosity ratio is lower



(b)

Fig. 4 (*continued*)

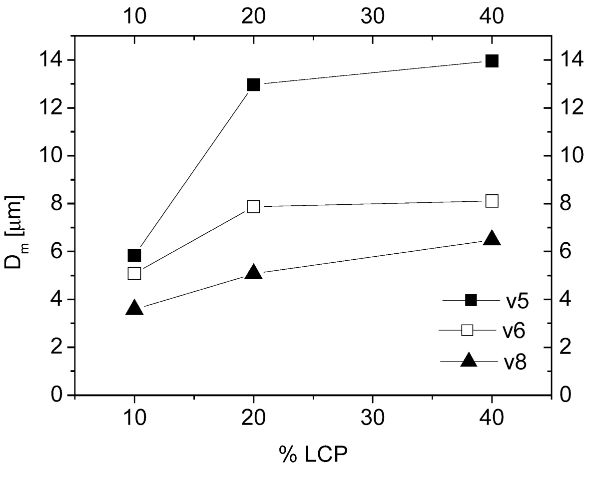


Fig. 5. Average droplet diameters for samples collected along the extruder of blends with 10, 20 and 40 wt% processed at 220 °C (lines are guides to the eyes).

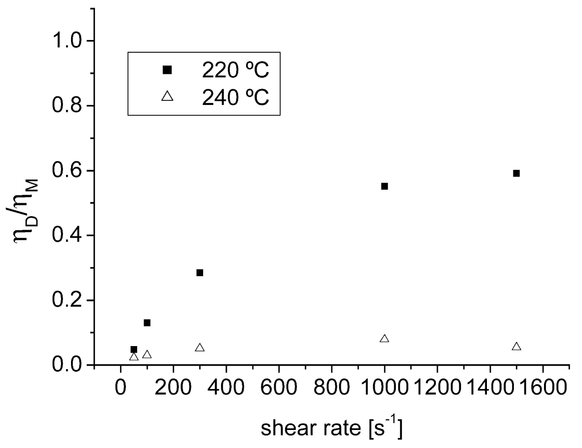


Fig. 6. Viscosity ratio between the disperse phase and the matrix (η_D/η_M) as a function of shear rate at 220 and 240 °C.

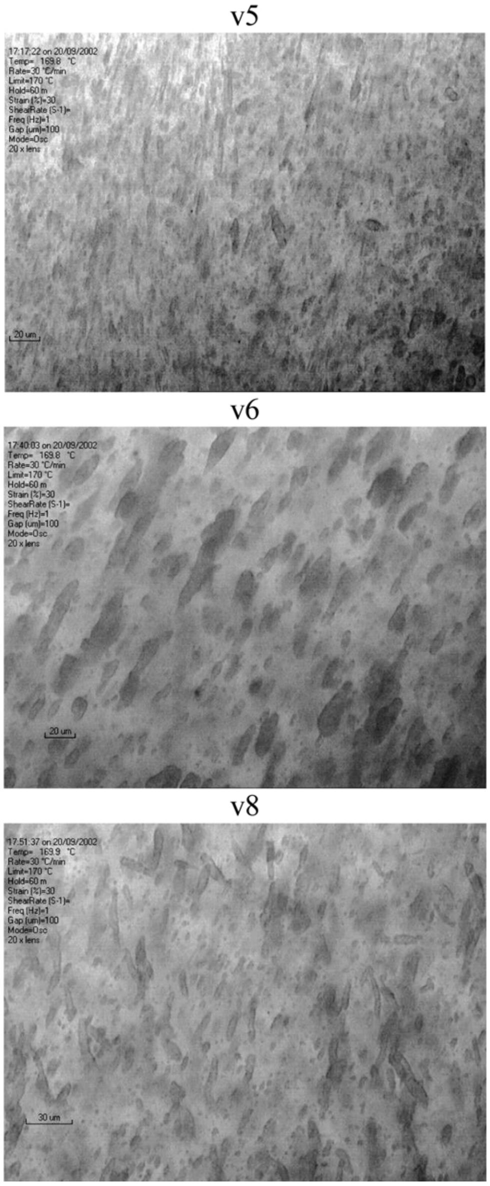


Fig. 7. Morphological evolution along the extruder length for the blend with 10 wt% LCP, at $T = 170$ °C (conducted using the Linkam optical shear system).

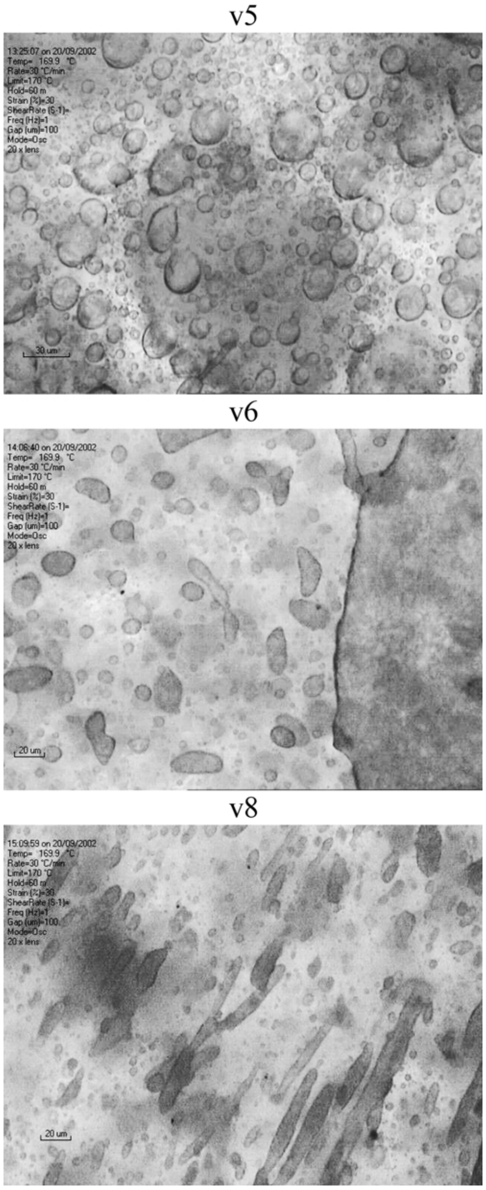


Fig. 8. Morphological evolution along the extruder length for the blend with 20 wt% LCP, at $T = 170$ °C (conducted using the Linkam optical shear system).

than 1, deformation of the LCP particles is to be anticipated provided that enough shear is applied in order to be possible to the viscous forces to overwhelm the interfacial forces. Since break-up processes are also possible for this viscosity ratio, it is expected that the blends with the higher LCP content will be those with the larger LCP structures, since the probability of coalescence will increase.

Since the shear rate increases from the beginning to the end of the extruder, an increase in the deformation of the LCP structures is expected along the extruder, with the consequent decrease in the mean diameter size. In principle, smaller average particle sizes, together with the fact that non-spherical particles yield higher apparent volume fractions than spherical particle, should yield an increase in interfacial area and a consequent increase in viscosity. However, in the case on non-compatibilised blends such as the ones studied in this work, lack of adhesion at the interface and the orientation of the disperse phase may become the dominant factor [30] and may actually decrease the viscosity.

In what regards elasticity in the case of non-compatibilised blends and due to the poor load transfer ability of the material through the interface, in principle the amount of energy stored by the material (G') should be higher for the samples with spherical structures and with lower aspect ratios, since this is the situation that minimizes interfacial area.

The evolution of both the storage and the loss modulus as a function of frequency was evaluated for the samples collected from valve 4 to valve 10 and for the final extrudates of the blends with 10, 20 and 40 wt% LCP content.

The analysis performed for the blend with 10 wt% LCP (Figs. 9 and 10) showed that, within experimental error, both the elastic modulus and the viscosity (η^*) remain approximately constant (or, at most, decrease slightly) as the material progresses along the extruder length. The storage modulus and the complex viscosity decrease, however, for the extrudates, which means that the differences are only noticeable when comparing the viscosity of samples with droplets and fibrils as the disperse phase.

The blend with 20 wt% LCP shows qualitatively similar results to the 10 wt% LCP one, i.e. there is a negligible (if at all) decrease in both the storage modulus (G') and the dynamic viscosity (η^*) along the extruder. However, once again, a decrease in both G' and η^* was observed for the final extrudates (Figs. 11 and 12).

For the blend with 40 wt% LCP, there are larger differences in viscosity along the extruder (see Figs. 13 and 14). This can be explained by the morphology present, namely by the combination of larger average particle size due to the increased LCP content and orientation.

3.3. Non-linear oscillatory rheology

Large amplitude oscillatory shear (LAOS) was applied to the different samples collected at different locations along the extruder in order to generate a non-linear response. A sinusoidal strain was applied for a given temperature and frequency and the resultant torque response was Fourier transformed. Doing so, a Fourier spectra was generated, consisting of several peaks, located at $3\omega_1$, $5\omega_1$, $7\omega_1$, etc. and also at the fundamental frequency ($\omega_1/2\pi$). Each one of these peaks is described by means of a amplitude (a_n) and a phase (ϕ_n), where n is the multiple of the fundamental frequency. The non-linear character was obtained from the relative intensity between the third harmonic ($3\omega_1/2\pi$) and the fundamental frequency ($\omega_1/2\pi$) and is represented by the normalized quantity $I(3\omega_1/2\pi)/I(\omega_1/2\pi) := I_{3/1}$; the higher this relative intensity, the more non-linear the response.

The evolution of the relative intensity of the third harmonic over the fundamental frequency with the applied strain amplitude was obtained for all the samples, from valve 4 to the final extrudate. As expected, this type of experiments proved to be very sensitive to the LCP content (clearly more so than linear oscillatory rheology), with large differences being observed for the evolution of the 20 and, especially, the 40 wt% LCP blends along the extruder. Comparing the evolution of the $I_{3/1}$ as a function of the applied strain amplitude (γ_0) for the samples collected at different locations along the extruder, shown in Figs. 15–17, significant differences were observed for intermediate and high strain amplitudes only ($\gamma_0 > 1.0$). In what regards the degree of non-linearity, it decreases markedly along the extruder, especially for the samples with higher LCP content. For example, when comparing samples collected at valve 4 and at the die it can be noticed that valve 4 displays higher non-linearity.

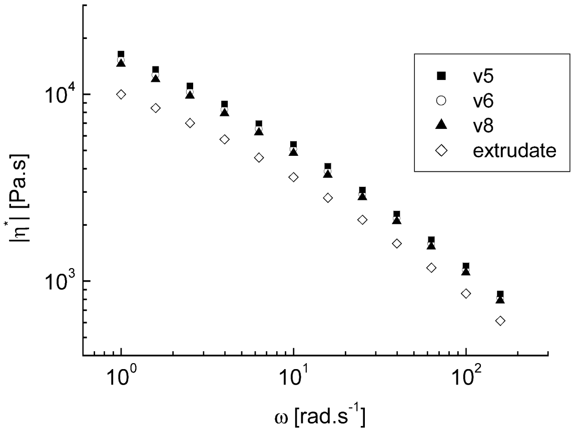


Fig. 10. Evolution of the complex viscosity along the extruder length for the blend with 10 wt% LCP, at $T = 170$ °C.

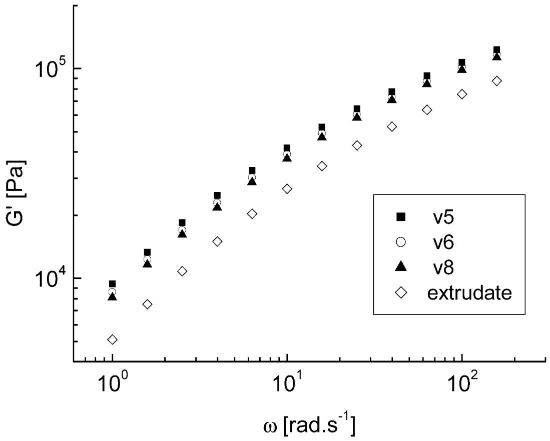


Fig. 9. Evolution of the storage modulus along the extruder length for the blend with 10 wt% LCP, at $T = 170$ °C.

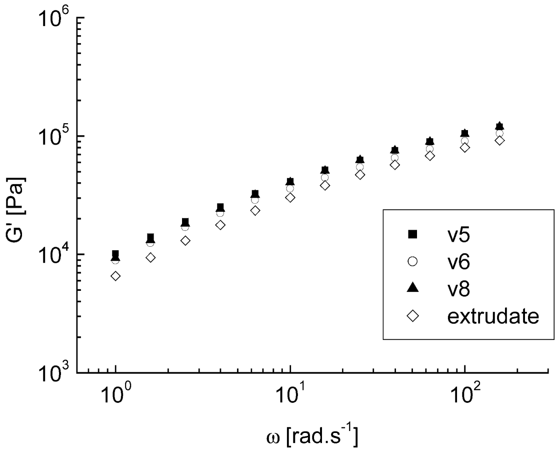


Fig. 11. Evolution of the storage modulus along the extruder length for the blend with 20 wt% LCP, at $T = 170$ °C.

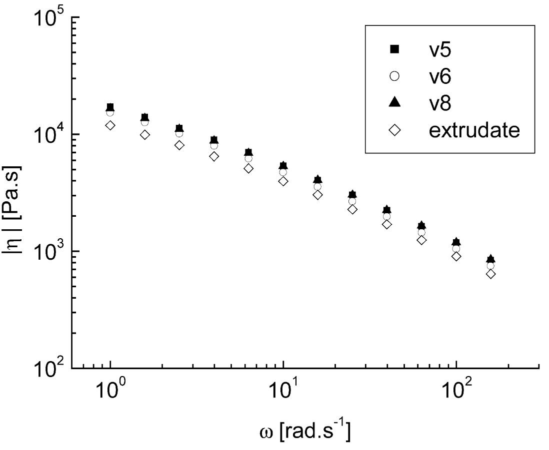


Fig. 12. Evolution of the dynamic viscosity along the extruder length for the blend with 20 wt% LCP, at $T = 170$ °C.

At this point of the compounding, the extruder configuration is constituted by a reverse-conveying element that is responsible for an increase in the residence time of the material. Since the time available for the contact between the LCP structures is increased in this region, an increased coalescence of the LCP structures is expected to be obtained, that would lead to an increase in the mean diameter size and to the appearance of LCP structures with spherical shapes, as could be observed in Fig. 2(a). Therefore, the compression moulded discs obtained from these samples possess LCP structures with higher mean diameters than those observed, for example, for those prepared from the final extrudates (see Fig. 7). According to the capillary number definition (Eq. (1)) the higher the radius of the LCP structures, the higher will be the capillary number. Therefore, the deformation will be easier for the samples collected at the beginning of the extruder, since these are the ones with the highest mean diameter. So, these were the samples for which one expects the highest degree of non-linearity. When the material crosses the region of the screw containing a set of kneading blocks, the deformation level is intermediate between that observed at the reverse-conveying elements and the one at the die. In this region, deformation of the LCP structures at the kneading blocks is higher than the observed at the conveying and reverse-conveying elements, leading to a decrease of the mean LCP dimensions. Therefore, the non-linearity for the samples collected at valve 8, for instance, is lower than that observed for the samples collected at valve 5. Nevertheless, the lowest non-linearity was obtained for the samples collected at the end of the extruder. This is the condition for which higher deformations were achieved and, as a consequence, the samples collected at this point possess a disperse phase, consisting of droplets with similar volume, but higher aspect ratio than that observed for the samples removed at the beginning and at the middle of the compounding process.

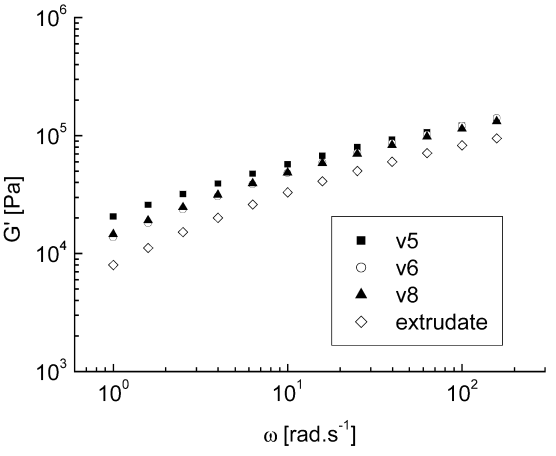


Fig. 13. Evolution of the storage modulus along the extruder length for the blend with 40 wt% LCP, at $T = 170$ °C.

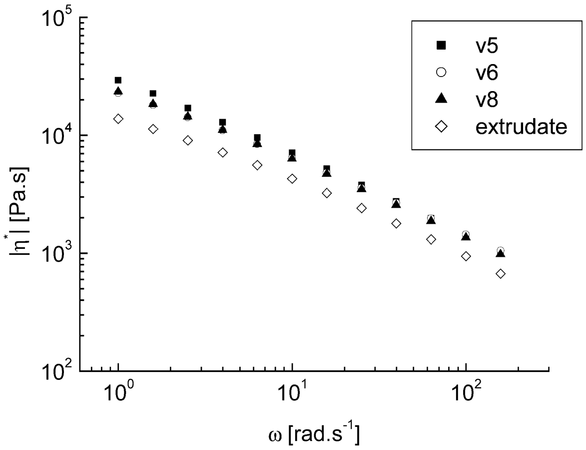


Fig. 14. Evolution of the dynamic viscosity along the extruder length for the blend with 40 wt% LCP, at $T = 170$ °C.

4. Conclusions

The morphological evolution of polymer blends upon

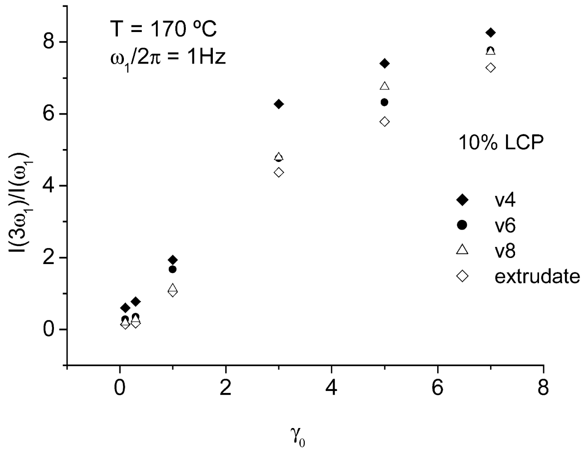


Fig. 15. Increase in $I(3\omega_1)/I(\omega_1)$ with the applied strain amplitude for the different samples collected along the extruder length (blend with 10 wt% LCP, at $T = 170$ °C).

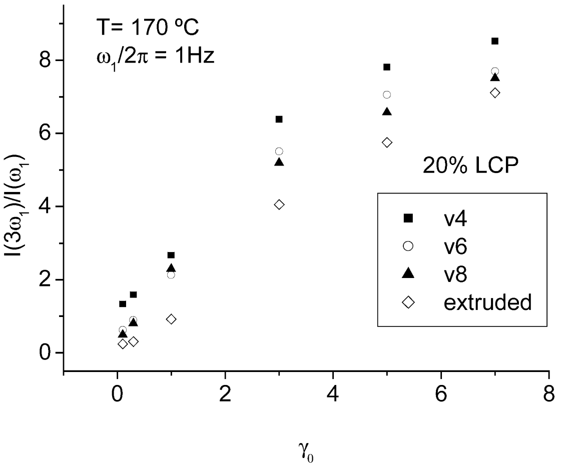


Fig. 16. Increase in $I(3\omega_1)/I(\omega_1)$ with the applied strain amplitude for the different samples collected along the extruder length (blend with 20 wt% LCP, at $T = 170$ °C).

processing depends largely on the processing conditions, namely the temperature, the shear rate, the screw speed, throughput, screw configuration and temperature profile.

The increase in the LCP content gives rise to extrudates with different morphologies, but the morphological evolution along the extruder length seems to occur similarly for all the different blends, always leading to an extrudate in which the disperse phase appears as fibrillar structures dispersed in the polypropylene matrix and oriented along the flow direction. During extrusion the LCP structures can be described as spherical shapes, elongated shapes or fibrillar structures depending on the extruder position and thus on the shear rate applied. A special home-built collecting device system was used that allowed the collection of samples at different locations along the extruder length [20]).

The rheological behavior in the linear regime of samples collected at different locations along the extruder was investigated. The linear viscoelastic differences along the extruder are clearly related to the different morphologies obtained, as studied by optical and electron microscopy. These results were confirmed through rheological measurements in both the linear and non-linear regimes. In the linear regime, the storage modulus and the complex viscosity decrease very slightly along the extruder, although it presents a significant decrease in the case of the extrudates. Furthermore, the mechanical non-linearity (for constant frequency and strain amplitudes) decreases from the beginning to the end of the extrusion process, which is again related to the morphological evolution observed. The rheological measurements performed in the linear and especially in the non-linear regime (Fourier transform rheology) are important tools to quantify the morphological evolution during compounding and are essential for a better understanding of the mixing processes and to predict and control the final properties of the blend as generated by an extruder.

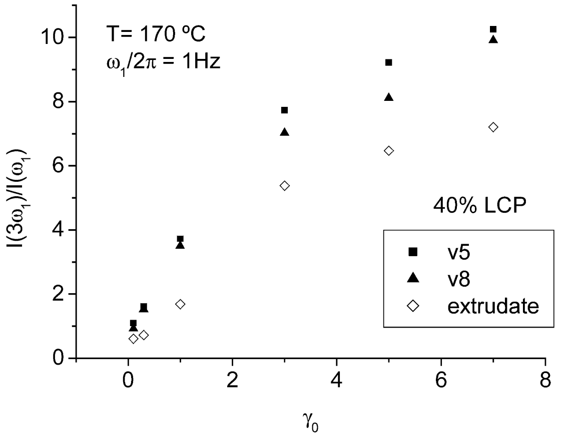


Fig. 17. Increase in $I(3\omega_1)/I(\omega_1)$ with the applied strain for the different samples collected along the extruder length (blend with 40 wt% LCP, at $T = 170$ °C).

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References

[1] Shi ZH, Utracki LA. Polym Engng Sci 1992;32:1824–33.
[2] Tyagi S, Ghosh AK. Polym Engng Sci 2002;42:1309–21.
[3] Potente H, Bastian M, Gehring A, Stephan M, Potschke PJ. Appl Polym Sci 2000;76:708–21.
[4] Potente H, Bastian M, Bergemann K, Senge M, Scheel G, Winkelmann Th. Polym Engng Sci 2001;41:222–31.
[5] Scott CE, Macosko CW. Polymer 1995;36:461–71.
[6] Lazkano JM, Peña JJ, Muñoz ME, Santamaría A. J Rheol 2002;46: 959–76.
[7] Postema AR, Fennis PJ. Polymer 1997;38:5557–64.
[8] Chan CK, Whitehouse C, Gao P, Chai CK. Polymer 1997;42: 7847–56.
[9] Kernick III WA, Wagner NJ. J Rheol 1999;43:521–49.
[10] Choi GD, Kim SH, Jo WH. Polym J 1996;28:527–34.
[11] Lee S, Man Hong S, Seo Y, Suk Park T, Sang Hwang S, Ung Kim K, Wook Lee J. Polymer 1994;35:519–31.
[12] Bordereau V, Shi ZH, Utracki LA, Sammut P, Carrega M. Polym Engng Sci 1992;32:1846–56.
[13] Shi ZH, Utracki LA. Polym Engng Sci 1992;32:1834–45.
[14] Huneault MA, Shi ZH, Utracki LA. Polym Engng Sci 1995;35: 115–27.
[15] Yoshikai K, Nakayama K, Kyotani MJ. Appl Polym Sci 1996;62: 1331–8.

[16] Datta A, Baird DG. Polymer 1995;36:505–14.
[17] Viswanathan R, Isayev AI. J Appl Polym Sci 1995;55:1117–29.
[18] Wano B, Samran J, Bualek-Limcharoen S. Rheol Acta 1998;37: 399–405.
[19] Boersma A, Van Turnhout J. Polymer 1999;40:5023–33.
[20] Machado AV, Covas JA, Van Duin M. J Appl Polym Sci 1999;71:135.
[21] Covas JA, Carneiro OS, Maia JM. Int J Polym Mater 2001;50(3–4): 445–67.
[22] Machado AV, Covas JA, Walet M, Van Duin M. J Appl Polym Sci 2001;80:1535–46.
[23] Van Duin M, Machado AV, Covas JA. Macromol Symp 2001;170: 29–39.
[24] Covas JA, Machado AV, Van Duin M. Adv Polym Technol 2000;19: 260–76.
[25] Wilhelm M, Maring D, Spiess HW. Rheol Acta 1998;37:399–405.
[26] Wilhelm M, Reinheimer P, Ortseifer M. Rheol Acta 1999;38: 349–56.
[27] Wilhelm M. Macromol Mater Engng 2002;287:83–105.
[28] Heino MT, Hietaoja PT, Vainio TP, Seppälä JV. J Appl Polym Sci 1994;51:259–70.
[29] Choi GD, Jo WH, Kim HG. J Appl Polym Sci 1996;59:443–52.
[30] Mustafa HU, Ishizuki M, Shige I, Suzuki H. Korea-Aust Rheol J 2003; 15:19–25.