

Rheological Conditions for the Development of Fibrils in Blends of Liquid Crystalline and Conventional Polymers

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ABSTRACT: In blends of liquid crystalline polymers (LCP) with conventional thermoplastics, the development of infinite, thin and highly oriented LCP-fibrils is very important for a substantial mechanical reinforcement of the blends. Such fibrils can be produced by processing a coarse mixture of LCP and polyethyleneterephthalate (PET) powders in an extrusion apparatus in which preferentially elongational, but only weak shear flows occur. The rheological conditions for the success of this process are explained.

INTRODUCTION

BLENDS OF THERMOTROPIC liquid crystalline (LCP) and conventional thermoplastic polymers have often been investigated; a short review has recently been published by the authors [1]. They have found novel applications in high precision parts, as for instance in telecommunications and data processing [2]. Added in low concentration, LCPs can lower the viscosity of a thermoplastic melt and, therefore, act as a processing agent [3,4]; in addition, the excellent mechanical properties of LCPs enable mechanical reinforcement of the thermoplastic matrix. In many cases, adhesion between the two components is low, but it can be improved by using compatibilizing agents [5,7] or by incorporating flexible segments into the stiff LCP-molecules [8,9], thus leading to a minor degree of compatibility.

Processing of the blends often leads to materials containing extended LCP-fibrils which are responsible for the reinforcement. These materials are usually referred to as "in-situ composites." They can be regarded as unidirectionally fiber reinforced; therefore, it should be possible to describe their mechanical properties by the well-known rule of mixtures:

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$$E_c = E_{LCP}V_{LCP} + E_mV_m$$

with E_c , E_{LCP} , and E_m being the elastic moduli of the composite, the LCP and the matrix, and V_{LCP} and V_m being the volume fractions, respectively. Obviously, high concentrations of LCP are required to achieve strong reinforcement.

However, at high LCP concentrations, only thick fibrils can be achieved in many cases which exhibit just a moderate overall degree of molecular orientation [10]. This phenomenon is probably due to the often-observed skin-core morphology with a high degree of molecular orientation only in the skin layer.

Therefore, it is valuable to develop a process by which fibrils with a very high degree of molecular orientation and exhibiting excellent mechanical properties can be produced at low concentrations of LCP. This might have a desirable side effect: Since LCPs are quite expensive, low concentrations will decrease the costs of the reinforced materials significantly.

CONVENTIONAL BLENDING

In many cases, LCP/thermoplastic blends are prepared in extruders, in which the minor component (LCP) gets more or less finely dispersed by strong shear flows. However, at very low LCP concentrations, when the effect of coagulation of the dispersed LCP droplets is nearly negligible (less than 5% of LCP, approx.), droplets with diameters of only a few microns are usually produced. It is obvious that such small droplets cannot be deformed into long fibrils, as they simply do not have the appropriate volume; in addition, interfacial tension makes any deformation of the droplets difficult. Thus, before discussing the extrusion process developed in this paper in more detail, we should point out that conventional extruders are unsuitable to produce in-situ composites with long fibrils at low concentrations of LCP. It has also been reported in the literature that gentle mixing techniques using lower shear rates, as, for instance, the application of static mixers with helical mixing elements, lead to better fibrillation [11].

The new extrusion process used in this work has been described elsewhere [12], but the principle will be explained here again very briefly.

MATERIALS

Polyethyleneterephthalate (PET, Tenite 7741, Eastman) was used as the thermoplastic matrix, and the selected LCP was Vectra B950, a wholly aromatic copolyesteramide [13] (Hoechst-Celanese).

EXTRUSION

Granules of both components were ground separately into more or less fine powders. In the mill, the LCP was disintegrated into fine fibers with a maximum length of 3 mm and some tens of micrometers in diameter. These powders were mixed with each other in the appropriate concentrations. The mixtures were processed in a small extrusion apparatus in which the melt is pressed by a piston

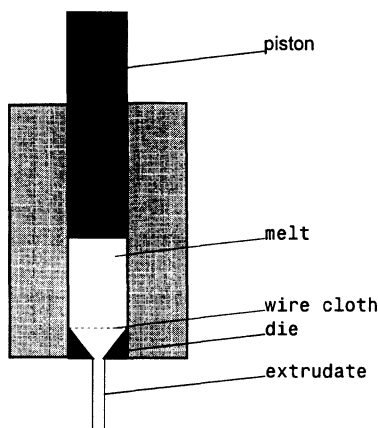


Figure 1. The apparatus used for extrusion. The mixture of LCP/PET powders is molten and then pressed by a piston through a conical die.

through a fine wire cloth (aperture width $63\ \mu\text{m}$), which mainly has a homogenizing effect, and then through a conical die (Figure 1). The force applied on the piston was kept constant. The extrusion temperature was fixed at 300°C .

MORPHOLOGY

Extrudates with concentrations of less than 5 wt.% of LCP contain fibrils with lengths in the range of several millimeters and diameters between two and four microns. Such an extrudate, molten in the hot stage at a temperature above the melting point of PET (252°C) and below the melting point of LCP (280°C), is shown in Figure 2. Extrudates with higher LCP concentrations (15 and 50 wt.% LCP) contain much thicker fibrils, which show lower birefringence (Figure 3). From this observation it was concluded that our extrusion procedure is indeed appropriate, especially for low concentrations of LCP. Variation of extrusion speed had little influence on the morphology. A detailed characterization of the blends is given in Reference [12], from which the main results should be mentioned again.

In spite of the high degree of molecular orientation in the fibrils and unusually high value for the interfacial shear strength of 100 MPa, as found via the fragmentation test, the mechanical reinforcement is still poor. However, this is due to the fact that the extrudates are still quite inhomogeneous: Bubbles are often found in the extrudates, since the extrusion apparatus offers no possibility for the air between the powder particles to escape from the melt.

DEVELOPMENT OF FIBRILS

The great advantage of using powders is obvious: the size of the LCP droplets in the melt is determined by the particle size of the LCP powder; there is no dependence on the LCP concentration. Compared with extruder-mixed blends, this dis-

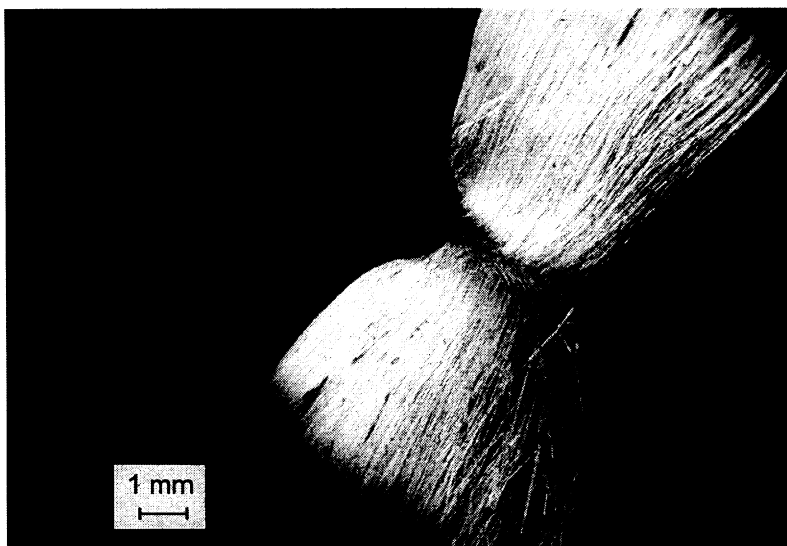


Figure 2. Light micrograph of an extrudate molten on a hot-stage. The infinite LCP fibrils show high birefringence between crossed polars; the PET melt is invisible. Here, the extrudate was stretched and the beginning of necking at the yield point is shown.

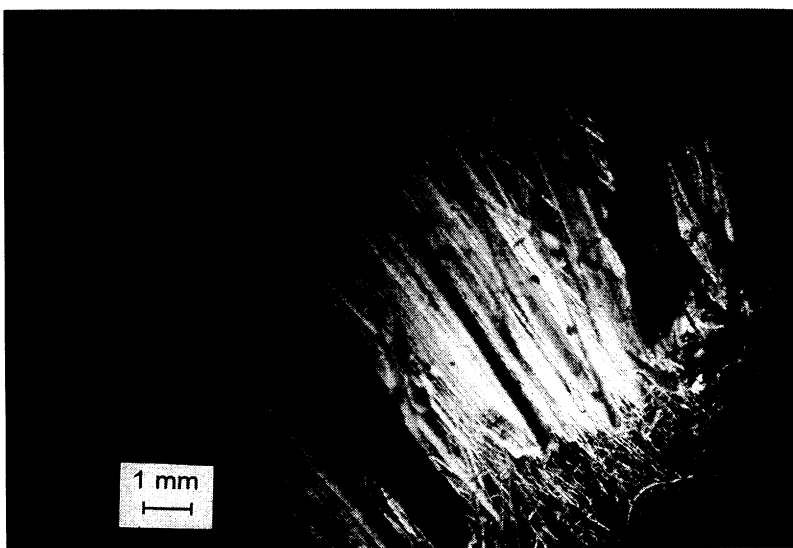


Figure 3. Light micrograph of an extrudate with 15 wt.% LCP. Compared with Figure 2, the birefringence is considerably lower.

person is coarser, and the LCP droplets have the appropriate volume to be deformed into the quasi-continuous fibrils described above. The question arises as to how the droplets are deformed into fibrils and how this process differs from the extrusion behavior of blends of two conventional thermoplastics.

To answer these questions, let us first consider the latter case—that both components are conventional thermoplastics, i.e., polymers with flexible chains, both being incompatible and the minor component being coarsely dispersed in a matrix of the other one. Two cases have to be distinguished: the viscosity of the matrix phase being lower than the viscosity of the dispersed phase and vice versa. In the first case, the droplet will hardly deform. In the second case, the droplet can be deformed into a fibril very easily. However, the molecular orientation of the dispersed polymer, if there is any, will be lost due to very rapid relaxation of the molecules, and the interfacial tension will disperse the fibril into a string of smaller droplets, which may be deformed again and again until an equilibrium between shear stress and interfacial tension is reached, as expressed by the capillary number Ca :

$$Ca = \tau R / \sigma = \eta \dot{\gamma} R / \sigma$$

with

τ = shear stress

R = radius of droplet

σ = interfacial tension

η = shear viscosity

$\dot{\gamma}$ = shear rate

From this we conclude that in the case of mixing two flexible polymers, to achieve optimal fibrillation the viscosities of the two components should be approximately equal.

Let us now consider the case that the dispersed component is an LCP: the typical structure of an LCP consists of so-called domains, inside of which the molecular orientation is largely homogeneous. Again, when the viscosity of the LCP is lower than the viscosity of the matrix, fibrillation occurs easily. We observed that these LCP fibrils are not dispersed into smaller droplets but remain stable in the melt for many hours at a temperature of 300°C, i.e., far above the melting point of the LCP, and there seems to be no decrease of their high birefringence. From the stability of these LCP fibrils, compared to fibrils of conventional thermoplastics, we conclude that for optimal fibrillation the viscosity of the LCP should indeed be lower than that of the matrix. This is in agreement with several investigations on the effect of LCP/matrix viscosity ratio on fibrillation reported in References [14,15]. Reasons for the stability of the LCP fibrils are explained as follows.

Compared with conventional thermoplastic polymers, LCPs exhibit very slow relaxation mechanisms [16]. Therefore, a molecular orientation developed in an extrusion process as described above might not have enough time to disappear before the extrudate solidifies outside the extrusion apparatus. However, relaxation

of an oriented LCP needs to be explained, since it is completely different from relaxation of flexible polymers. As mentioned above, the molecular orientation inside the so-called domains is rather homogeneous. The direction of orientation is usually referred to as the *director*. The borderlines between the domains are thin layers in which the director changes its direction. Here the liquid crystalline structure is distorted, which is an energetically unfavorable state. It would be interesting in this context to discuss the energy of distortion with respect to the interfacial tension between the components; however, there is no consistent theory to calculate the energy of distortion for polymeric liquid crystals, the theory of Leslie and Ericksen being valid only for low molecular weight LCPs [17,18].

Thus, if a high degree of molecular orientation is induced over a macroscopic distance—as, for instance, by an extrusion apparatus—the relaxation of an LCP means that remaining distortions are reduced, the borderlines between the domains vanish, and the liquid crystalline structure becomes more perfect. To summarize: the fibrillar state with high molecular order as well as orientation is the energetically most favorable state of an LCP. This is probably the most important difference between LCPs and conventional polymers consisting of flexible chains. Therefore, in the hypothetical case that the interfacial tension between both components disperses the LCP fibril into a string of small spherical droplets, the liquid crystalline structure would be distorted, and compared to a fibril consisting of a polymer with flexible chains, additional energy is needed to destroy the fibril, which is the reason for its high stability.

INFLUENCE OF TYPE OF FLOW AND VISCOSITY

Shear viscosities were measured using a capillary with $L/D = 10$. The temperature was the same as for extrusion, 300°C. No end corrections were used, since their validity for LCPs is doubtful. The results are presented in Figure 4. We observed that at low shear rates, the viscosity of the LCP is much higher than that of the PET matrix, which, in good agreement with the literature, exhibited an almost Newtonian behavior over the entire range of shear rates [19]. According to these data, no fibrillation should occur. This apparent contradiction convinced us that elongational rather than shear flows are responsible for fibrillation. Regarding the deformation of the LCP droplets into fibrils, it is obvious that elongational flow, as we find in our converging die, is much more effective than shear flow. Furthermore, it is well-known that shear flow of liquid crystals can lead to so-called *director tumbling*, unless the shear rate is very high. In this case, the director turns infinitely, and the LCP's overall molecular orientation is decreased [20], an effect that does not occur in elongational flows. From the observed high birefringence of the fibrils and the connected high degree of molecular orientation, we conclude that director tumbling plays no role in our extrusion process. Consequently, elongational flows and the ratio of the elongational viscosities of LCP and matrix play the decisive role for the observed fibrillation. Since the elongational viscosity of the LCP is in our case obviously lower, while the shear viscosity is higher than that of the PET matrix, we find that there is no direct connection between the two types of flow, as reported in Reference [14].

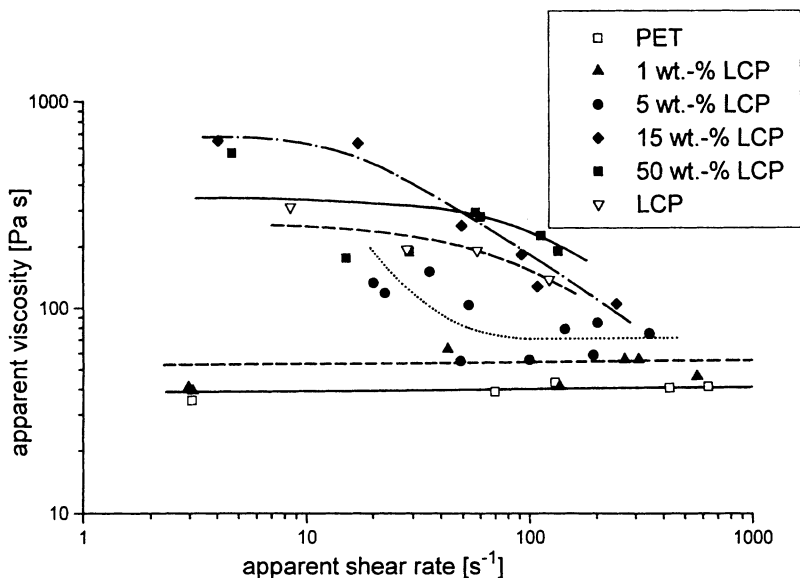


Figure 4. Results of shear-viscosimetric measurements, carried out using a capillary ($L/D = 10$) at 300°C. The viscosity of the pure LCP is higher than that of the blend, which should have made the formation of fibrils impossible (see text). Viscosities of the blends are determined by phase separation effects and show high experimental scatter (not described in the text).

SUMMARY

For optimal fibrillation of LCP in a thermoplastic matrix, the following conditions have to be fulfilled:

- The LCP has to be dispersed coarsely in the matrix. This can be achieved by using LCP powders of appropriate particle size. Dispersions produced in extruders or similar devices, in particular if the concentration of LCP is low, are in many cases too fine; the droplets do not have the appropriate volume to be deformed into fibrils.
- Elongational flow is needed for the formation of fibrils. Not only is it much more effective for the deformation of the LCP droplets but it also leads to higher degrees of molecular orientation of the LCP fibrils as compared with shear flow. Elongational flows can be achieved, for example, by using a conical die in an extruder.
- The elongational viscosity of the LCP has to be lower than the elongational viscosity of the matrix. It is not advisable to use shear viscosimetric data instead of elongational viscosimetric values. However, little experimental data for the elongational viscosities of LCPs can be found in the literature, and they often give inconsistent results [21].

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