Quasi-Continuous Fibrils in Blends of Liquid Crystalline and Thermoplastic Polymers at Low LCP Concentration

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ABSTRACT: A new technique for blending liquid crystalline polymers (LCPs) with thermoplastic polymers is described. With poly(ethylene terephthalate) as the matrix and Vectra B950 as the LCP, fibers containing quasi-continuous LCP-fibrils can be produced even when the LCP-concentration is very low (1 wt.-% LCP or less). Fragmentation tests show excellent bonding between the components. The elastic modulus of the LCP-containing fibers is significantly increased.

INTRODUCTION

MUCH RESEARCH WORK on liquid crystalline polymers has been done in recent years. Excellent mechanical properties, low melt viscosities, and the ability to form highly oriented fibers and films make LCPs an interesting engineering material. Blending them with conventional thermoplastic polymers can enhance the mechanical properties of the matrix significantly. A short review summarizing the recent literature about these blends is given in [1].

The formation of thin LCP-fibrils in the matrix leads to a strong reinforcement. Parameters important for this process are the viscosities of the two components (the viscosity of the LCP should be much lower than that of the matrix [2,3]), the interfacial tension, and the applied mixing technique [4].

Obviously, in many investigations materials and processing parameters do not fit together. For example, if the interfacial tension between the two components is very high, processing in an extruder may be unsuitable for this type of blend: Due to the high shear rates, very finely dispersed particles with an average size of just a few microns in diameter are produced that can not be deformed into long fibrils. Usually the elastic modulus of these blends is a little bit higher than that of the pure matrix, but the tensile strength may even be lower because the adhesion between the components is often poor. With increasing concentration of LCP in the blend, the probability of coalescence of particles rises and fibrillation

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becomes more probable. Therefore, long fibrils are often observed only above a critical concentration of approximately 20 wt.-%.

EXPERIMENTAL

The LCP used in this work was Vectra B950 (Hoechst Celanese), a fully aromatic copolyesteramide; the matrix was poly(ethylene-terephthalate) Tenite 7741 (Eastman). For fragmentation tests, extruded fibers were stretched and melted on a Mettler hot stage FP52 at a temperature of 265°C, which is between the melting points of the two components. Length and diameter of the fragments were measured using a Leitz Ortholux II polarizing microscope, which was also taken for morphological observations. Tensile tests were carried out on an Instron 1121 machine.

Processing

The components were separately ground in a mill with a rotating knife. PET was sieved to get a powder as homogeneous as possible. The LCP was disintegrated into fine fibers with a maximum length of 3 mm and some tens of micrometers in diameter. In the same mill the powders were mixed, with LCP-concentrations of 0.1, 1.0, 5.0 and 15.0 wt.-%, respectively.

These mixtures were molten at 300°C and pressed with a piston first through a fine wire cloth (aperture width 63 μm) and then through a V-shaped die. The extrusion apparatus is shown schematically in Figure 1.

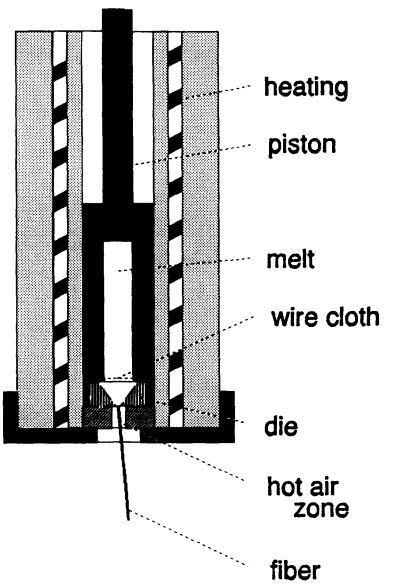

Figure 1. *Scheme of the extrusion apparatus.*

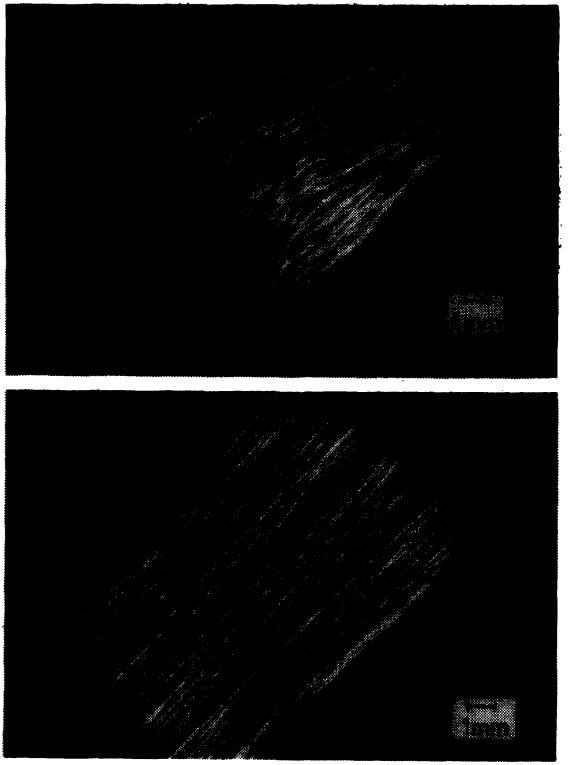

Figure 2. *Light micrographs of PET fibers with 0.1 (top) and 1.0 wt.-% (bottom) LCP content, respectively.*

Morphology

The light microscopic pictures show quasi-continuous LCP fibrils which are aligned almost perfectly (see Figure 2) for all concentrations examined. The morphology is influenced by the LCP concentration in the blend and by the cooling conditions following the extrusion: Spinning into air of ambient temperature results in the formation of thick and uneven LCP fibrils with diameters of approximately 10 μm. In the case that a metal ring produces a zone of hot air below the die, as shown in Figure 1, the fibrils become very thin, about 2.5 μm in diameter, if the concentration is 5.0 wt.-% or less. If the LCP concentration is as high as 15 wt.-%, relatively thick and branched fibrils together with thin fibrils are observed, which may be caused by coalescence of the LCP particles. These fibrils show lower birefringence between crossed polars.

Fragmentation Test

The fragmentation test is a well-known method method to calculate the inter-

facial shear stength between the fiber and the matrix in a composite material. A single fiber is imbedded in the matrix and stretched to the point where the fiber is broken into fragments of various lengths which are determined by the quality of adhesion. The interfacial shear strength can then be calculated following the Kelly-Tyson equation:

$$\tau = \frac{\sigma_F d_F}{2l_c}$$

τ interfacial shear strength
σ_F tensile strength of the fiber
d_F fiber diameter
l_c critical length

In the present case, instead of a single fiber a great number of fibrils is incorporated in each specimen. However, since their concentration is very low, it can be assumed that their mutual influence is negligible. Furthermore, the diameter varies from fibril to fibril. Therefore, the calculations have to be carried out for each diameter separately.

Drawn specimens from the tensile tests were melted on the hot stage and the microscopic pictures were transmitted to a video screen, where the dimensions of the fragments could easily be measured. Figure 3 shows an example for such a fragmented specimen.

The fragment lengths fulfill a Gaussian distribution in the case that the diameters are in the range between 2.5 and 3 μm. The distribution function for the fragments with a diameter around 2 μm is asymmetric, including a great number of very small or even spherical LCP particles. These spherical entities can also be observed in all probes before fragmentation and seem to be the smallest existing particles, the dimensions of which are determined by shear stress, interfacial tension, and the viscosity ratio between the two components when passing

Figure 3. *Fragmented fibrils in a PET-fiber with 0.1 wt.-% LCP.*

Table 1. Critical fragment lengths.

Diameter	Concentration		
	0.1 wt.-% LCP	1.0 wt.-% LCP	5.0 wt.-% LCP
2.5 μm	$n = 52$	$n = 71$	$n = 73$
	8.8 μm $< l_c <$ 12.0 μm	10.4 μm $< l_c <$ 13.2 μm	12.9 μm $< l_c <$ 16.3 μm
	4.9 μm $< \sigma <$ 7.2 μm	5.1 μm $< \sigma <$ 7.2 μm	6.2 μm $< \sigma <$ 8.6 μm
3.0 μm	$n = 42$	$n = 42$	$n = 40$
	11.9 μm $< l_c <$ 16.2 μm	12.2 μm $< l_c <$ 15.6 μm	17.8 μm $< l_c <$ 22.5 μm
	5.6 μm $< \sigma <$ 8.7 μm	5.8 μm $< \sigma <$ 9.1 μm	5.9 μm $< \sigma <$ 9.4 μm

through the meshes of the wire cloth. LCP particles with a diameter around 2 μm were therefore excluded from the following calculations.

For a Gaussian distribution, the parameters of average and standard deviation, μ and σ, respectively, are given by

$$\mu = \bar{x} \pm t\frac{s}{\sqrt{n}}$$

$$\sigma = s\sqrt{\frac{n-1}{\chi^2}}$$

$\bar{x}$ average
s standard deviation
n sample size
t, χ^2 values can be taken from any statistical textbook, here [5].

Based on a confidence level of 95%, the values for the critical fragment length, l_c, lie within the calculated limits listed in Table 1.

The corresponding values of the critical fragment length of the blends containing 0.1 wt.-% LCP and 1 wt.-% LCP, respectively, are nearly identical. This proves that the mutual influence of the fibrils is negligible, as expected. The results of these tests could be united, as was shown by means of a statistical t-test. The results are listed in Table 2. In the case of the blends with 5 wt.-% LCP, the fragments are significantly longer. The fibrils obviously influence and reinforce each other; i.e., one of the basic prerequisites for the fragmentation test is not fulfilled. The resulting values of the interfacial shear strength are also presented in Table 2. As expected, they are nearly identical for both diameters.

Tensile Test

Tensile tests were carried out with a gauge length of 12 mm and a speed of 10 mm/min. The fibers with LCP-concentrations of 0.1 and 1.0 wt.-% were too inho-

Table 2. Critical fragment lengths after unification of corresponding fragmentation tests and resulting interfacial shear strengths.

Diameter 2.5 μm
n = 123
10.3 μm < l_c < 12.0 μm
112 MPa > τ > 97 MPa
Diameter 3 μm
n = 84
12.4 μm < l_c < 15.0 μm
112 MPa > τ > 93 MPa

Table 3. Results of the tensile tests.

	PET	Blend with 5.0 wt.-% LCP		Vectra B950
σ_{yield} [MPa]	61 ± 7	54 ± 14	σ_{break} [MPa]	928 ± 262
ϵ_{yield} [%]	4.3 ± 2.2	3.3 ± 1.0	ϵ_{break} [%]	1.6 ± 0.6
E [GPa]	1.7 ± 0.2	2.1 ± 0.6	E [GPa]	68 ± 17

mogeneous to achieve reasonable results. Table 3 summarizes the values of elastic modulus, stress and strain at yield for PET and the blend with 5 wt.-% LCP as well as stress and elongation at break for pure Vectra (including standard deviations).

A strong increase of the elastic modulus of PET is obtained when blended with 5.0 wt.-% LCP; however, the value is lower than the rule of mixtures would predict. The yield stress and strain of the blend are even lower than that of pure PET.

CONCLUSIONS

The processing technique presented in this paper allows fibers to be produced from LCP/thermoplastic blends with quasi-continuous LCP-fibrils inside the matrix. The material that remained between the wire cloth and the die does not contain any fibrils, but finely dispersed particles, proving that the cloth is needed only to homogenize the material. Therefore, fibrillation has its origins inside or below the die. However, the rheological processes are not completely understood at the moment.

As shown by the fragmentation test, adhesion between the phases is very high. Possibly, there might be some chemical reaction at the interphase as observed by Magagnini et al. on Vectra B950/polycarbonate blends [6]. Some doubts exist as to whether the tensile strength of pure Vectra measured in the tensile test (see Table 3) can be used for calculation of the interfacial shear strength, since the degree of molecular orientation might be different from that in the blends. We will answer this question of orientation by x-ray experiments in the near future.

The elastic modulus is significantly enhanced by addition of only 5.0 wt.-% of LCP, but less so than would be expected according to the rule of mixtures. The yield stress and strain of the blend are a little bit lower than for pure PET, probably due to inhomogeneities of the fibers caused by the broad distribution of particle sizes in the powders used or to bubbles that were found in the fibers in some regions.

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