

The Effect of Mixing Shear Rate on the Properties of Liquid Crystalline Polymer/Polyethylene Terephthalate Blends

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Received 11 March 1999; accepted 31 August 1999

ABSTRACT: The effect of mixing speed of a batch mixer on the properties of liquid crystalline polymer/polyethylene terephthalate (LCP/PET) blends is investigated through two techniques: scanning electron micrographs to examine morphological changes, and tensile testing to determine the mechanical property dependence of the degree of mixing. The results of the two methodologies are well correlated, indicating that the increased degree of mixing of the blend, which is a function of the mixing speed, can be related directly to improved mechanical properties. The results are discussed in the light of existing theories on polymer mixing. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1783–1787, 2000

Key words: polymer blends; mixing speed; degree of mixing

INTRODUCTION

In recent years, interest has grown in an alternative pathway to new material systems that exploits the almost infinite variety of alloys, blends, and composites that can be formed from existing polymeric materials. In these systems, microstructure is as important as the molecular structure in determining the limits of performance. For all polymeric materials, microstructure is intimately tied to the material experience enroute to final fabrication. Proper understanding of the ultimate product properties demands a full and quantitative treatment of the relationship between material experience and machine environment during processing.

A liquid crystalline polymer (LCP) is capable of forming highly oriented crystalline structures

when subjected to shear and/or elongational flow above its melting point. The mechanical properties of LCP products are close to those of fiber-reinforced composites. However, due to high molecular orientation in the flow direction, their ultimate properties in the direction transverse to flow are usually lower. The addition of LCP to a second thermoplastic (TP) component may improve its processability¹ and reduce its cost—retaining however, to a large extent the exceptional material properties for which LCPs are known. The LCP/TP blends are referred to variously as *in situ* composites,^{1–3} self-reinforcing composites,⁴ or molecular composites.⁵ Recent blending technology has made it possible to prepare blends of LCP and thermoplastics to form *in situ* composites where the mechanical properties are enhanced,¹ well above those of the neat thermoplastics.

Polyethylene terephthalate (PET) is a very well-known engineering thermoplastic that is widely used in packaging and other applications. Its ad-

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Journal of Applied Polymer Science, Vol. 75, 1783–1787 (2000)
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vantages include low cost and ease of processing. However, it does not compete well with the best barrier materials, and its tensile properties fall short in certain applications. Recent research has shown that the properties of PET can be enhanced by a factor of two to five with the addition of 10–15% LCP.⁶

There are conflicting reports concerning the influence of mixing methods on the mechanical properties of self-reinforcing composites. According to Isayev and Modic,⁴ the method of mixing (whether by single screw extruder, or by twin screw extruder) significantly affects the mechanical properties of the blends. According to these authors, blends prepared with a static Koch mixer have superior mechanical properties over those obtained by mixing in an internal Banbury mixer. The rpm of the screw extruder was also reported to have a major influence on the morphology and mechanical properties of the extrudate.⁷ Kiss² and Baird et al.,¹ on the other hand, found no significant improvement in the tensile modulus or strength of the blend they studied, as a result of the blending technique.

The main goal of our present study is to investigate the effect of the mixing speed, on the degree of mixing and the ultimate mechanical properties of blends of LCP and PET, using a batch mixer. Various methods were used to assess the extent of mixing and its effect on the properties of the blends. These include scanning electron microscopy (SEM) to study mixing-dependent morphological development, and tensile test to correlate the mechanical property changes with the degree of mixing.

EXPERIMENTAL

Batch Mixing of LCP/PET Blends

An aromatic liquid crystalline polymer (Vectra A950 RX from Hoechst Celanese) was mixed with an injection molding grade PET (Shell Chemical) in a 300 cc Brabender batch mixer, with a rubber mixing blade. The amount of polymer added to the mixer for each mixing run was about 250 cc. The concentration of LCP for all blends was fixed at 15% by weight, with no addition of a compatibilizer. Mixing was conducted at 280°C over a time period of 3 min. The mixing temperature of 280°C was determined from preliminary tests, and was found to be the lowest possible temperature needed to ensure minimum degradation,

but high enough to melt the LCP. The components were thoroughly dried in a vacuum oven at around 60°C for 24 h before mixing. Five blends were prepared by varying mixing speeds from 30 to 90 rpm in 15 rpm increments.

The speed of the mixer was calibrated using a Mitutoyo digital tachometer before and during the mixing experiments to ensure accurate and reproducible mixing speeds from batch to batch. The prepared blends were dried and kept in separate sealed plastic bags for further analyses.

Specimen Preparation for Tensile Testing

Mechanical properties may be directly related to the microstructure developed from different extents of mixing of LCP in PET as referenced in the introduction of this paper. The extent of mechanical property change, resulting from the mixing operation, was investigated by conducting tensile tests on compression molded test specimens. A simple plaque mold was designed and constructed for compression molding. The mold was a two-piece combination, one piece is a metal sheet (3.18 by 14.65 by 0.5 cm) having a rectangular cut in the center with the dimensions of 1.27 by 10.16 by 0.01 cm; the other is a solid metal sheet cover. The compression molded samples were opaque indicating that PET has crystallized. The mechanical properties of the LCP/PET blends as well as the pure samples of PET and LCP were measured using an Instron universal tensile testing machine. Tensile modulus was measured from the initial slope of the stress–strain curve.

Viscosity Measurement

Viscosity information is useful in determining the processability of the PET/LCP blends. The apparent viscosity was measured using a Monsanto automatic capillary rheometer. Viscosities for the pure PET and three blends compounded at 30, 60, and 75 rpm, respectively, were measured at 260°C. The results are shown in Figure 1. All measurements were conducted in a shear rate range of 1000–5000 s⁻¹. The materials were dried in the same manner described earlier, before every viscosity measurement.

RESULTS AND DISCUSSION

As shown in Figure 1, the viscosities of the blends are significantly lower than those of the PET com-

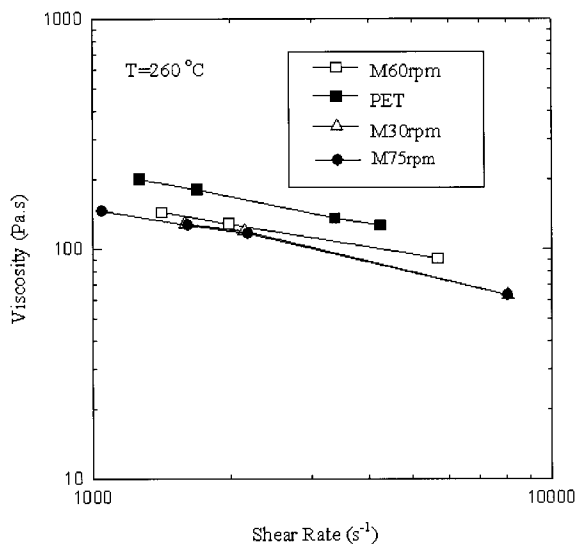


Figure 1 Log-log plot of viscosity versus shear rate for LCP/PET blends at 260°C, for different mixing speeds. For comparison, the results for pure PET are also plotted.

ponent. This is consistent with findings in the literature, indicating that along with the benefits mentioned earlier, inclusion of LCP also reduces melt viscosity, hence enhancing its processability.

The curves for 30 and 75 rpm blends fall together, indicating that mixing speed does not affect viscosity significantly. The curve for 60 rpm deviates slightly from those of 30 and 75, but it is still far below that of pure PET.

SEM Analysis

In theoretical studies,^{8,9} the term “uniform particle distribution” is generally accepted as an indication that a mixture is perfectly random. Prior to the start of the mixing process, the components are assumed to be completely separated and the particles of the individual components are indistinguishable from one another. As mixing progresses, these agglomerates are first ruptured, followed by separation of the fragments from each other, and finally the distribution of the ultimate particles throughout the melt. This is referred to in the literature as dispersive mixing,¹⁰ as opposed to distributive mixing,¹⁰ which does not involve the breaking up of particles. Several optical methods have been used to capture various stages of degree of mixing and miscibility of polymer blends,¹¹ including light scattering, high power optical microscopy,¹² and scanning electron

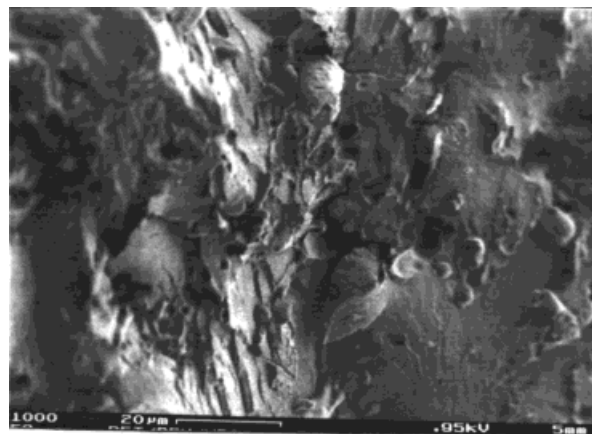


Figure 2 SEM photo of 15% LCP/PET blend mixed at 30 rpm in a Brabender batch mixer. The figure shows poor mixing of the LCP and PET components. The dispersed phase of LCP is seen as spherical particles in the photo.

microscopy. The scanning electron microscopy technique was used in the present studies to determine, qualitatively, the degree of mixing of the blends, and hence the effect of mixing speed on the degree of mixing through changes in morphology of the blend. Analyses were conducted for three different samples prepared at 30, 60, and 90 rpm, respectively. The SEM microphotographs are presented in Figures 2, 3, and 4, respectively.

Figure 2 shows rather large, nearly spherical particles of the minor LCP phase dispersed in the PET matrix. As we increase the mixing speed, we see further evidence of dispersive mixing, where the relatively large spherical particles seen in



Figure 3 Same as Figure 2 at a mixing speed of 60 rpm. In this photo, the sizes of the spherical particles seen in Figure 2 have decreased.

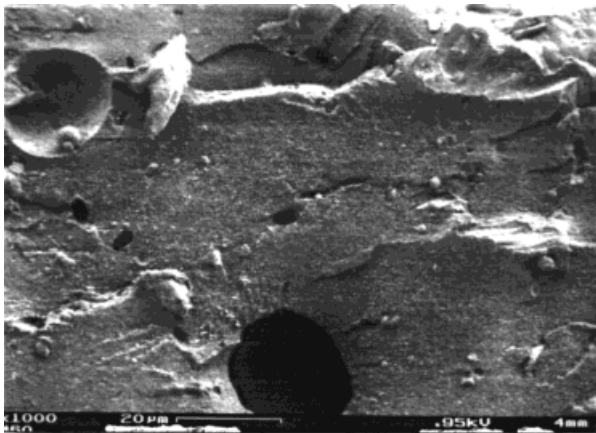


Figure 4 Same as Figure 2 at a mixing speed of 90 rpm. Note the improved mixing has resulted in a fine morphology. The spherical particles seen in Figure 2 are barely discernible.

Figure 2 are now broken into much smaller sizes (Fig. 3). As we increase the mixing speed from 60 to 90 rpm, we see that the dispersed particles have been further reduced to barely discernible sizes, which are uniformly distributed throughout the matrix (Fig. 4).

There have been some concerns expressed regarding transesterification reaction that might occur during the mixing process. According to the available literature, transesterification reaction could lead to enhanced compatibility between the polymer blends.^{13,14} The fact that the blends remain incompatible throughout the mixing speed ranges indicates that no transesterification reaction has taken place. Furthermore, according to Heino and Sepalla,¹³ transesterification reaction between Vectra A950 and PET can occur only in the presence of certain catalysts, such as Sb_2O_2 , stannous octoate, or zinc acetate.

Tensile Modulus Dependence of Mixing Speed

Figure 5 shows a plot of tensile modulus as a function of mixing speed. The figure also shows two data points corresponding to the pure PET and LCP. The pure LCP datum was taken from the design manual of Hoechst Celanese Corporation.¹⁵ This figure clearly shows that the modulus increases with the mixing speed. Furthermore, although we do not expect the intensive mixing to result in the formation of fibers from the LCP components, which could lead to optimal properties as one would from extrusion processes, nevertheless Figure 5 shows a gradual increase of the

tensile modulus, and toughness, with increasing mixing speed.

An alternative method of assessing the effect of the degree of mixing on the mechanical properties of the blend is by measuring the toughness of the blend. This result is also shown in Figure 5. Here, the toughness is the area under the tensile stress–strain curve, calculated at 4% strain. In a similar study but using the number of passes through a twin screw extruder as a measure of degree of mixing, Baird et al.¹ reported that the toughness of PEI/LCP (Ultem/LCP) blends increased with the number of passes. Figure 5 shows that increasing the degree of mixing of the blends also increases the toughness of the material, thus corroborating the results of Baird et al. The toughness for pure PET, molded under identical conditions as the blend, was about 2250 KJ/m^3 ; this datum is also shown in Figure 5.

CONCLUSIONS

This work shows that the degree of mixing of LCP/PET blend can be related directly to the mixing speed of the batch mixer. This effect was assessed through two methodologies: tensile testing to determine the mechanical property dependence of the degree of mixing, and SEM to examine morphological changes. The results from all

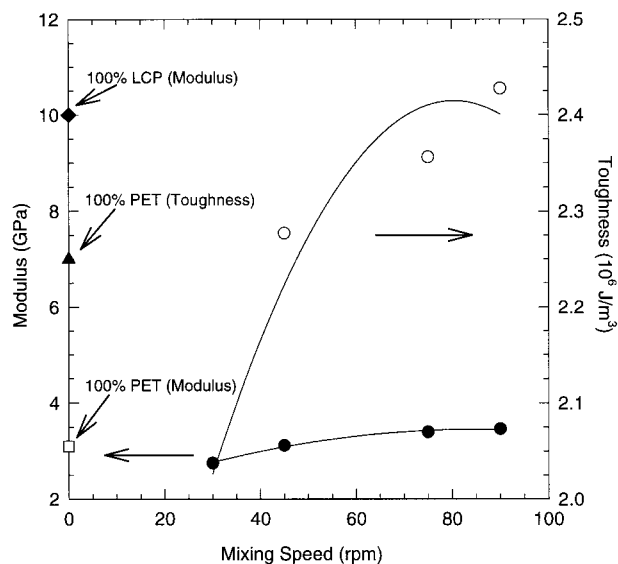


Figure 5 Figure 5 Tensile modulus and toughness versus mixing speed for 15% LCP/PET blends. (●) tensile modulus, (○) toughness (area under stress–strain curve), and (◆) tensile modulus for 100% LCP.

the techniques are well correlated, indicating that increasing the mixing speed increases the degree of mixing of the blends.

The SEM analyses were performed at Stevens Institute of Technology using a LEO 982 SEM machine. We are grateful to Stevens Institute of Technology for permission to use its SEM.

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