CONTINUOUS ULTRASONIC PROCESS FOR PREPARATION OF PET/LCP BLENDS

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CONTINUOUS ULTRASONIC PROCESS FOR PREPARATION OF PET/LCP BLENDS

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Abstract

Wholly aromatic polyester, LCP, was blended with PET to produce self-reinforced composites using an ultrasonically assisted single screw compounding extruder. Ultrasonic intensity was varied to induce in-situ compatibilization in the blends and was found to decrease pressure, and affect morphological, rheological and mechanical properties. PET and LCP homopolymerization, as well as their copolymerization through possible esterification/ transesterification reactions leading to an increase in their viscosities and mechanical properties was observed in the melt state under certain conditions.

Introduction

Liquid crystalline polymers (LCP) have excellent mechanical properties in addition to dimensional and chemical stability. These materials form in-situ composites during processing under elongational flow and are starting to replace traditional fiber reinforced systems [1, 2]. Combined with their ease of processing, LCPs are ideal for applications in aerospace, automobile, marine and other markets requiring high performance composites [2, 3].

The widespread use of LCPs is hindered by their high cost, promoting the study of their blends with conventional thermoplastic polymers. However, commercial LCPs are immiscible with many thermoplastic polymers. The challenge in the processing of thermoplastic/LCP blends is to increase the interfacial adhesion between the blend components while preserving the in-situ fiber formation. An optimum amount of compatibilization is necessary to fully utilize these blends [2, 4].

Various researchers have attempted to compatibilize blends of commercial LCPs with thermoplastics [2, 4-6]. Among the methods they used are the addition of blockcopolymers, catalysts, and acids into the blends as well as prolonged annealing. In the case of polyester/LCP blends, transesterification in the melt state after prolonged annealing creates copolymers with molecular affinity to both phases of the blends [2, 4].

High power ultrasound acting on the melt is known to cause degradation and molecular weight buildup, depending on amplitude and the polymer used [7]. The effect of ultrasound has also been studied in immiscible polymer blends. High power ultrasound was found to promote radical formation leading to copolymerization in rubber-rubber, rubber-plastic blends [7] and in PA6/PP blends [8]. A significant amount of homopolymerization of PA6 through polycondensation reactions was found in PA6/PP blends [8]. These reactions occur during melt processing in an extruder at very short residence times.

The study of the ultrasonic treatment of polyester/LCP blends is of particular interest as the continuous compatibilization of these blends is of great commercial value [9]. In this article, we study the effects of high power ultrasound on the rheology, morphology, and mechanical properties of pure PET, LCP and their blends.

Experimental

Materials

The materials used in this study were LCP (Vectra A950, Ticona) and PET (Eastapak PET 7352, Eastman Chemical Company). Both resins were in pellet form and were dried at 120^{o}C in a vacuum oven for 24 h before use.

Preparation of PET/LCP Blends

For the blending of PET and LCP, a new ultrasonic single screw extruder was designed as shown in Figure 1. The extruder (KL100, Killion) has a diameter of 25.4 mm and L/D ratio of 33:1. The barrel temperature was set at 260°C in the feeding section and 285°C in all other zones. Pressure was recorded at a point just prior to ultrasonic treatment. A screw speed of approximately 15 RPMs, yielding a mass flow rate of 1kg/hr under flood feeding was used. The resulting mean residence time in the ultrasonic treatment zone was 7 s. The extruder had three mixing sections, two before the ultrasonic treatment zone and one after. This allowed for increased homogeneity of the melt before and after sonication.

Two ultrasonic units operating at a frequency of 20 KHz and variable amplitudes (0-10 μm) were used. Water cooled horns transferred the ultrasound to the melt.

Impact bars (63.50 x 12.70 x 3.18 mm^3, ASTM D 256-05) and dumbbell shaped mini tensile bars (63.50 x 9.53 x 1.52 mm^3, ASTM D 638-03) were injection molded simultaneously using a Van Dorn 55 injection molding machine. The barrel temperature setup was the same as in extrusion; the mold was kept at room temperature. A clamping force of 55 tons and an injection speed of 150 mm/s were used in all cases.

A compression molding press (Carver 4122) was used to prepare discs for rheological testing. Discs of 2 mm thickness and 25 mm diameter were molded at 280°C for PET and all blends and 300°C for pure LCP, at a pressure of 23 MPa.

Rheological Measurement

An Advanced Rheometric Expansion System (ARES, TA Instruments) was used in oscillatory shear mode with parallel plate geometry. Strain amplitude was fixed at 2% and dynamic frequency sweep experiments with angular frequency (ω) from 0.1 to 100 s^{-1} were performed at 280°C. PET and all blends were tested under nitrogen atmosphere, while pure LCP, which was found not to degrade, was tested under air. The complex viscosity ($|\eta^*|$), dynamic storage (G') and loss (G'') moduli were obtained. All rheological measurements are an average of four runs.

Morphological Studies

Morphological studies of the blends were carried out on cryofractured injection molded mini tensile bars using a Hitachi S-2150 scanning electron microscope (SEM).

Mechanical tests

An Instron 5567 tensile tester was used to study the tensile properties of injection molded mini tensile bars following ASTM D 638-03. A 30 kN load cell was used for testing at 5 mm/min constant crosshead speed. Young's modulus was obtained using an extensometer with 7.62 mm gauge length. As the extensometer created a physical weakness in the samples, tensile tests to obtain strength and elongation at break were carried out without it. A minimum of 6 samples were used for each test.

Impact testing of the injection molded samples was carried out using an Izod impact tester (Testing Machines Inc.) with a 907 g load for the blends, and a 4536 g load for pure LCP. As the samples were too brittle with notching, unnotched specimens were used. ASTM D-256-05 procedure was followed except for notching. Pure PET did not break without notching. Therefore, its impact strength could not be compared with that of the blends. Accordingly, its value was not reported.

Results and Discussion

Processing and Rheology

Figure 2 shows the pressure before the ultrasonic treatment zone and the ultrasonic power consumption as a function of ultrasonic amplitude. Greater ultrasonic power consumption was achieved at an amplitude of 10 μm in 70/30 and 60/40, and at an amplitude of 7.5 μm in 80/20 PET/LCP blends, signifying increased effect of ultrasound.

The pressure continuously decreases with amplitude. This is caused by acoustic cavitation in melt, resulting in both permanent and thixotropic changes in viscosity. In addition to these effects, there is a possible slip of polymer melt along the solid surface, leading to a decrease in pressure [8]. However, the viscosities of pure PET as well as 90/10, 80/20 and 60/40 PET/LCP blends were found to be higher after treatment at an amplitude of 7.5 μm, indicating that the thixotropic and slip effects are dominating in extrusion. The increase of viscosity is evidently due to esterification of PET and copolymerization at the interface in the melt state.

Figure 3 shows the concentration dependence of viscosity at frequencies of 1 and 100 s^{-1}. PET viscosities at these frequencies are the same, indicating its Newtonian behavior. On the other hand, the LCP phase exhibits shear thinning behavior. This explains why the viscosity of the blends is lower at $\omega = 100$ s^{-1} for high LCP concentrations [2, 10]. It is seen that the viscosity of the 90/10 and 80/20 PET/LCP blends is less than that of the pure components. This is due to LCP acting as a flow modifier [2, 11]. Orientation of the LCP phase in the flow direction reduces melt viscosity, as observed in both capillary and rotational rheometry experiments by Gotsis and Baird [10].

Figure 4 shows the effect of ultrasonic treatment on the storage modulus versus loss modulus of PET/LCP blends at an amplitude of 7.5 μm. It is seen that the elasticity of the blends increases with LCP concentration. Moreover, ultrasonic treatment of 90/10, 80/20 and 70/30 PET/LCP blends at an amplitude of 7.5 μm increases G' with respect to G´´, causing a further increase in elasticity.

Mechanical Properties

Figures 5 and 6 show the Young's modulus and tensile strength of PET/LCP blends treated at different ultrasonic amplitudes. In general, the blends become stronger but more brittle with the addition of LCP. Improvements in the tensile strength of 80/20 PET/LCP blends and Young's moduli of both 80/20 and 70/30 PET/LCP blends were recorded at an amplitude of 7.5 μm. Figure 7 shows the tensile toughness and impact strength of PET/LCP blends treated at different ultrasonic amplitudes. Toughness of the

90/10 PET/LCP blends increased substantially at 10 μm. These improvements in the tensile properties of the ultrasonically treated blends are partially due to homopolymerization of the pure PET, as evident from rheological data. The improvements in mechanical properties could also be related to transesterification reactions as a result of ultrasonic treatment, leading to improved adhesion between PET and LCP.

Figure 8 shows the effect of ultrasonic treatment on the Young's modulus, tensile and impact strengths of neat LCP. All these mechanical properties are found to improve with ultrasonic treatment at certain amplitudes.

Tensile strength of 283 MPa was achieved for LCP treated at an amplitude of 7.5 μm. This is a significant improvement over a tensile strength of 244 MPa for as-received sample, and 262 MPa for sample extruded without ultrasonic treatment. The higher tensile strength reported above for as-received sample in comparison with value provided by manufacturer is due to greater skin region in injection molded mini tensile bars. [12]

Impact strength of pure LCP was 346 kJ/m^2 after ultrasonic treatment at an amplitude of 7.5 μm. The impact strength of as-received sample was 244 kJ/m^2, while that of sample extruded without ultrasonic treatment was 261 kJ/m^2. The improvements in the tensile and impact strengths of LCP indicate a possibility of homo-polymerization under the effect of ultrasound. Other researchers identified solid state polymerization as the cause of increased tenacity of LCP fibers after prolonged heat treatment [2, 3, 13]. As opposed to heat treatment, the ultrasonically induced homo-polymerization reactions in LCP take place in the melt state at very short residence times as also shown for other polymers [7, 8].

Morphology

SEM micrographs of moldings of PET/LCP blends revealed spherical droplets in the core, and highly elongated fibers of various diameters in the skin region. The skin region formed a substantial portion of the injection molded mini tensile bars as a result of their small cross sectional area.

Figure 9 shows the SEM micrographs of the skin and core regions of 90/10 PET/LCP blends before and after ultrasonic treatment. Without ultrasonic treatment, the surface of LCP droplets in the core region is smooth, showing little interaction with PET. On the other hand, 90/10 PET/LCP blend treated at an amplitude of 7.5 μm showed hairy structures on the surface of LCP droplets in the core region, indicating an improved adhesion between the PET and LCP phases. However, it should be noted that the hairy structures were also seen in the ultrasonically treated and untreated 80/20 PET/LCP blends. At higher LCP concentrations, hairy structure could not be observed due to smaller LCP droplet size in the core region and the presence of fibrillar structures in both the core and skin regions. Furthermore, phase domains could not be clearly identified in blends treated at an amplitude of 10 μm.

Conclusions

The ultrasonic treatment of PET/LCP blends leads to improvements in the mechanical properties of the homo-polymers and some blends. The increase in the viscosity and mechanical properties of neat PET and LCP, as well as some of their blends at certain amplitudes, points toward homo- and copolymerization. The increase in viscosity of PET after ultrasonic treatment is attributed to possible esterification reaction. The presence of hairy structures on the surface of LCP droplets in the core region of 90/10 PET/LCP blends after ultrasonic treatment at an amplitude of 7.5 μm illustrates the improved adhesion between the PET and LCP phases, and possible copolymer formation under the action of ultrasound. Low residence times in the ultrasonic zone and energy saving due to reduced pressure render ultrasonic extrusion a viable method for the compatibilization of thermoplastic polymer/thermotropic LCP blends. Further refinement of processing conditions could allow one to achieve greater enhancements in the performance of LCP, and its blends with PET.

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Keywords

Ultrasound, LCP, PET, blend, compatibilization.

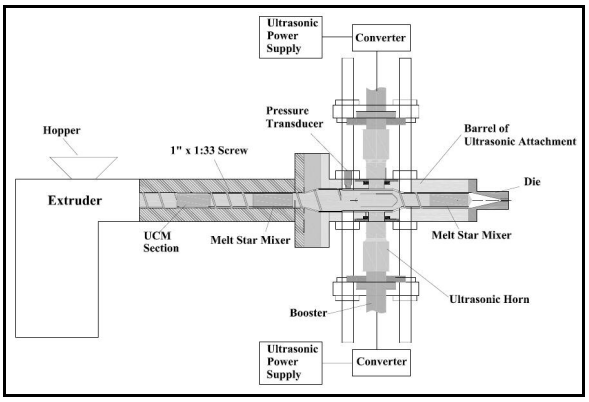


Figure 1. The ultrasonic extruder

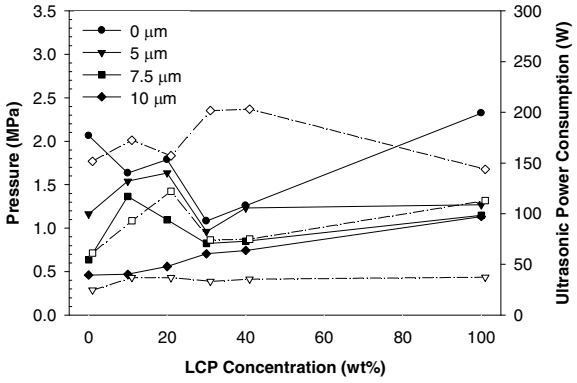


Figure 2. Pressure before ultrasonic treatment zone (filled symbols) and ultrasonic power consumption (open symbols) versus LCP concentration at different ultrasonic amplitudes. Values of ultrasonic power consumption at same concentration shifted along abscissa for clarity.

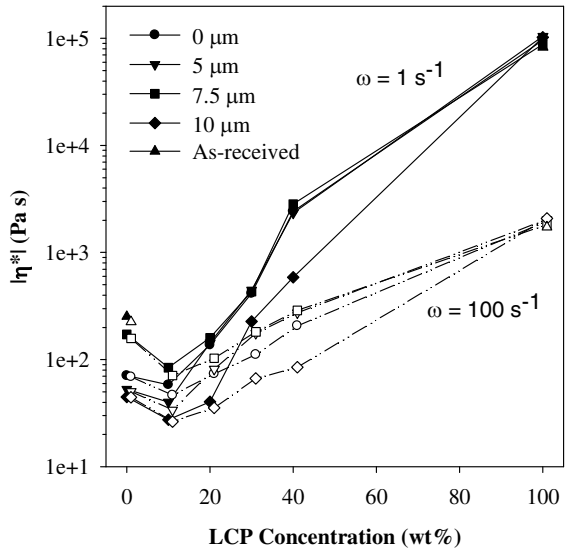


Figure 3. Complex viscosity versus LCP concentration at frequencies of 1 s^{-1} (filled symbols) and 100 s^{-1} (open symbols) for PET/LCP blends treated at different ultrasound amplitudes. Viscosity values at ω = 100 s^{-1} at same concentration shifted along abscissa for clarity.

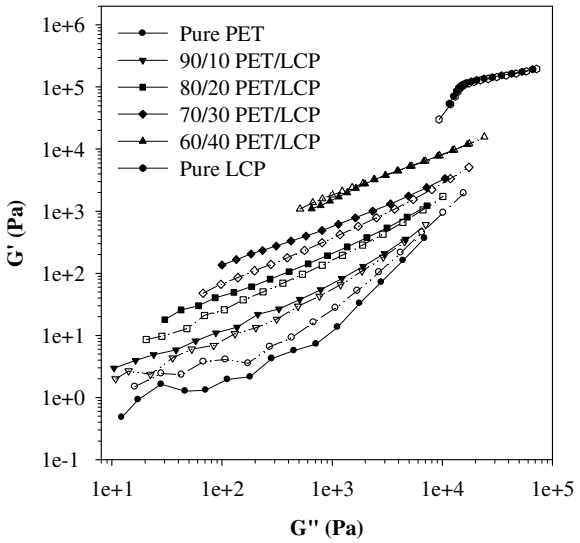


Figure 4. G' versus G" for PET/LCP blends without (open symbols) and with ultrasonic treatment at an amplitude of 7.5 μm (filled symbols).

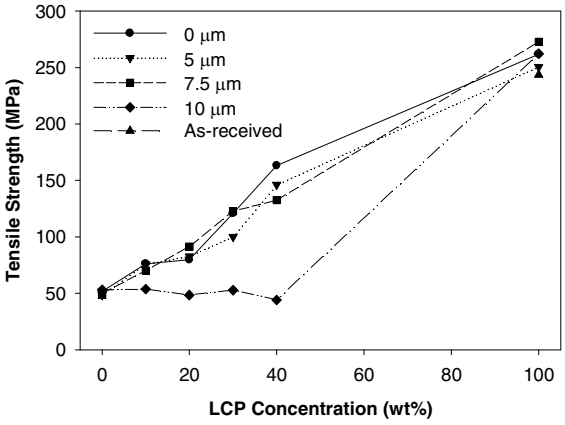


Figure 5. Tensile strength versus LCP concentration of PET/LCP blends treated at different ultrasonic amplitudes.

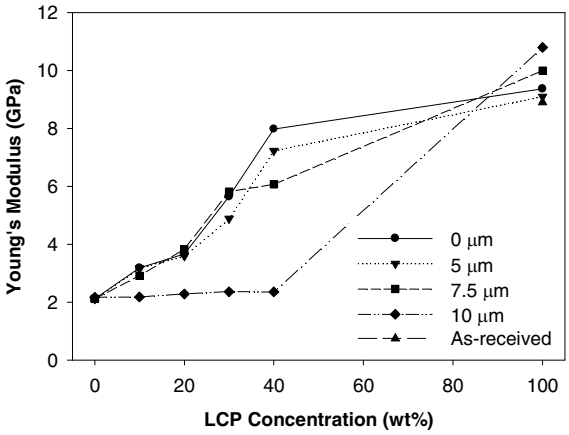


Figure 6. Young's modulus versus LCP concentration of PET/LCP blends treated at different ultrasonic amplitudes.

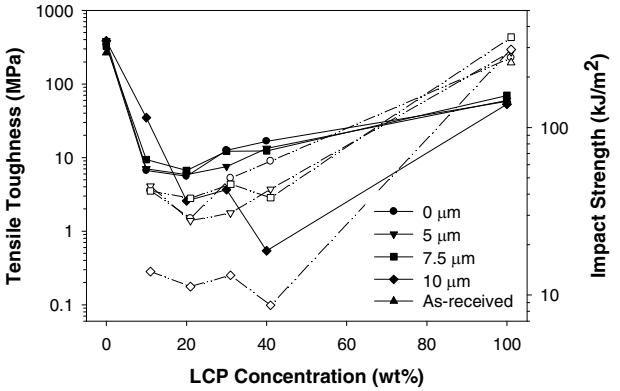


Figure 7. Tensile toughness (filled symbols) and impact strength (open symbols) versus LCP concentration of PET/LCP blends treated at different ultrasonic amplitudes. Impact strength values at same concentration shifted along abscissa for clarity.

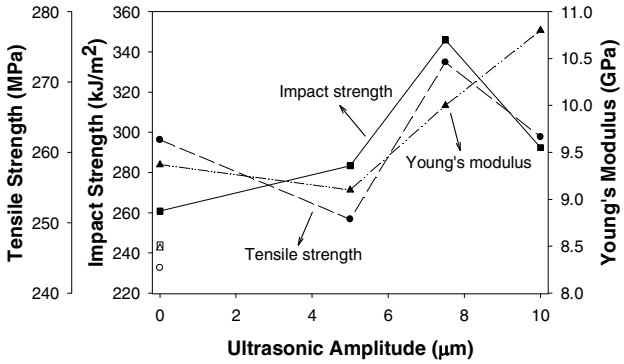


Figure 8. Tensile and impact strengths, and Young's modulus of LCP versus ultrasonic amplitude for extruded (filled symbols), and as-received (open symbols) samples.

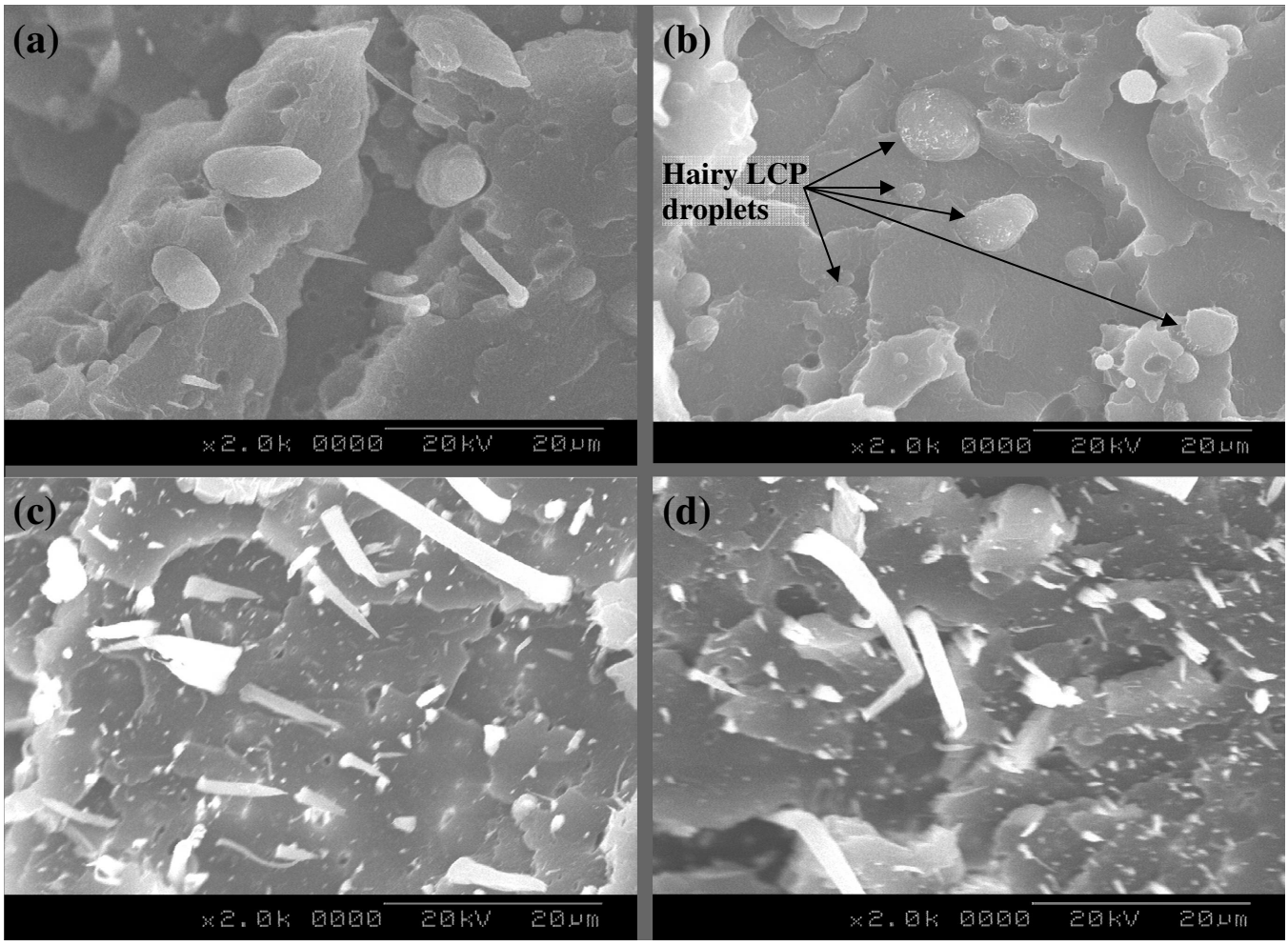


Figure 9. SEM micrographs of 90/10 PET/LCP blends. (a) untreated core region, (b) core region treated at an ultrasonic amplitude of 7.5 μm, (c) untreated skin region, (d) skin region treated at an ultrasonic amplitude of 7.5 μm.