

In Situ Compatibilization of PEN/LCP Blends by Ultrasonic Extrusion

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ABSTRACT: *In situ* compatibilization of immiscible blends of PEN and thermotropic LCP was achieved by the ultrasonically-aided extrusion process. Ultrasonically-treated PEN underwent degradation, leading to a decrease of its viscosity. Viscosity of LCP was unaffected by ultrasonic treatment. Because of reduced viscosity ratio of PEN to LCP at high amplitude of ultrasonic treatment, larger LCP domains were observed in molding of the blends. LCP acted as a nucleating agent, promoting higher crystallinity in PEN/LCP blends. Ultrasonically-induced copolymer formation was detected by MALDI-TOF mass

spectrometry in the blends. Ultrasonic treatment of 90/10 PEN/LCP blends improved interfacial adhesion in fibers spun at intermediate draw down ratios (DDR), improving their ductility. The lack of improvement in the mechanical properties of fibers spun at high DDR after ultrasonic treatment was attributed to the disturbance of interfacial copolymer by high elongation stresses.

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INTRODUCTION

Blending of wholly aromatic liquid crystalline polymers (LCP) with thermoplastics produces *in situ* reinforced composites with superior properties and could yield an economical advantage over neat LCP. However, such blends are commonly immiscible and thus brittle. To achieve mechanically superior blends, fine LCP fibrillation and good interfacial adhesion are required. Factors affecting the *in situ* formation of reinforcing LCP fibrils, as reviewed in Ref. ¹ include volume fractions and viscosity ratio of the components, as well as processing conditions.

Compatibilization of LCP/thermoplastic blends has been achieved by the addition of block-*co*-polymers,² insertion of flexible groups on LCP main chain,³ addition of catalysts or prolonged annealing,⁴ and addition of acid.⁵ Polyester/LCP blends can undergo transesterification reactions in the melt state through annealing and mixing for long times, resulting in generation of copolymers that improves their miscibility.⁴ Recently, the effect of the ultrasonic extrusion on the rheology, mechanical properties, and morphology of PET/LCP blends was studied.⁶ It was found that ultrasonication in the melt caused

homopolymerization of the PET phase at an ultrasonic amplitude of 7.5 μm . Improvements in the mechanical properties of the LCP and some blends were also observed with ultrasonic treatment of certain amplitudes. The observed improvements were attributed to enhanced LCP fibrillation and improved interfacial adhesion in the blends with ultrasonic treatment.

Ultrasonication in the melt leads to polymer chain scission and recombination with the dominating effect depending on chemical structure and ultrasonic amplitude.⁷ High power ultrasound was found to promote reactions at short residence times leading to copolymerization in rubber–rubber and rubber–plastic blends,⁸ as well as PA6/PP⁹ and PET/PEN blends.¹⁰ At the same time, homopolymerizations of PA6 and PET were, respectively, observed in PA6/PP⁹ and PET/PEN blends.¹⁰ The present article studies the effects of ultrasonic treatment during extrusion of PEN/LCP blends. It is aimed to explore the possibility of development of a rapid process for transesterification of this blend. Rheological, thermal, mechanical, and morphological properties, as well as the chemical structure of components and blends are investigated to determine the nature of transformations occurring during ultrasonically aided extrusion.

MATERIALS

The liquid crystalline polymer (LCP) was a wholly aromatic copolyester (Vectra A950, Ticona) containing 73% hydroxybenzoic acid and 27% hydroxy

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naphthoic acid. Polyethylene naphthalate (VFR 40046, Shell Chemical Company, I.V. of 0.64 dL g^{-1}) was chosen as the matrix in the blends. Both resins were acquired in pellet form.

Preparation of PEN/LCP blends

Resins were dried at 120°C in a vacuum oven for 24 h prior to use. The pure LCP was prepared in the ultrasonic single screw extruder as previously described.¹¹ The mixing section after the ultrasonic treatment zone of the extruder¹¹ was replaced with screw flights to reduce thermomechanical degradation during extrusion in the current study.

The barrel temperature was set at 260°C in the feeding zone and 300°C in all other zones. Pressure, temperature, and ultrasonic power consumption were recorded by a data acquisition system (Dataq Instruments, DI-715-U). The ultrasonic amplitude was varied in the range of 0–10 μm . To prevent overheating of the ultrasonic system, each horn was cooled with tap water at a flow rate of $0.3 \text{ cm}^3 \text{ min}^{-1}$. Streamlined reliefs on the inner surface of the barrel guided the polymer melt to flow only through two channels having a thickness of 2.54 mm between the ultrasonic horns and the screw shaft.

Under flood feeding conditions at a screw speed of 10 rpm, a mass flow rate of 1 kg h^{-1} was obtained for PEN and the blends. The screw speed used to obtain the same flow rate for pure LCP was 15 rpm. The exiting melt was run into a water bath at room temperature, dried, and then chopped into particles in a grinder (Weima, WSL180/180).

Impact bars ($127 \times 12.7 \times 3.2 \text{ mm}^3$) and dumbbell-shaped mini-tensile bars ($63.5 \times 9.5 \times 1.5 \text{ mm}^3$, ASTM D 638-03) were injection-molded simultaneously using a Van Dorn 55 HP-2.8F injection molding machine. The barrel temperature was set at 285°C in all zones except the feeding zone, which was set at 260°C . The mold temperature was 27°C . Other injection molding parameters were: a clamping force of 55 tons, an injection speed of 15 cm s^{-1} , a holding pressure of 4 MPa that was applied for 5 s, and a cooling time of 25 s.

Fibers were spun upon extrusion from a capillary rheometer (Rosand RH7, Malvern Instruments) at a barrel temperature of 300°C . A capillary die having a length of 24 mm and a diameter of 1.5 mm was used. Plunger speed was constant at 10 mm min^{-1} . The distance from the exit of the capillary die to the motor shaft, on which a take up bobbin having a diameter of 287 mm was mounted, was set at 36 cm. The take up device (Model 12A5BEP, B and B Motor and Control Corp, NY) consisting of 1 : 20 geared motor (130V DC, 186 W, 1.8 Amp) had electronically controlled variable speed (0–125 rpm), and

produced a torque of 8.5 Nm. Fibers were collected without any take up, and at draw down ratios (DDR) of 45, 76.5, and 112.5.

Rheological measurement

A capillary rheometer (Rosand RH7, Malvern Instruments) with a capillary of length, L , to a diameter, d , ratio $L/d = 24$ and a diameter of $d = 1 \text{ mm}$ was used for viscosity measurements at 300°C . The apparent viscosity and apparent shear rate was obtained. Viscosity had a standard deviation of 10%.

Differential scanning calorimetry

A differential scanning calorimeter (DSC-29210, TA instruments, New Castle, DE) was used to determine the thermal behavior of materials at a heating rate of 10°C from room temperature to 300°C under N_2 atmosphere at a N_2 gas flow rate of 50 mL min^{-1} . A sample of 5–8 mg crimped in aluminum hermetic pan was used. Results of the second heating run were reported to erase thermal history experienced in processing. The crystallinity (X_c) was determined by subtracting the enthalpy of cold crystallization (ΔH_{cc}) from the enthalpy of fusion (ΔH_f) of PEN, dividing that by the enthalpy of fusion of the perfect crystal (103.4 J g^{-1} for PEN¹²), and normalizing the result with respect to PEN content in the blend.

Dynamic mechanical analysis

Dynamic mechanical analysis (Pyris Diamond DMA, Perkin-Elmer-Seiko Instruments) was performed at a frequency of 1 Hz in the tensile mode at a heating rate of 2°C min^{-1} under nitrogen atmosphere. Samples cut from mini-injection molded tensile bars were tested by heating from room temperature to 140°C with an accuracy of 1°C .

Mass spectroscopy

Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectroscopy was performed to identify chemical changes occurring with ultrasonic treatment. MALDI-TOF measurements were carried out on a Bruker Ultraflex III TOF/TOF (Bruker Daltonics, Billerica, MA), equipped with a Nd:YAG laser emitting at a wavelength of 355 nm. All spectra were measured in the positive reflector mode. The instrument was calibrated prior to each measurement with an external standard PMMA. Polymer solution of 10 mg mL^{-1} ratio in pentafluorophenol was prepared. To dissolve the LCP, the solutions were heated to 80°C and sonicated for 6 h in an ultrasonic bath

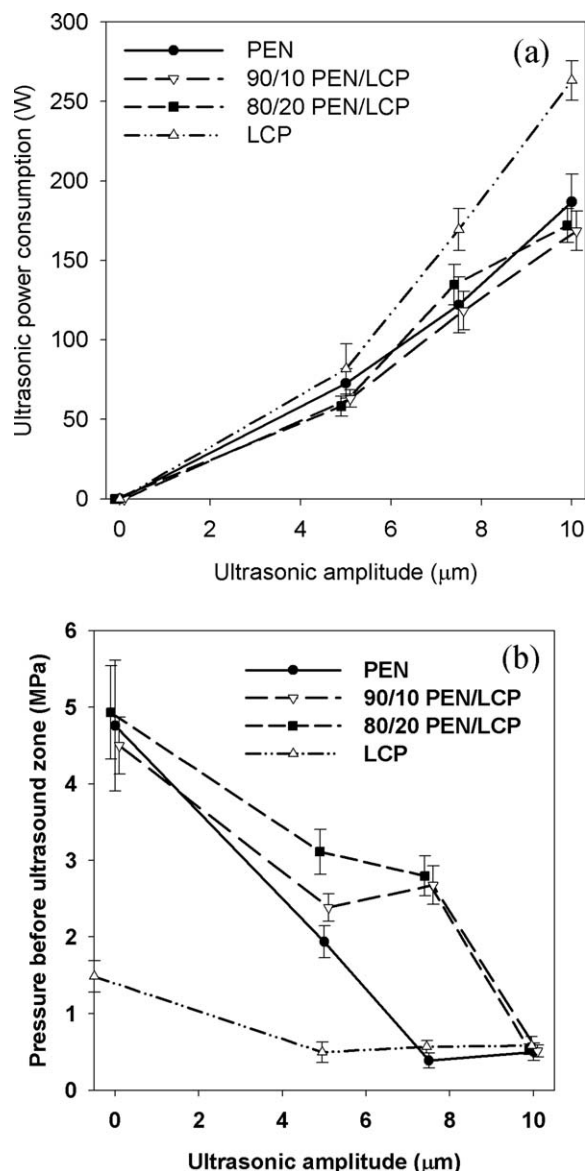


Figure 1 Ultrasonic power consumption (a), and pressure before the ultrasonic treatment zone (b) versus ultrasonic amplitude for PEN, LCP and PEN/LCP blends (values shifted along abscissa for clarity).

(Branson, Danbury, CT). T-2-(3-(4-*t*-butyl-phenyl)-2-methyl-2-propenylidene) malononitrile (DCTB) matrix (20 mg mL^{-1}) in THF, and NaTFA cationizing agent (10 mg mL^{-1}) in THF were mixed in 1 : 1 ratio, and $0.5 \mu\text{L}$ of the final mixture was deposited on microtiter plate wells (MTP 384-well ground steel plate). After the spots were dried, $0.5 \mu\text{L}$ of a solution of LCP or PEN/LCP blends was deposited on the top of the matrix and salt layer. After drying, $0.5 \mu\text{L}$ of matrix/salt mixture was deposited on top of the samples, and let dry. The sample thus "sandwiched" between the layers of matrix improved ionization of samples and hence the resolution of MALDI-TOF spectra.

Mechanical testing

The injection-molded mini-tensile bars were tested in an Instron Tensile Tester 5567 (Norwood, MA) following ASTM D 638-03. A crosshead speed of 5 mm min^{-1} , a 10-kN load cell, and an extensometer with a gauge length of 7.62 mm were used. The reported values are averages of a minimum of five samples, with a standard deviation of 10%.

Injection-molded impact bars, which were cut into two equal pieces labeled dead-end (DE) and gate-end (GE) to conform to the size specifications of ASTM D 256-05, were tested using an Izod impact tester (Testing Machines, Ronkonkoma, NY). Unnotched moldings of pure PEN and LCP were tested at a load of 4536 g, while unnotched moldings of the blends were tested at a load of 907 g, following ASTM D-256-05. As the difference between DE and GE samples were statistically insignificant for PEN and the blends, only their averages were reported.

Morphological studies

Morphological studies on injection moldings were performed using SEM (Hitachi S-2150) on cryogenically fractured mini-tensile bars. The morphology of fibers was studied with a field emission SEM (JSM7401F, Jeol, Tokyo, Japan). Specimens were sputter-coated with silver before imaging. Interfacial thickness in the blends was measured from high magnification field emission SEM micrographs by taking the average of a minimum of 20 measurements.

RESULTS AND DISCUSSION

Processing characteristics

Figure 1(a) shows the average net power consumption of the two ultrasonic horns after the subtraction of zero power consumption, determined with the horn in air. Ultrasonic power consumption increases with ultrasonic amplitude, and is the highest for treatment of LCP.

Figure 1(b) shows the pressure before the ultrasonic treatment zone of extruder as a function of ultrasonic amplitude. Without treatment, the pressure is lowest for LCP due to its lower viscosity than those of PEN and the blends, as shown by rheological measurements reported below in Figure 2. The pressure decreases with ultrasonic amplitude. The decrease in pressure in the presence of ultrasonic oscillations is due to a combination of permanent and thixotropic changes in viscosity, in addition to a possible slip of polymer melt along the solid surface of horns.⁷ Consequently, it is not possible to separate ultrasonically-induced chain scission or recombination reactions from pressure readings.

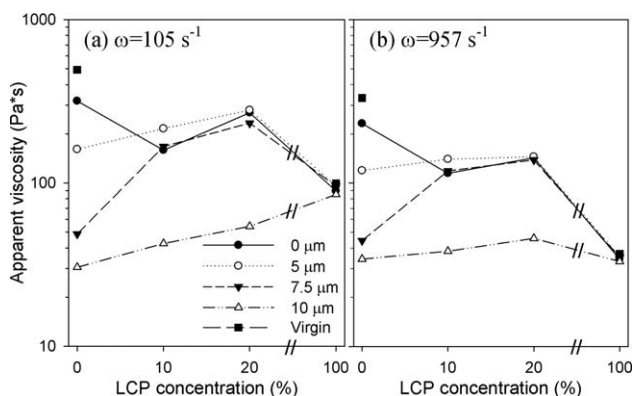


Figure 2 Apparent viscosity versus concentration for PEN, LCP and PEN/LCP blends at different ultrasonic amplitudes at apparent shear rates of 105 s^{-1} (a) and 957 s^{-1} (b). Lines connecting data to pure LCP are drawn for convenience.

It can be observed from Figure 1(b) that the pressure decrease in PEN/LCP blends is less than that in the components with ultrasonic treatment at amplitudes of 5 and $7.5 \mu\text{m}$. This indicated that ultrasound affects PEN/LCP blends differently than the components, suggesting the occurrence of interchange reactions between PEN and LCP.

Rheology

Figure 2 illustrates the composition dependence of viscosity at different ultrasonic amplitudes at apparent shear rates of 105 (a) and 957 s^{-1} (b). By comparing Figure 2(a,b), it is seen that LCP shows the greatest shear thinning behavior. The viscosities of virgin (as-received) PEN and LCP are higher than those of the extruded samples without ultrasonic treatment. While viscosity of PEN was observed to decrease at all amplitudes of treatment due to its degradation, viscosity of LCP and PEN/LCP blends was, respectively, observed to slightly and significantly decrease with treatment only at an amplitude of $10 \mu\text{m}$. Since the ultrasonic power consumption at amplitudes 5 and $7.5 \mu\text{m}$ is about the same for pure PEN and the blends, it follows that ultrasonic energy not only leads to chain scission in blends, but also induces recombination of active chain ends to form copolymers, as discussed later in this article.

Thermal analysis

Differential scanning calorimetry (DSC) studies were performed on extrudates of PEN and PEN/LCP blends to observe changes in their thermal behavior with ultrasonic treatment. Differences in processing time-temperature history were removed by using DSC results obtained after heating and cooling the samples. Glass transition (T_g), melting (T_m), and cold

crystallization (T_{cc}) temperatures, and percent crystallinity (X_c) of PEN and the blends are shown in Table I. X_c was determined after subtraction of PEN cold crystallization enthalpy from the melting enthalpy and normalization with respect to PEN content in the blends. The substantial increase in crystallinity of PEN at ultrasonic amplitudes of 7.5 and $10 \mu\text{m}$ and PEN/LCP blends at an ultrasonic amplitude of $10 \mu\text{m}$ is seen. Also, the substantial decreases in the T_g and T_{cc} of PEN with ultrasonic treatment at amplitudes of 7.5 and $10 \mu\text{m}$, and that of the blends at an amplitude of $10 \mu\text{m}$ were observed. This indicated degradation of PEN. The fact that T_g and T_{cc} showed no decrease in blends with treatment at an amplitude of $7.5 \mu\text{m}$ may indicate the occurrence of recombination reactions.

Heat flow versus temperature curves during DSC second heating for PEN, 90/10 PEN/LCP, and 80/20 PEN/LCP without and with ultrasonic treatment at an amplitude of $10 \mu\text{m}$ are plotted in Figure 3. Cold crystallization temperature of untreated PEN/LCP blends was lower than that of untreated PEN indicating that LCP acted as a nucleating agent for PEN crystallization.¹³ In addition, the cold crystallization temperatures of PEN and blends were observed to decrease substantially an amplitude of $10 \mu\text{m}$. This indicated degradation of PEN phase, as lower molecular weight polymer chains have greater mobility and crystallize faster.¹⁴ No changes in the melting point of PEN and PEN/LCP blends were observed.

Dynamic mechanical analysis

Figure 4 shows the effect of ultrasonic amplitude on the $\tan \delta$ temperature dependence in the glass transition temperature range, as obtained by DMA. There are strong $\tan \delta$ peaks in this temperature range for PEN and PEN/LCP blends and a weak

TABLE I
Glass Transition (T_g), Cold Crystallization (T_{cc}), and Melting Temperature (T_m), and Crystallinity (X_c) in DSC Second Heating for PEN and PEN/LCP

DSC 2nd heating runs		T_g ($^{\circ}\text{C}$)	T_{cc} ($^{\circ}\text{C}$)	X_c (%)	T_m ($^{\circ}\text{C}$)
PEN	Virgin	125	214.3	3.8	270.4
	$0 \mu\text{m}$	122.8	204.8	4.5	269.6
	$5 \mu\text{m}$	123.3	204.6	2.2	270.3
	$7.5 \mu\text{m}$	120.5	178.5	21.9	269.8
	$10 \mu\text{m}$	120.6	179.2	20.0	270.1
90/10 PEN/LCP	$0 \mu\text{m}$	122.2	172.4	21.4	269.3
	$5 \mu\text{m}$	121.7	176.4	20.9	268.9
	$7.5 \mu\text{m}$	123.0	174.8	17.5	268.7
	$10 \mu\text{m}$	119.7	165.5	35.4	269.5
80/20 PEN/LCP	$0 \mu\text{m}$	122.8	177.4	16.2	268.7
	$5 \mu\text{m}$	121.9	175.3	20.6	269.1
	$7.5 \mu\text{m}$	121.2	172.2	22.0	268.7
	$10 \mu\text{m}$	120.0	170.9	28.1	269.1

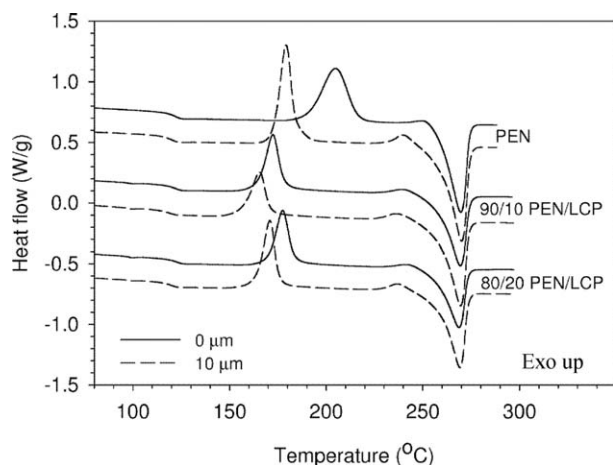


Figure 3 Heat flow versus temperature curves during second heating in DSC for PEN, 90/10 PEN/LCP and 80/20 PEN/LCP without and with ultrasonic treatment at an amplitude of 10 μm.

peak for LCP. As seen, temperatures corresponding to $\tan \delta$ peaks of ultrasonically-treated samples shift to a lower temperature for treated samples, indicating a reduction in T_g of PEN and blends after treatment. Loss tangent behavior also supported conclusion on degradation of PEN at amplitudes of 7.5 and 10 μm, and in 90/10 and 80/20 PEN/LCP blends at an amplitude of 10 μm. At these conditions, the $\tan \delta$ peak value was also observed to increase, indicating loss of elasticity with ultrasonic treatment at the specified amplitudes. The decrease in T_g signifies a substantial decrease in the molecular weight of pure PEN at amplitudes of 7.5 and 10 μm and in PEN/LCP blends at 10 μm. The glass transition temperatures of PEN/LCP blends corresponding to the $\tan \delta$ peaks were summarized in Table II. It can

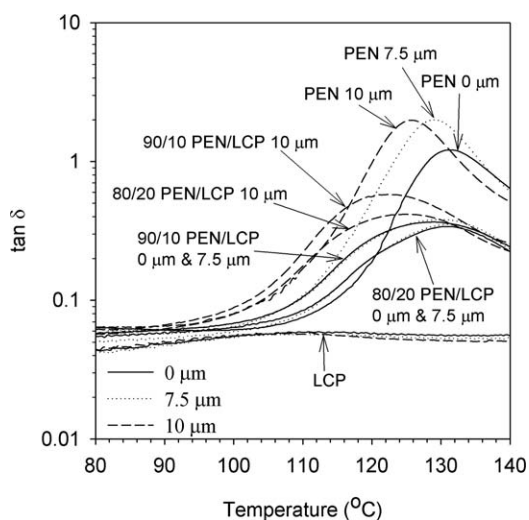


Figure 4 Loss tangent versus temperature for PEN, LCP, and blends, without and with ultrasonic treatment at amplitudes of 7.5 and 10 μm.

TABLE II
Glass Transition Temperature of PEN, LCP, and Blends without and with Ultrasonic Treatment, as Determined from $\tan \delta$ Peaks in DMA

T_g (°C)	PEN	90/10 PEN/LCP	80/20 PEN/LCP	LCP
Virgin	130	—	—	107
0 μm	131	126	130	107
5 μm	130	127	130	106
7.5 μm	129	128	129	106
10 μm	126	122	124	106

be observed that the glass transition temperatures obtained by DMA show similar trend as those obtained by DSC, but were somewhat higher, as expected.¹⁵ In contrast to DSC data that did not show T_g values of untreated and ultrasonically-treated LCP, DMA data show $\tan \delta$ peaks corresponding to T_g at about 107°C.

Mass spectroscopy

Copolymerization of LCP (HBA/HNA copolymer) and PEN is expected to occur by transesterification, leading to the formation of HBA/HNA-*co*-PEN copolymer, as shown in Figure 5. It should be noted that it is not necessary for the newly formed copolymer to be a block copolymer. It could also be random copolymer through a series of recombination reactions.

Figure 6 shows the MALDI-TOF mass spectra both of PEN, LCP, and 90/10 PEN/LCP without and with ultrasonic treatment at an amplitude of 10 μm in the m/z range of 1630–1715. Mass spectra of PEN and LCP were altered with ultrasonic treatment, indicating chemical changes such as degradation of higher molecular weight chains through chain scission, as was also indicated by viscosity data depicted in Figure 2. Mass spectra of 90/10 PEN/LCP exhibited peaks that were not present in PEN or LCP without and with ultrasonic treatment. It follows that these new species must be produced by chemical reactions between PEN and LCP. Evidently, these species are PEN-LCP copolymers. With ultrasonic treatment at an amplitude of 10 μm, the mass spectra of the blend indicated the presence of new copolymer species. Also, change in the distribution of some copolymer peaks already present without treatment becomes sharper after ultrasonic treatment. These changes in the mass spectra of the blend with ultrasonic extrusion revealed an enhancement of the PEN/LCP copolymer formation under treatment. However, the particular copolymer species corresponding to each peak could not be identified due to the complexity of the possible combinations of PEN, HBA, and HNA chains with different end groups.

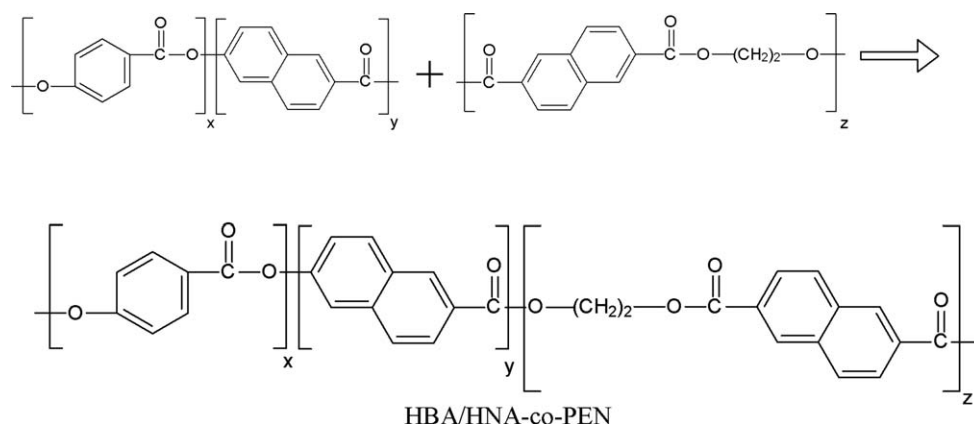


Figure 5 Structure of PEN/LCP copolymers expected to be formed by transesterification reaction of PEN and LCP.

Mechanical properties

Injection moldings

Figure 7 shows the effect of ultrasonic treatment on the tensile strength (a) and Young's modulus (b) of PEN, LCP, and their blends. These properties for the untreated blends are higher in comparison with prior studies,¹⁶ due to higher orientation and greater portion of the skin layer in molded mini-tensile bars as compared to larger injection-molded tensile specimens.¹⁷ While the Young's modulus and tensile

strength of PEN and PEN/LCP blends are not affected by treatment at ultrasonic amplitudes of 5 and 7.5 μm , they decreased with treatment at 10 μm . However, significant improvements in properties of pure LCP were observed with ultrasonic treatment at an amplitude of 7.5 μm . These improvements were attributed to chemical changes in LCP with ultrasonic treatment, as was shown by MALDI-TOF study.

Figure 8 shows the effect of ultrasonic amplitude on the elongation at break (a) and unnotched Izod

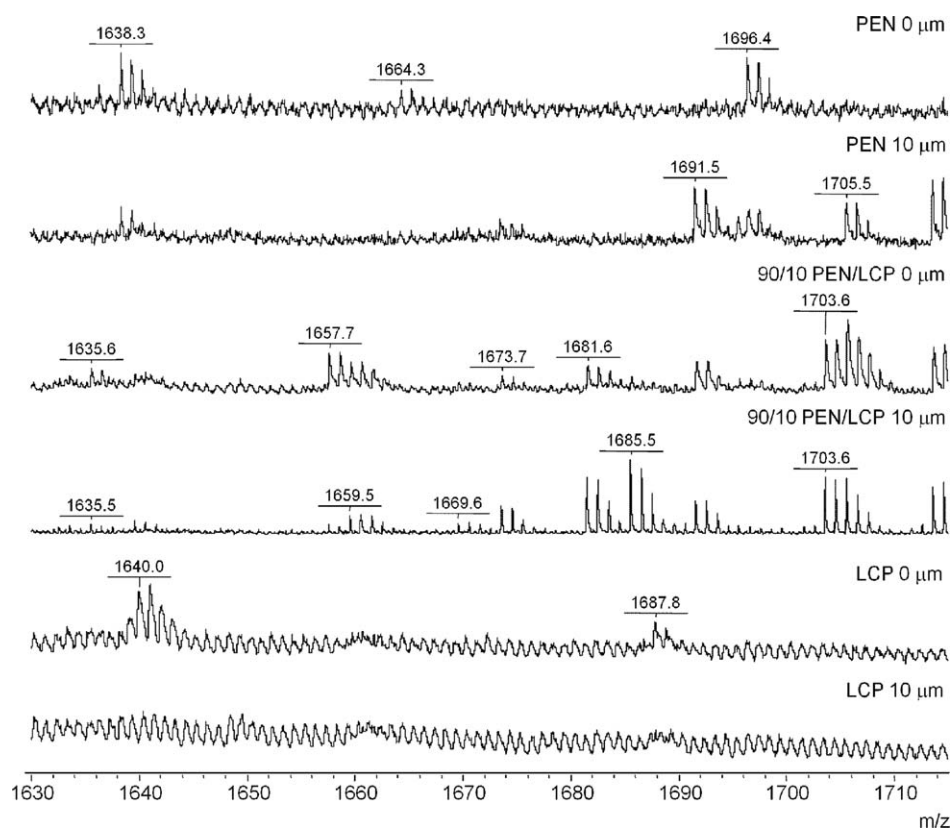


Figure 6 MALDI-TOF mass spectra of PEN, 90/10 PEN/LCP, and LCP, without and with ultrasonic treatment at an amplitude of 10 μm in m/z range of 1630–1715.

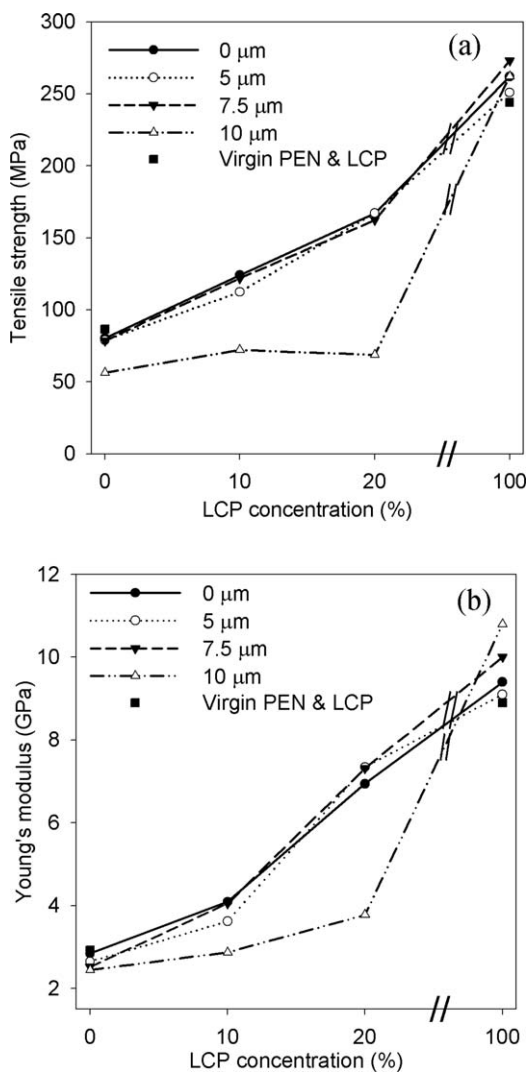


Figure 7 Tensile strength (a) and Young's modulus (b) of moldings of PEN/LCP blends versus LCP concentration without and with ultrasonic treatment at various amplitudes. Lines connecting 20% LCP concentration to pure LCP are drawn for convenience.

impact strength (b) of PEN, LCP and their blends. It should be noted that PEN shows yielding at all processing conditions except with treatment at an amplitude of 10 μm . A blend of 90/10 PEN/LCP treated at an amplitude of 7.5 μm also exhibited yielding. The elongation at break of 80/20 PEN/LCP blends was the lowest. The elongation at break of PEN and the blends decreased significantly with treatment at an amplitude of 10 μm , indicating their degradation.

As can be observed from Figure 8(b), the impact strength of pure PEN decreased with treatment at an amplitude of 7.5 μm , while that of 90/10 PEN/LCP blend was increased, indicating its improved compatibility as a result of copolymer formation by ultrasonically-induced recombination reactions as indicated by MALDI-TOF studies. However, the

impact strength of PEN and blends was observed to decrease at an amplitude of 10 μm . A reduction in LCP fibrillation in blends could be expected at this amplitude due to PEN degradation leading to a decrease of its viscosity. Generally, the reduced viscosity ratio of the matrix (PEN) to the dispersed phase (LCP) hinders fibrillation of the LCP phase.^{1,18,19}

Fibers

Fiber spinning of polymers typically leads to greater stiffness and strength than their injection moldings due to higher orientation.^{1,20} In general, LCP fibrils in blends were reported to be longer in fiber spinning than in injection moldings.²¹ The enhancement of fibrillation is expected to be more pronounced at higher LCP concentrations in fiber spinning.^{22–26}

The tensile strength, Young's modulus, and elongation at yield of PEN/LCP fibers spun at a DDR of

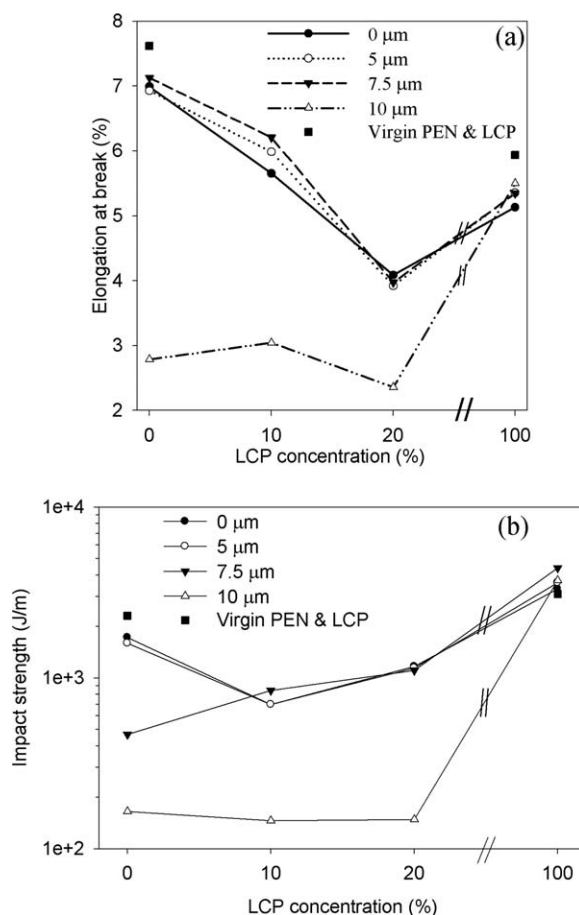


Figure 8 Elongation at break (a), and unnotched Izod impact strength (b) of moldings of PEN/LCP blends versus LCP concentration, without and with ultrasonic treatment at various amplitudes. Elongation at yield is reported for PEN and 90/10 PEN/LCP blends treated at 7.5 μm . Lines connecting 20% LCP concentration to pure LCP are drawn for convenience.

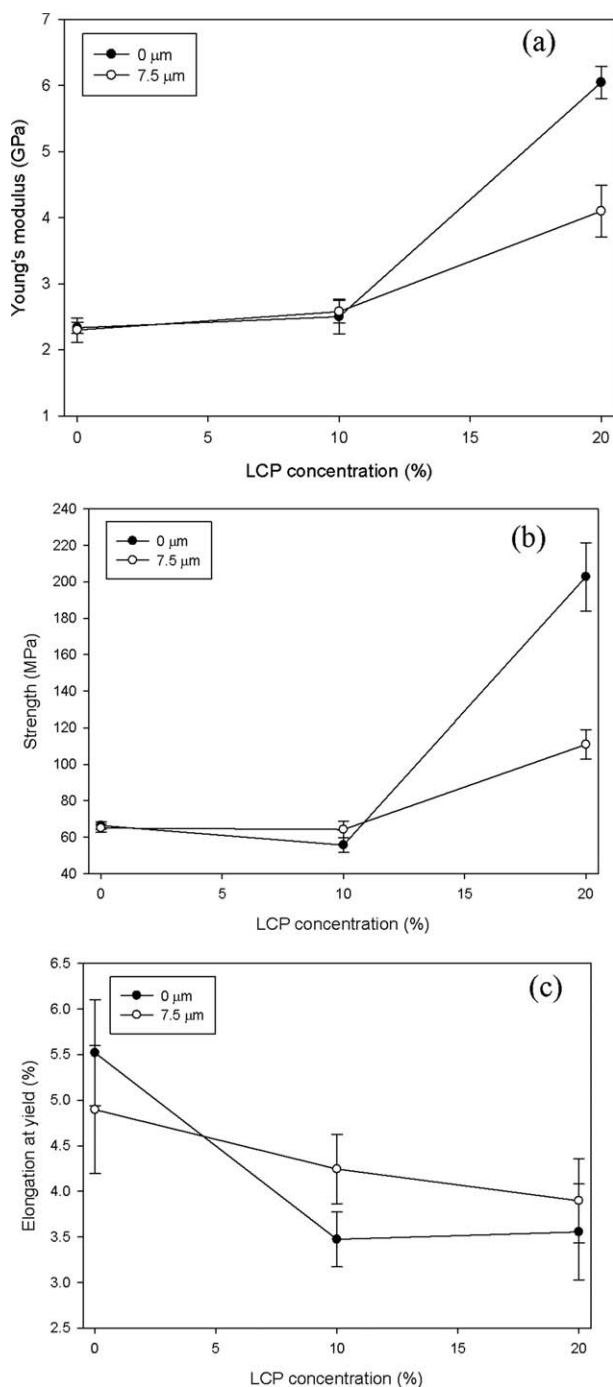


Figure 9 Young's modulus (a), strength (b), and elongation at yield (c) of PEN/LCP fibers spun at a DDR of 76.5 without and with ultrasonic treatment at an amplitude of 7.5 μm .

76.5 without and with ultrasonic treatment at an amplitude of 7.5 μm are shown in Figure 9. It should be noted that the 80/20 PEN/LCP blends exhibited brittle fracture. The tensile strength and Young's modulus of fibers increase with the addition of 20% LCP, while the elongation at yield decreases. There was no significant change in the Young's modulus and strength of PEN with the addition of 10% LCP.

The lack of improvement in these properties could be explained by the low extent of LCP fibrillation at this lower LCP concentration.^{22–26} Ultrasonic treatment of PEN/LCP blends at an amplitude of 7.5 mm had no significant effect on the Young's modulus of 90/10 PEN/LCP fibers spun at a DDR of 76.5, while it slightly improved their strength and elongation at yield. Fibers of 80/20 PEN/LCP blends spun at the same DDR exhibited a reduction in the Young's modulus and strength with ultrasonic treatment, while their elongation at break was not affected. The Young's modulus, strength, and elongation at break of LCP fibers were reported earlier.²⁷

The stress–strain plots of 90/10 PEN/LCP blends are shown in Figure 10 without (a) and with ultrasonic treatment at an amplitude of 7.5 μm (b). In the untreated blend, the strength and elongation at break were reduced at DDRs of 76.5 and 112.5 as seen from Figure 10(a). As also depicted in this figure undrawn 90/10 PEN/LCP blend exhibited the yielding behavior while all drawn fibers of this blend exhibited brittle fracture. However, similar to the untreated blend, undrawn 90/10 PEN/LCP fiber

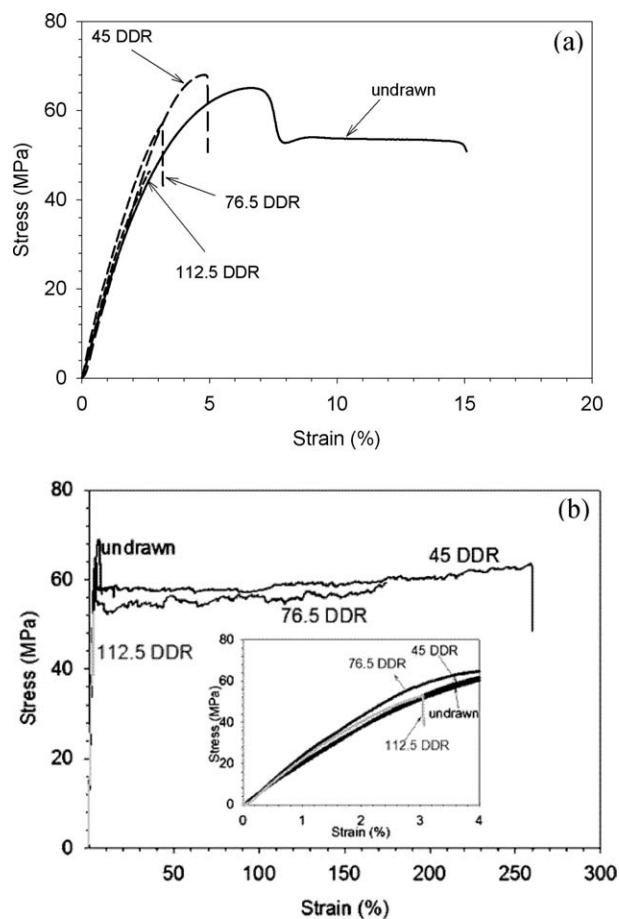


Figure 10 Stress versus strain curves for 90/10 PEN/LCP fibers at different DDRs, without (a) and with ultrasonic treatment at an amplitude of 7.5 μm (b). Insert indicates stress–strain curves up to a strain of 4%.

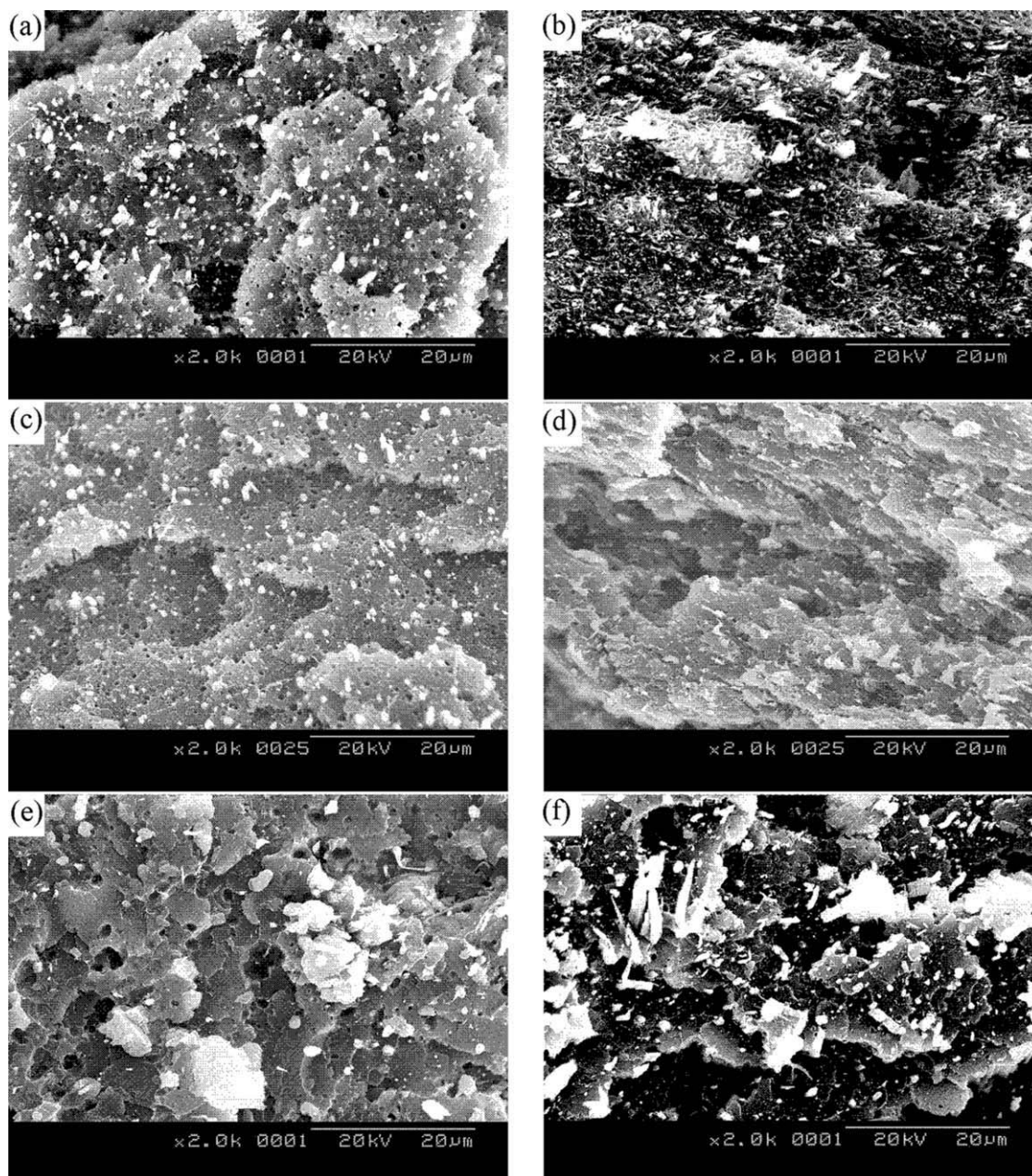


Figure 11 SEM micrographs of 80/20 PEN/LCP moldings in untreated core region (a), untreated skin region (b), core region treated at 7.5 μm (c), skin region treated at 7.5 μm (d), core region treated at 10 μm (e), skin region treated at 10 μm (f).

treated at an amplitude of 7.5 μm showed yielding behavior, as can be observed from Figure 10(b). The treated blend drawn at DDRs of 45 and 76.5 exhibited the ductile fracture while the ultrasonically-treated fiber drawn at a DDR of 112.5 was brittle. The improved elongation at break of 90/10 PEN/LCP blends with ultrasonic treatment at an amplitude of 7.5 μm indicated an enhanced compatibility of 90/10 PEN/LCP blends. This was due to *in situ* formed PEN/LCP copolymer, observed by MALDI-TOF MS, which improved interfacial stress transfer^{28,29} between PEN and LCP. The brittle frac-

ture at the high DDR of 112.5 for the treated blend could possibly be due to movement of the *in situ* formed copolymer away from the interface at a higher speed of elongation. It is expected that to compatibilize immiscible blends, *in situ* copolymer must reside at the interface.^{28,29}

Morphology

Injection moldings

Injection moldings of PEN/LCP blends exhibited spherical LCP droplets in the core, and elongated

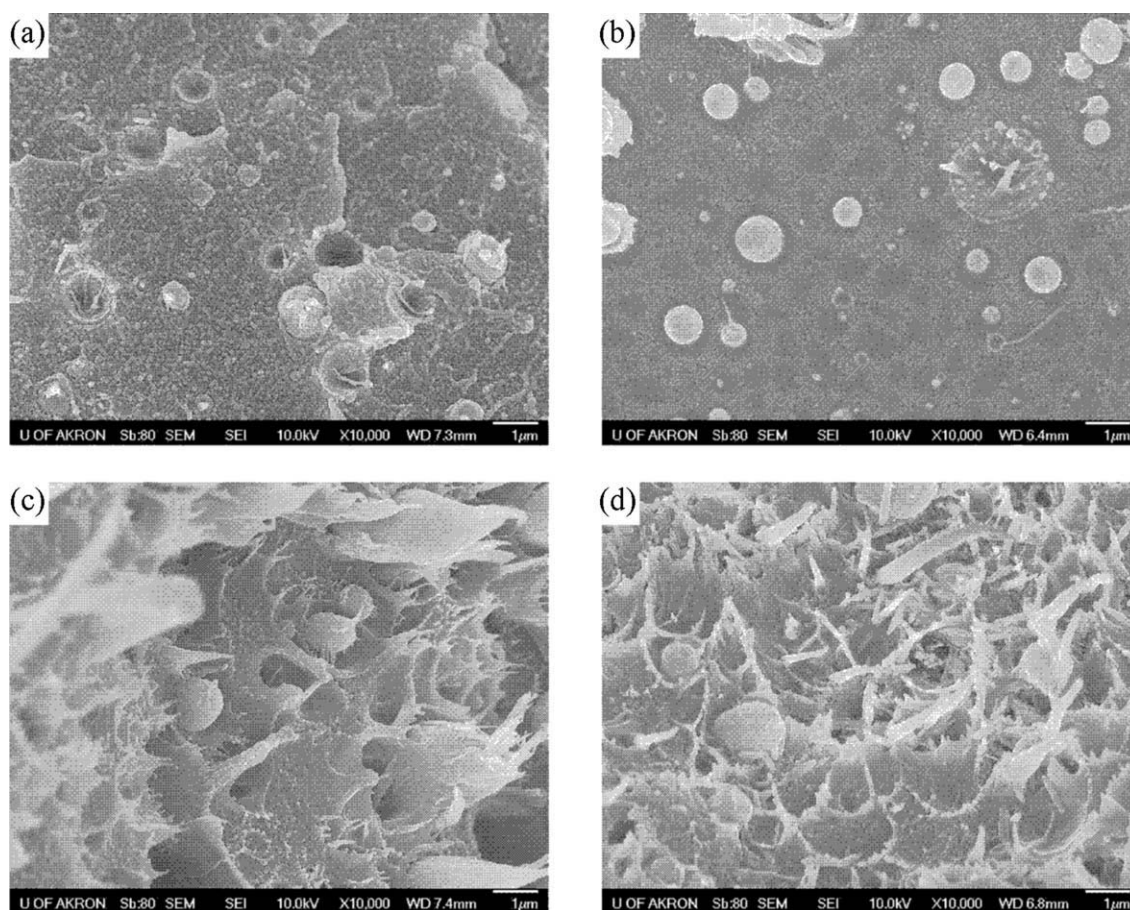


Figure 12 Field emission SEM micrographs at a magnification of 10,000x for fibers at DDR of 45 for PEN/LCP blends at concentrations of 90/10 without treatment (a), 90/10 with treatment at an amplitude of 7.5 μm (b), 80/20 without treatment (c), 80/20 with treatment at an amplitude of 7.5 μm (d).

LCP particles of various diameters in the skin region. In general, the skin region formed a substantial portion of the molded mini-tensile bars. Figure 11 shows the effect of ultrasonic treatment on the core (a, c, e) and skin (b, d, f) regions of molding of 80/20 PEN/LCP blends indicating this effect. The sizes of LCP droplets in the core and fibrils in the skin were observed to increase with treatment at an ultrasonic amplitude of 10 μm [Figs. 11(e,f)]. The viscosity ratio of the PEN matrix to the dispersed LCP phase determines LCP deformation in their blends.^{1,18,19} Because of the degradation of PEN with ultrasonic treatment at 10 μm , the viscosity ratio of PEN to LCP is significantly reduced. This led to reduced LCP fibrillation in PEN/LCP blends leading to the reduction of mechanical properties.

Fibers

Figure 12 shows the SEM micrographs of fibers of 90/10 (a, b) and 80/20 (c, d) PEN/LCP blends at a DDR of 45, without (a, c) and with ultrasonic treat-

ment at an amplitude of 7.5 μm (b, d). Clearly, fibers of 80/20 PEN/LCP exhibited greater LCP fibrillation than those of 90/10 PEN/LCP. However, the extent of LCP fibrillation was not affected by ultrasonic treatment at an amplitude of 7.5 μm .

Figure 13 shows higher magnification SEM micrographs of fibers of 90/10 (a, b) and 80/20 (c, d) PEN/LCP blends at a DDR of 45, without and with ultrasonic treatment at an amplitude of 7.5 μm . While fibrils are clearly present in the blends containing 20% LCP, largely undeformed LCP droplets were observed in 90/10 PEN/LCP blends. The lack of LCP fibrillation was also responsible for the lack of improvement in the Young's modulus and strength of 90/10 PEN/LCP fibers. The observed poor fibrillation in 90/10 PEN/LCP blends can be attributed to the lower LCP concentration in this blend. LCP fibrillation was also shown to improve with increasing LCP concentration.²²⁻²⁶

To quantify the interfacial effect in PEN/LCP blends, the interface in the extruded fibers (DDR = 1) of blends without and with treatment at an amplitude of 10 μm were analyzed.

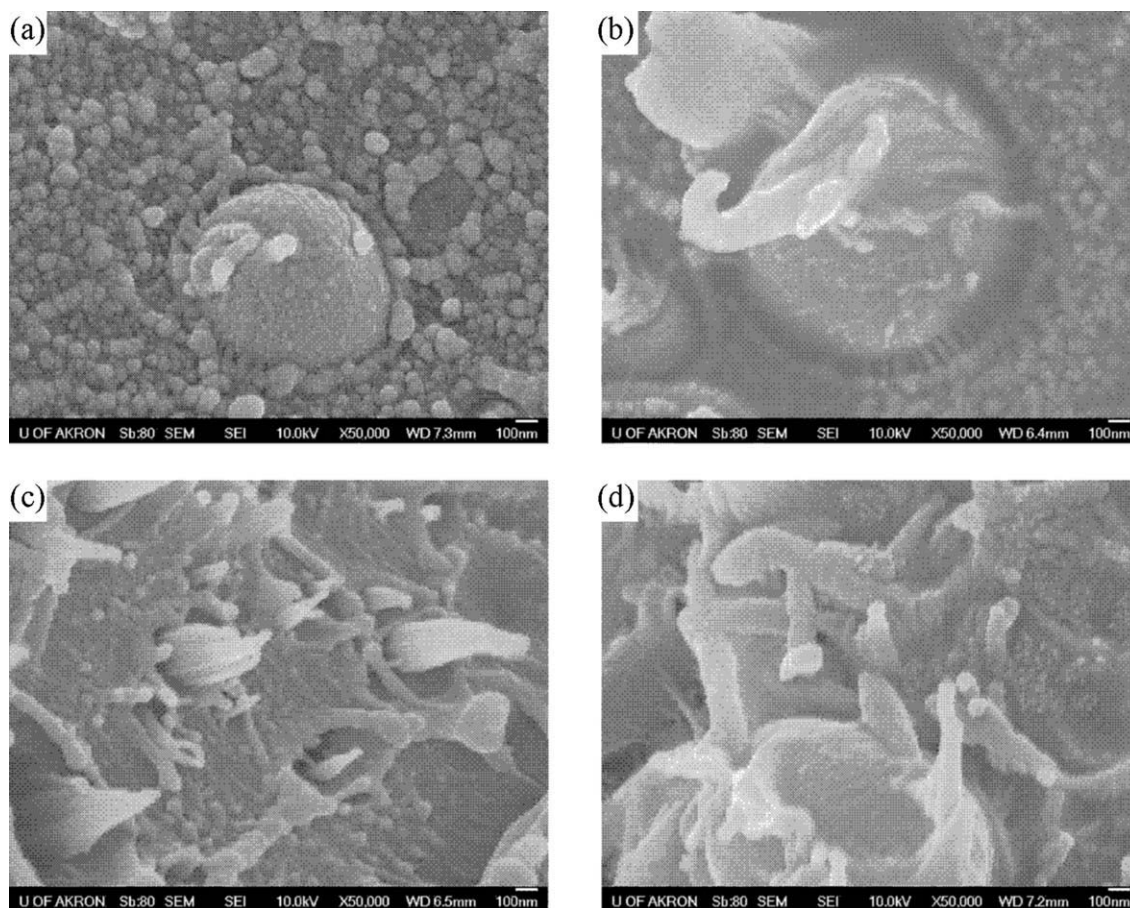


Figure 13 Field emission SEM micrographs at a magnification of $\times 50,000$ for fibers at a DDR of 45 for PEN/LCP blends at concentrations of (a) 90/10 without treatment, (b) 90/10 with treatment at an amplitude of $7.5 \mu\text{m}$, (c) 80/20 without treatment, (d) 80/20 with treatment at an amplitude of $7.5 \mu\text{m}$.

In particular, Wu's relation was used for calculation of interfacial tension³⁰:

$$\gamma_{12} = 55a_I^{-0.86} \quad (1)$$

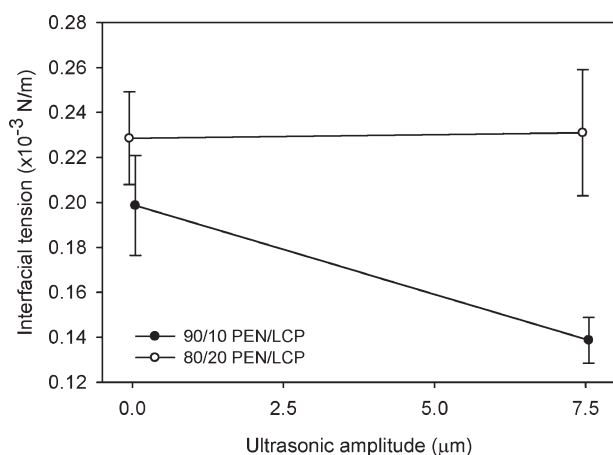


Figure 14 Interfacial tension of PEN/LCP blends without and with ultrasonic treatment at an amplitude of $7.5 \mu\text{m}$, with the error bars indicating 95% confidence intervals.

where γ_{12} is the interfacial tension expressed in dyn cm^{-1} , and a_I is the measured interface thickness in Angstroms.

The interfacial tension calculated from average interface thicknesses observed by SEM micrographs of PEN/LCP blends are presented in Figure 14 along with 95% confidence intervals. Values of the interfacial tension for PEN/LCP blends without treatment were higher than those reported in literature using the same method for PET/LCP ($0.18 \times 10^{-3} \text{ N m}^{-1}$) and PBT/LCP ($0.06 \times 10^{-3} \text{ N m}^{-1}$) blends for which the LCP phase was a 18/82 PET/HBA copolymer.³¹ A reason for the higher interfacial tension of untreated PEN/LCP blends could be the greater rigidity of PEN, as compared to PET and PBT. While interfacial tension was similar for untreated 90/10 and 80/20 PEN/LCP blends, it was observed to decrease significantly with treatment at an amplitude of $7.5 \mu\text{m}$ in 90/10 PEN/LCP blend. This decreased interfacial tension caused by improved interfacial adhesion with ultrasonic treatment, leading to the presence of a diffuse interphase. Ultrasonic treatment was not observed to influence the interfacial tension of 80/20 PEN/LCP blends. This

could be due to presence of larger LCP domains and consequently reduced total surface area for reactions at greater LCP concentration.

CONCLUSIONS

PEN/LCP blends were prepared in the ultrasonically aided extruder at a flow rate of 1 kg h^{-1} . Ultrasonic treatment led to reduced pressure during extrusion, and reduced viscosity of PEN. In 90/10 and 80/20 PEN/LCP blends, the viscosity and mechanical properties decreased with treatment at an ultrasonic amplitude of $10 \text{ }\mu\text{m}$. The glass transition temperature of pure PEN and PEN in the blends was also reduced with treatment at an amplitude of $10 \text{ }\mu\text{m}$.

LCP acted as a nucleating agent in PEN/LCP blends. Crystallinity of PEN increased with ultrasonic treatment at amplitudes of 7.5 and $10 \text{ }\mu\text{m}$, while that of PEN in the blends increased with treatment at an amplitude of $10 \text{ }\mu\text{m}$. At the same conditions, an increase in the value of $\tan\delta$, and a shift in T_g to lower temperatures was observed. These changes were solely attributed to the degradation of PEN. The observed lack of degradation of blends at an amplitude of $7.5 \text{ }\mu\text{m}$ even in the presence of degradation of PEN in blends was due to enhanced recombination reactions caused by ultrasonic treatment. MALDI-TOF mass spectroscopy revealed the presence of PEN/LCP copolymers without and with ultrasonic treatment. However, ultrasonic treatment of 90/10 PEN/LCP blends was shown to induce a greater copolymer formation.

The 90/10 PEN/LCP blends treated at an amplitude of $7.5 \text{ }\mu\text{m}$ indicated improved interfacial adhesion due to *in situ* compatibilization. Under this condition, improvements were recorded in the impact strength and elongation at yield of moldings and elongation at break of fibers. The elongation at yield of this blend was also slightly improved at an amplitude of $5 \text{ }\mu\text{m}$. Ultrasonic treatment at an amplitude of $10 \text{ }\mu\text{m}$ led to grossly undeformed LCP domains in the core and skin regions of blends. The latter suggested that any beneficial effects of exchange reactions were masked by the lack of fibrillation caused by reduced viscosity ratio of PEN to LCP at an amplitude of $10 \text{ }\mu\text{m}$.

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