

Studies on a Terephthalic Acid and Dihydroxydiphenyl Sulfone Liquid Crystalline Copolymer and Its Composites with Different Thermoplastics

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ABSTRACT: A liquid crystalline polymer (LCP) was synthesized by an interfacial polycondensation reaction at room temperature from terephthaloyl chloride and *p,p'*-dihydroxydiphenyl sulfone. The LCP synthesized was so stable and molecularly rigid that it did not show any phase transition until it degraded at about 320°C. Composites of the LCP with polycarbonate (PC), polystyrene (PS), and sulfonated polystyrene (SPS) were formed by compression molding at a temperature at which the thermoplastic matrix was in the melt state. They were thermally analyzed by differential scanning calorimetry. Tensile specimens were cut from the compression-molded plates, and mechanical tests were performed. The morphology of the material systems was studied by performing scanning electron microscopy analysis on cryogenically fractured specimens. For LCP/PS and LCP/SPS systems, a sharp two-phase morphology was formed, which suggested poor interfacial adhesion. The tensile strength of both systems decreased with LCP addition. The LCP/PC system also revealed a two-phase morphology; however, the interfaces between the LCP domains and the PC matrix were not so well defined, showing better interfacial adhesion than the two previous systems studied. Stronger bonding between the LCP and PC resulted in a significant improvement in the mechanical behavior of PC by LCP addition. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 645–652, 1997

Key words: liquid crystalline polymer; polymer composite; polystyrene; polycarbonate; sulfonation; nitration; mechanical properties

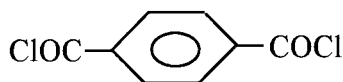
INTRODUCTION

Liquid crystalline polymers (LCPs) represent a new class of materials with unique chemical and physical properties based on unique molecular relationships. Exceptional strength and stiffness, low coefficient of thermal expansion, chemical resistance, and excellent electrical and optical properties are some of the features of LCPs.^{1–3}

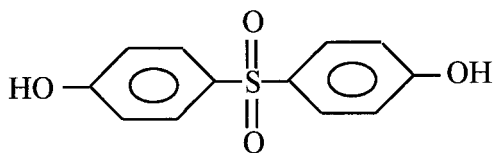
The first LCPs were synthesized in 1959 by Eareckson⁴ as a set of copolyesters from various acid chlorides and bisphenols. Several other LCPs have been synthesized since then. In 1975, Roviello and Sirigu⁵ synthesized a low-molar-mass LCP, *p,p'*-di-hydroxy- α,α' -di-methyl benzalanine. In 1981, Mansour et al.⁶ synthesized some new polyarylates and copolyarylates. They utilized several monomers, of which dihydroxydiphenyl sulfone, bisphenol A, resorcinol, and terephthaloyl chloride were the common ones used. In 1981, Antoun et al.⁷ prepared a few thermotropic

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Terephthaloyl chloride



Dihydroxy diphenyl sulfone

Figure 1 Structural formulae of the monomers used to produce LCP.

LCPs that contained mesogenic units interconnected by flexible spacers along the main chain. Gupta et al., in 1983,⁸ synthesized various aliphatic-aromatic copolyesters by interfacial polycondensation. Skovby et al., in 1990,⁹ synthesized wholly aromatic liquid crystalline main chain polyesters derived from terephthalic acid and (1-phenylethyl) hydroquinone modified with *p*-hydroxybenzoic acid. Some new types of polyaramides were synthesized by Kricheldorf et al. in 1992.¹⁰ The two monomers used were 1,4-diaminobenzene and terephthalic acid. Aromatic substituents of various lengths were also incorporated to create a new class of polyaramides. Despite relatively long substituents, meltable polyaramides were never obtained. However, two homopolyaramides and two copolyaramides showed a good solubility in pure *N*-methylpyrrolidone and compatibility with poly(vinylpyrrolidone). Li et al., in 1994,¹¹ synthesized thermotropic liquid crystalline copolyesters by molten-state copolycondensation from 1,4-, 1,5-, and 2,7-naphthalenediol units with terephthalic acid, *p*-acetoxyben-

zoic acid, and poly(ethylene 2,6-naphthalene dicarboxylate). Chang et al., in 1995,¹² synthesized three different thermotropic liquid crystalline polyesters. The first LCP consisted of diad aromatic ester-type mesogenic units and the hexamethylene spacers along the main chain. The second was a wholly aromatic polyester having alkoxy side groups on the terephthaloyl moiety. The third was a copolymer consisting of triad aromatic ester-type mesogenic units and two different spacers: tetramethylene and hexamethylene units.

While many macroscopic properties of LCPs are extremely advantageous, blends/composites formed by their inclusion in less expensive isotropic materials have recently received considerable attention for their strong potential for technological applications ranging from structural to electronics and nonlinear optics at a reduced material cost.^{2,12-23} It was the objective of this study to design and synthesize an LCP and investigate the thermal, morphological, and mechanical properties of its composites with various thermoplastics.

EXPERIMENTAL

Materials

The LCP was synthesized as a copolymer of terephthaloyl chloride (TC) and *bis*(4-hydroxy phenyl) sulfone (also called dihydroxydiphenyl sulfone [DHDPS]). It was expected that these monomers would result in a rigid rod-like structure, imparting thermotropic liquid crystallinity.²⁴ TC was used rather than its precursor terephthalic acid because acid chlorides are more reactive than their precursor carboxylic acids.⁶ The structural formulae of the two basic monomers are given in Figure 1. It was also expected that the oxygen atoms of the —SO₂— and the —CO₂— links would form hydrogen bonding with the hydrogen atoms attached to N or O present in the thermo-

Table I Operating Conditions for the Plate Fabrication Process

Material System	Operating Temperature (°C)	Operating Time (min)	Annealing Temperature (°C)	Annealing Time (min)
PC and PC/LCP	225	6	165	30
PS and PS/LCP	225	6	165	30
SPS and SPS/LCP	215	6	165	30
NPS and LCP/NPS	225	6	165	30

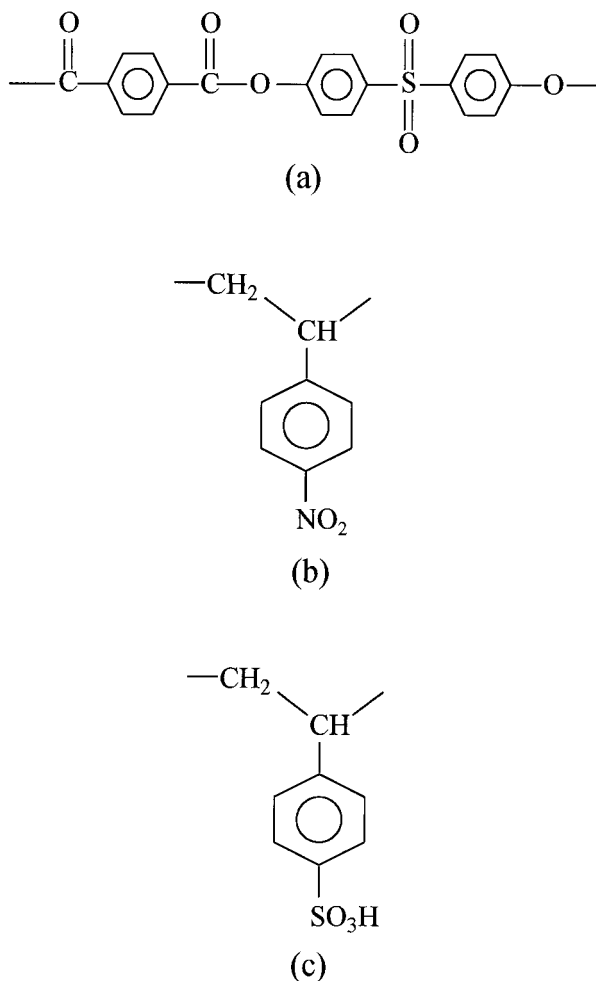


Figure 2 Structural formulae of the repeat units of (a) LCP, (b) SPS, and (c) NPS.

plastic when the LCP is incorporated in a thermoplastic improving the interfacial adhesion.

LCP synthesis was performed with toluene as the solvent.⁴ An equimolar ratio of the monomers were used. DHDPS (0.05 mol) was weighed out and dissolved in 100 mL of 0.1M NaOH. It was

then diluted with 300 mL of water. The solution was charged in a blender. Then, 3 g of sodium dodecyl sulfate in 30 mL of water was added to the blender while it was stirred slowly. It acted as a dispersing agent in the reaction. On the other hand, 0.05 mol of TC was dissolved in 150 mL of toluene and the solution was also charged in the blender. The reaction mixture was then blended at high speed for 5 min. The reaction was carried out at room temperature. The reaction mixture was then poured into an excess of acetone so as to coagulate the product. After leaving the system overnight, the slurry was filtered off and washed with an excess of water to remove occluded salts and detergent. This was followed by repeatedly washing with methanol and acetone to remove unreacted monomers and toluene. The nematic nature of the LCP (as dissolved in sulfuric acid) was confirmed by threaded-Schlieren texture observed by polarized optical microscopy.

The thermoplastics used in this study were polycarbonate (PC) supplied by the BDH Company, polystyrene (PS) supplied by SABIC, and modified polystyrene by nitration and sulfonation. PS was sulfonated according to the procedure of Makowski et al.²⁵ by attaching an $-\text{SO}_3\text{H}$ group at the para position of the benzene ring in the repeat unit of PS. The sulfonating group was attached because it was expected to improve the interfacial adhesion by forming hydrogen bonding with the LCP chain in the composites of PS and LCP. It has also been reported that about 8% sulfonation is achieved through that procedure.²⁵

PS was also modified according to the procedure given by Gauthier and Eisenberg,²⁶ by the attachment of the $-\text{NO}_2$ group at the para position of the benzene ring in the repeat unit of PS, with pure PS, nitrobenzene, and an equivolume ratio of concentrated nitric acid and concentrated sulfuric acid. The addition of the polarizing group

Table II Experimental (EXP) and Calculated (CALC) Values of Percentages of Elements Present in LCP, NPS, and SPS

Material	% C		% H		% N		% S	
	EXP	CALC	EXP	CALC	EXP	CALC	EXP	CALC
LCP	60.8	63.1	3.4	3.2			8.8	8.5
NPS	63.7	64.4	4.7	4.69	9.4	9.39		
SPS	55.37	52.17	4.52	4.34			1.9	17.4 ^a

^a Based on 100% sulfonation.

Table III Melting and/or Degradation Temperatures of the Polymers Used

Temperature	PC	PS	SPS	NPS	LCP
Melting (°C)	220	220	210	280	
Degradation (°C)	285	280	240	300	320

(—NO₂) was also expected to induce compatibility in the composites of PS and LCP.

Composite Fabrication

The possibility of solution blending the LCP and the thermoplastics (PC, PS, nitrated PS [NPS], sulfonated PS [SPS]) was checked first. Various solvents such as chloroform, acetone, dimethyl formamide, tetrahydrofuran, phenol, acetic acid, concentrated sulfuric acid, dimethyl sulfoxide, and 1,2-dichloroethane were tried. None of these trials was satisfactory. Composites of LCP with the thermoplastics were then fabricated by compression molding at a temperature above the melting point but below the degradation temperature of the thermoplastics. Sheets of about 0.7 mm in thickness were casted from PC, PS, NPS, SPS, and composites of 1, 5, 10, and 25% LCP with

these thermoplastics. The details of the procedure follow.

The LCP and the thermoplastic powders were first mixed roughly (in proportion) in a micromilling machine for about 5 min. Meanwhile, two stainless steel plates were wrapped separately with aluminum foil. This was done to keep the sheets from sticking onto the steel plates during compression molding. A square metallic mold (11.5 × 11.5 cm) was placed on one of the steel plates covered with aluminum foil. The composite powder was then evenly spread in the mold, and the system was placed in the compression molding machine (Wabash, Model 75-2424-4TM). Enough time was given for the thermoplastic to melt. Then, the second steel plate was placed on the mold and the whole system was compressed at a specified temperature for a fixed time. The system was then cooled to a lower temperature, which was maintained for a specified duration. After that, the system was cooled to room temperature and the pressure was released. The operating parameters used for different composite systems are given in Table I.

Table IV Glass Transition Temperatures of LCP/PS, LCP/SPS, and LCP/PC Composite

Material System	T_g (°C)
LCP/PS	
0/100	105
1/99	105
5/95	105
10/90	104
25/75	104
100/0	
LCP/SPS	
0/100	102
1/99	103
5/95	103
10/90	103
25/75	104
100/0	
LCP/PC	
0/100	145
1/99	147
5/95	147
10/90	147
25/75	148
100/0	

Characterization

Elemental analysis was performed on LCP, SPS, and NPS by a Carlo Erba Elemental Analyzer.

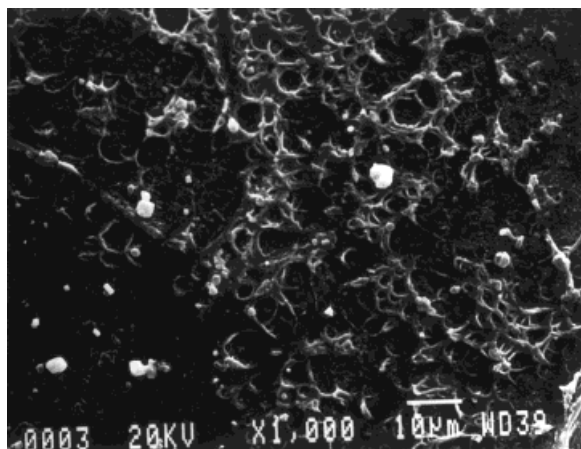


Figure 3 SEM micrograph of a fracture surface of an LCP/PS system.

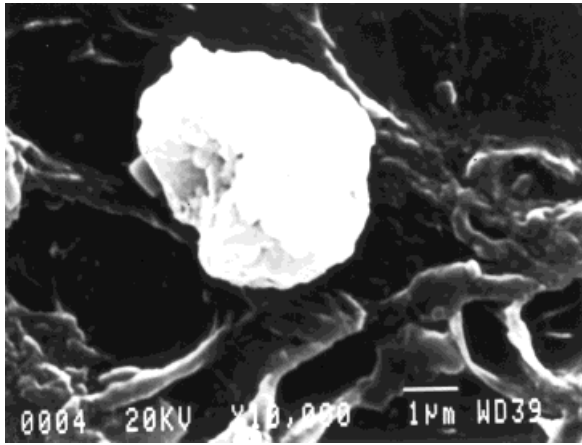


Figure 4 SEM micrograph of a fracture surface of an LCP/PS system showing the sharp interface boundary around an LCP particle.

Melting and/or degradation points for the materials were determined with an Electrothermal Melting Point Apparatus. Glass transition temperatures were determined by means of a differential scanning calorimeter (Perkin Elmer DSC-4) under an inert atmosphere of argon. The heating rate was 20°C/min, and the temperature range covered was from 50 to 320°C. The mechanical properties were obtained with an Instron 1196 mechanical testing system. The tensile tests were conducted at a displacement rate of 0.1 mm/min. The samples for the tensile tests were cut from compression-molded plates (and milled) as per specifications given in ASTM Standard D 638M-89 (Type M II).²⁷ The arithmetic average and the standard deviation of the tensile properties were calculated with four samples. All mechanical tests

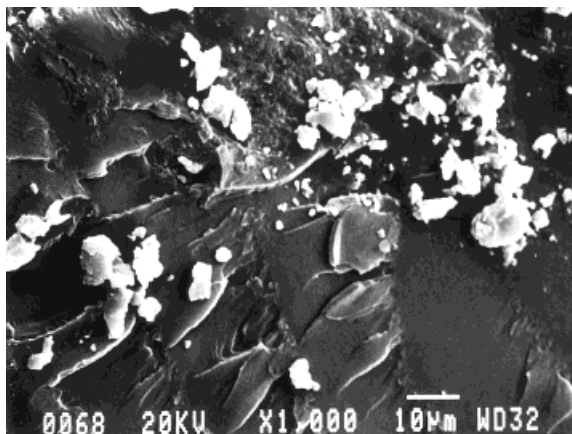


Figure 5 SEM micrograph of a fracture surface of an LCP/SPS system.

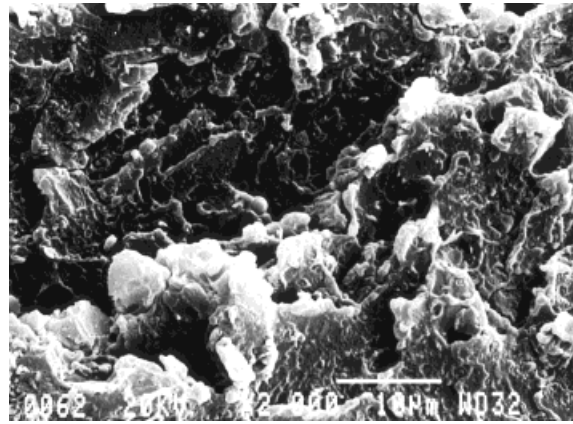


Figure 6 SEM micrograph of a fracture surface of an LCP/PC system showing a two-phase morphology.

were carried out at room temperature. To investigate the interfacial adhesion between the LCP and the thermoplastics, fractured surfaces at cryogenic temperature (in liquid nitrogen) and tensile fractured surfaces were observed by scanning electron microscopy on a JSM-840 scanning microscope.

RESULTS

Structures of LCP, NPS, and SPS

The structural formulae of the repeat units of LCP, SPS, and NPS are given in Figure 2. Calculated (from the structures in Fig. 2) and experimentally determined weight percentages of elements present in LCP and NPS were not signifi-



Figure 7 SEM micrograph of a fracture surface of an LCP/PC system showing not very well-defined interfaces between an LCP particle and the PC matrix.

Table V Tensile Properties of LCP/PS, LCP/SPS, and LCP/PC Composites

Material System	Tensile Modulus (MPa)	Tensile Strength (MPa)
LCP/PS		
0/100	1,728 ± 147	28.44 ± 5.07
1/99	1,933 ± 143	19.94 ± 1.29
5/95	1,661 ± 193	16.28 ± 2.38
10/90	1,668 ± 266	11.29 ± 1.06
LCP/SPS		
0/100	2,013 ± 175	32.29 ± 5.40
1/99	2,008 ± 110	27.80 ± 2.32
5/95	1,890 ± 391	20.71 ± 1.31
10/90	1,957 ± 129	20.76 ± 3.49
25/75	1,979 ± 285	16.54 ± 3.43
LCP/PC		
0/100	1,527 ± 121	32.83 ± 2.30
1/99	1,488 ± 98	32.25 ± 2.17
5/95	1,491 ± 97	40.01 ± 5.18
10/90	1,624 ± 61	31.44 ± 3.17
25/75	1,822 ± 347	30.69 ± 8.24

cantly different, as listed in Table II. However, for the case of SPS, about 11% sulfonation was achieved, which was a little higher than the level of sulfonation (8%) reported by Makowski et al.²⁵

Thermal Analysis

The melting/degradation points for LCP, SPS, NPS, PC, and PS are listed in Table III. These two temperatures were important in determining the processing temperature range for plate fabrication. In the case of NPS, degradation and melting occurred simultaneously. Therefore, composite fabrication was not possible for the LCP/NPS system. In the case of LCP, melting temperature was not observed. The LCP started to degrade at around 320°C. For that reason, a pure LCP plate was also not possible to fabricate.

Table IV lists the glass transition temperatures (T_g 's values) as a function of composition for the LCP/PS, LCP/SPS, and LCP/PC systems. Pure LCP did not have a T_g , and no significant change in T_g was observed as the weight percentage of LCP was increased for all three of the systems studied.

Morphological and Mechanical Characterization

For the LCP/PS system, a sharp/distinct two-phase morphology was formed (as shown in Figs.

3 and 4), which suggested poor interfacial adhesion. For the LCP/SPS system, SEM again revealed poor bonding between the LCP and the SPS by exhibiting well-defined interfaces between them (Fig. 5). However, a composite plate of 25% LCP/SPS, unlike 25% LCP/PS, was formed, which could be an indication of some improvement in the interfacial bonding by low-level (11%) sulfonation of PS. The LCP/PC system also revealed a two-phase morphology, as shown in Figure 6; however, the interfaces between the LCP and the PC were not well defined (Fig. 7), showing better interfacial adhesion than both the LCP/PS and the LCP/SPS systems.

The strong adhesion between PC and LCP is believed to be due to the partial charges present in the functional groups of PC (O—CO—O) and LCP (OC—O), resulting in strong physical interaction between the two polymers with partial or full miscibility. The extent of miscibility could be examined if melt or solution blending of the polymers were possible. The possibility of chemical reaction at the interface of any of the material systems studied is believed to be remote.

The study on morphology was complemented by characterizing the associated mechanical properties. The data with standard deviations are sup-

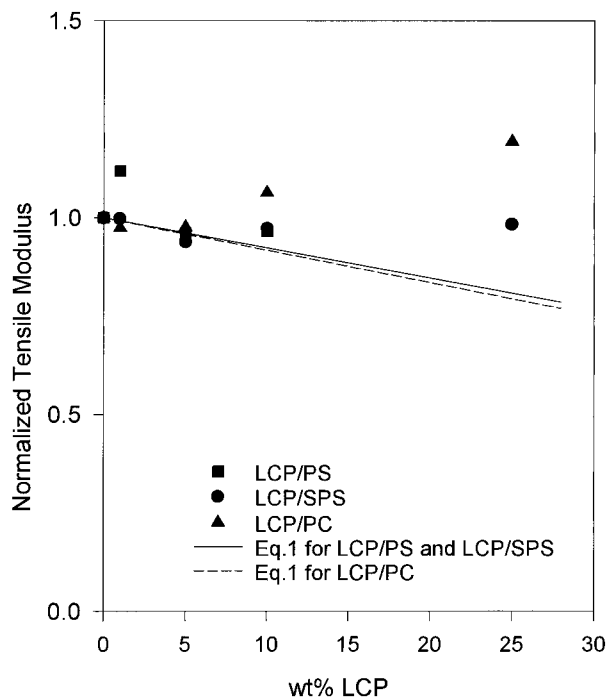


Figure 8 Tensile modulus (normalized by the modulus of pure thermoplastic) versus LCP content for LCP/PS, LCP/SPS, and LCP/PC systems.

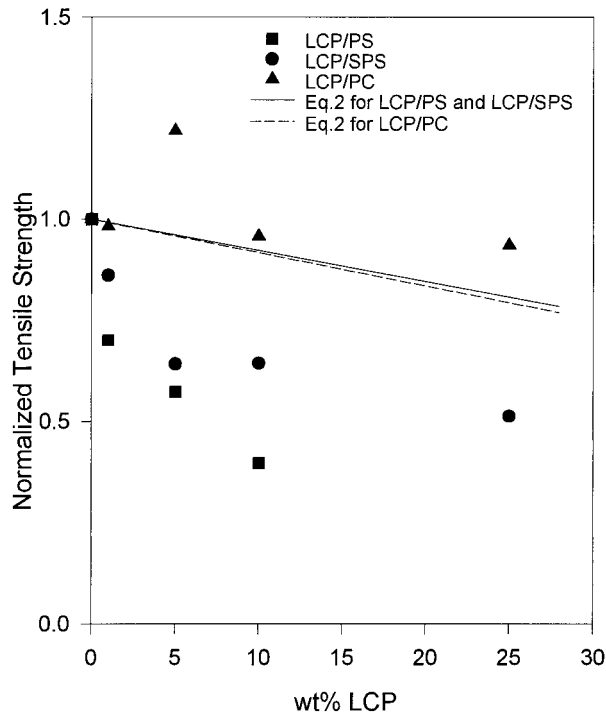


Figure 9 Tensile strength (normalized by the strength of pure thermoplastic) versus LCP content for LCP/PS, LCP/SPS, and LCP/PC systems.

plied in Table V. Plots of average modulus and strength (as normalized by the pure thermoplastic property) versus LCP content for the LCP/PS, LCP/SPS, and LCP/PC systems (combined for easier comparison) are given in Figures 8 and 9. Also given in the plots is the prediction by the rule of mixtures for the case of no adhesion between the LCP and the thermoplastic. If the interfacial adhesion does not exist between the LCP and the thermoplastic, the volume occupied by the LCP can mechanically be regarded as voids and the simple rule of mixtures yields the following equations for the composite modulus (E_c)²⁸ and composite strength (σ_c).^{29,30}

$$E_c = (1 - V_f)E_m \quad (1)$$

$$\sigma_c = (1 - V_f)\sigma_m \quad (2)$$

where V_f represents the volume fraction of the fiber (reinforcement), LCP, and E_m and σ_m are the tensile modulus and strength of the pure thermoplastic matrix, respectively.

The tensile tests performed on the LCP/PS system showed a sharp decrease in strength with an increase in LCP content (Fig. 9), while composite modulus values were close to the predicted values

for the case of no interfacial adhesion between the LCP and the PS (Fig. 8). This is because the rule of mixtures does not take into account the discontinuities (interfaces between LCP particles and the thermoplastic) in the material at which the stresses are intensified (when there is no adhesion between the LCP and the thermoplastic matrix or when the bond fails at some stress level for the case of some interfacial bonding), resulting in cracking and failure at a stress level quite below the predicted strength. On the other hand, the modulus is related to the stiffness of the material before fracture and thus is not significantly affected by the discontinuities at the LCP/thermoplastic interfaces.

The strength of the LCP/SPS composite also decreased by an increase in LCP content; however, the composite strength for any composition was higher for the LCP/SPS system than for the LCP/PS system (Fig. 9). The composite modulus, on the other hand, did not change significantly with LCP addition, even with the addition of 25% LCP (Fig. 8). Note that the formation of a composite plate with 25% LCP was not possible for the LCP/PS system.

Unlike the LCP/PS and LCP/SPS systems, no significant decrease either in modulus or in strength was observed for the LCP/PC system (Figs. 8 and 9). Instead, as a result of stronger interfacial bonding, the addition of LCP to PC generally increased the tensile modulus and the strength of compression-molded plates. However, the higher the LCP content was, the lower the improvement was. This was possibly due to non-uniformities in mixing/dispersion/wetting at high LCP concentrations.

SUMMARY AND CONCLUSIONS

The LCP which was formed by an interfacial polycondensation reaction from TC and DHDPS was so stable and molecularly rigid that it did not melt but degraded at about 320°C. Mixtures of the LCP with PC, PS, and SPS were first tried to be solution blended. Various solvents were tried, but not one solvent was found to dissolve both the LCP and the thermoplastic. LCP/thermoplastic systems were then processed by compression molding at a temperature at which the thermoplastic matrix was in the melt state. The composites of LCP/PC and LCP/SPS were formed in 1, 5, 10, and 25% weight percentages of LCP. However, the 25% LCP/PS system could not be fabricated, pos-

sibly because of the lack of proper interfacial bonding. The nitration of PS was also tried, but it was not possible to process it because the melting and degradation of nitrated PS occurred simultaneously.

Both LCP/PS and LCP/SPS systems revealed two-phase morphology with well-defined interfaces between the LCP and the thermoplastic, which suggested poor interfacial adhesion. However, a composite plate of 25% LCP/SPS, unlike 25% LCP/PS, was formed, which could be an indication of some improvement in the interfacial bonding by the sulfonation of PS. The strength of both composites decreased by an increase in LCP content; however, the composite strength for any composition was higher for the LCP/SPS system than for the LCP/PS system.

The LCP/PC system also revealed a two-phase morphology; however, the interfaces between the LCP domains and the PC matrix were not so well defined, indicating better interfacial adhesion than the two previous systems studied. The strong bonding between the LCP and PC resulted in a significant improvement in the mechanical behavior of PC by LCP addition. Future work will investigate the possibility of synthesizing the LCP as meltable (i.e., processable in the melt state) by introducing flexible spacers, side chains, or kinks in the main chain of the LCP molecule.

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