

Synthesis and Characterization of Semi-Interpenetrating Liquid Crystalline Polymer Networks LCP/PAN

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ABSTRACT: A new type of interpenetrating polymer network based on a liquid crystalline polymer: a semi-interpenetrating liquid crystalline polymer network comprising the liquid crystalline polymer (LCP) PET/60PHB and crosslinked polyacrylonitrile (PAN) (for short: semi-ILCPN LCP/PAN) was successfully prepared. The compatibility and thermal properties of the semi-ILCPNs with different amounts of the crosslinking agent were investigated by FTIR, SEM, DSC, and TGA. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 349–354, 1998

Key words: IPN; semi-IPN; LCPs; ILCPN; semi-ILCPN

INTRODUCTION

Polymer blends of thermotropic liquid crystalline polymers (TLCPs) with thermoplastics have provoked increasingly focused interests for their great potentiality for high-performance composites with superior mechanical properties, ease of processability, and good thermal stability.^{1–4} However, their practical application in product design and engineering has been restricted by the poor compatibility between the TLCPs and the thermoplastic matrix due to self-aggregation and phase separation which result in rough dispersion and poor adhesion of the interfaces toward each other.^{5,6} Three different approaches have been used previously for enhancing the compatibility between liquid crystalline polymers (LCPs) and thermoplastic polymers including (1) the synthesis of block copolymers consisting of the rigid-rod LCP and flexible nonliquid crystalline polymer segments^{7–10} and used as a compatibilizer, (2) the preparation of graft copolymers with rigid-rod backbones and the flexible side chains used as a

compatibilizer,¹¹ (3) the selecting of TLCP and polymer matrix pairs with active sites that can promote specific interactions, such as acid/base or hydrogen bonding.¹² Based on the extensive and systematic studies on the conventional IPNs,^{13–15} we believe that interpenetrating liquid crystalline polymer networks (ILCPNs)¹⁶ might also be another promising effective method for enhancing the compatibility between LCPs and thermoplastics. It is well known that the phase separation in IPNs might be restricted to different extents by the crosslinks, so that we could expect to control the microphase dimension of the system of TLCPs/thermoplastics and obtain high mutual dispersity blend systems.

PET/60PHB, a well-known thermotropic liquid crystalline copolyester with a rigid aromatic unit and a flexible methylene spacer, has been studied extensively since the initial work of Jackson and Kuhfuss.^{17–19} By varying the molar ratio of the aliphatic-containing poly(ethylene terephthalate) (PET) to the *p*-hydroxybenzoic acid (PHB) block, one can obtain TLCPs with a range of melting points and physical properties. Liquid crystalline behavior is observed only in a copolyester of at least 35% molar PHB. The optimum mechanical properties (strength, modulus, impact) and

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minimum viscosity are obtained in a copolyester of 40/60 molar ratio, namely, PET/60PHB. Therefore, PET/60PHB was chosen as a LCP component of semi-ILCPNs throughout our research work.

In this article, we describe the method of synthesizing a new kind of IPN based on LCPs: semi-ILCPN LCP/PAN. The purpose of this work was to develop a new approach for enhancing the compatibility of LCPs with the thermoplastic matrix in order to offer a new possibility of making specialty polymer blends. The effect of the content of the crosslinking agent of PAN on the morphology and thermal properties of semi-ILCPNs was investigated by FTIR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Furthermore, studies on other semi-ILCPN systems such as semi-ILCPN LCP/PC and semi-ILCPN LCP/PS are being undertaken in our laboratory.

EXPERIMENTAL

Materials

p-Hydroxybenzoic acid (PHB) was recrystallized from hot water and dried under a vacuum at 60°C. Acrylonitrile (AN) and the crosslinker ethylene glycol dimethacrylate (EGDMA) were purified by distillation under a vacuum. Azobisisobutyronitrile (AIBN) was recrystallized from acetone and dried under a vacuum. Dimethyl terephthalate (DMT), ethylene glycol (EG), and acetic anhydride (Ac₂O) were used without purification, and the PET oligomer was prepared by the method described in ref. 20.

Synthesis of Liquid Crystalline Polymer PET/60PHB

An appropriate amount of the PET oligomer, PHB, Ac₂O, and the catalyst Zn(OAc)₂·2H₂O were added into a three-neck flask. The reaction mixture was heated to 140°C for 1 h under nitrogen; then, the reaction temperature was increased gradually to 230 and 275°C in 60 and 30 min, respectively, and kept at 275°C for another 30 min. Afterward, the reaction system was evacuated to 2 mmHg in 1 h and kept at this pressure about 30 min. The final product was extracted in a Soxhlet with DMF for 24 h and dried under a vacuum at 70°C for 48 h. The inherent viscosity of PET/60PHB was 0.912 dL/g measured at a

concentration of a 0.5 dL/g solution in a phenol/1,1,2,2-tetrachloroethane mixture (1 : 1 w/w) at 25°C.

Synthesis of Semi-ILCPN LCP/PAN

The sequential semi-ILCPN LCP/PAN preparation procedure utilized can be described as follows: To speed up the swelling process, the LCP PET/60PHB was first swollen in a solvent mixture of DMF/trifluoroacetic acid (1 : 2 w/w) which was subsequently removed, then LCP was swollen with acrylonitrile containing the crosslinking agent EGDMA and 0.8% AIBN as the initiator. The swollen LCP was removed from the remaining solution by filtering and put into a glass ampule. Evacuated and flushed with nitrogen three times, the ampule was sealed under a N₂ atmosphere and then placed in a water bath for polymerization *in situ* at 60°C for 24 h and 90°C for 4 h, respectively. With the formation of the crosslinked PAN network interlocked with LCP, a semi-ILCPNs sample was obtained. Each sample was extracted with DMF and trifluoroacetic acid, respectively, to remove any unreacted AN monomer, uncrosslinked PAN, and LCP which did not interpenetrate with the PAN network. All semi-ILCPN samples were dried at 70°C for 3 days under a vacuum before characterization.

Characterization of semi-ILCPN LCP/PAN

The FTIR spectra were collected on a Nicolet 750 FTIR spectrometer. The DSC and TGA were performed on a DuPont 1090B thermal analyzer under a nitrogen flow at a heating rate of 20°C/min. A Hitachi S-450 scanning electron microscope (SEM) was used for the fractured surface observation of semi-ILCPN LCP/PAN films obtained by hot compression at 220°C under a N₂ atmosphere. The fractured surface was sputtered with a 150 Å layer of evaporated gold before entering the SEM. The degree of swelling was determined by the equation $(w_s - w_d)/w_d$,²¹ where w_s is the weight of the swollen LCP and w_d is the weight of the dried LCP. The weight measurements were carried out by using an electronic balance with an error of ±0.001 g and the final value is an average of three determinations.

RESULTS AND DISCUSSION

The PET/60PHB was synthesized by an *in situ* acetylation reaction²⁰ in which the PET oligo-

Table I Thermal Characteristics of Samples with Different Contents of EGDMA of PAN from DSC and TGA Measurements

Samples	EGDMA (wt %)	DSC		TGA ^a
		T_{g1} (°C)	T_{g2} (°C)	T_{id} (°C)
PAN 1	0.5		101	270
PAN 2	1.0		102	276
PAN 3	2.0		105	303
LCP(PET/60PHB)		64		434
Blend ^b	0.5	64	101	268
Semi-ILCPN 1 ^b	0.5	67	101	284
Semi-ILCPN 2	1.0	70	98	299
Semi-ILCPN 3	2.0		91	333

^a The initial decomposition temperature.

^b The weight ratio of the LCP and PAN in the blend and all semi-ILCPNs is 32/68.

mers, PHB, Ac₂O were used. It is found that compared with Jackson and Kuhfuss's method¹⁷ used in the preparation of PET/PHB the *in situ* acetylation method can provide a faster reaction rate and the copolyester with a higher inherent viscosity can be obtained simultaneously. The T_g of PET/60PHB that we synthesized was 64°C (see Table I), lower than that which Jackson and Kuhfuss obtained. This is presumably due to the lower inherent viscosity of the PET oligomers ($\eta_{inh} = 0.146$ dL/g) that we used in the synthesis of PET/60PHB. A similar T_g for this copolyester was also reported by Takase et al.²² and Stachowski and Dibenedetto.²³

Different from the preparation of a conventional sequential IPN, for which polymer network I is swollen with the second monomer II plus its own crosslinking agent and initiator and then polymerized *in situ*, here, the LCP PET/60PHB was first preswollen in a solvent mixture and then was swollen with the monomer AN containing the crosslinker EGDMA and the initiator AIBN, by which a slightly flocculent swollen PET/60PHB was obtained and the maximum degree of swelling of this copolyester in AN was up to 1.47. Finally, this is followed by the polymerization and crosslinking of PAN *in situ*. Most of solvent mixture could be removed by filtering under pressure reduction after preswelling; only about 6% still remained in the reaction system, which did not affect the radical polymerization of AN.

FTIR is a useful tool which can provide some information about the interactions between chains. The interactions between LCP and PAN in semi-ILCPNs were confirmed using FTIR spectroscopy. Figure 1 illustrates the FTIR difference

spectra of semi-ILCPNs and the blend consisting of PET/60PHB and PAN minus pure LCP. From Figure 1, we could find that the difference spectrum of the blend sample minus pure LCP was completely identical with that of PAN, while the FTIR difference spectrum of semi-ILCPNs minus pure LCP was becoming more complex than the spectrum of PAN, clearly indicating that an interaction caused by interpenetrating has, in fact, taken place between LCP and PAN during the preparation of these semi-ILCPNs, which could result in enhancement of compatibility of LCP with PAN.

Investigations^{24–26} on the blends of polymers revealed that the glass transition behavior of blends is affected mostly by the compatibility between polymers. If two polymers are miscible and form a homogeneous mixture, only one T_g that is intermediate between the T_g 's of polymers 1 and 2 would exist. If separate, distinct phases occur, each phase should exhibit its own independent thermal response. Thus, two T_g 's corresponding to the T_g 's of the component polymers should occur. In the case of partially miscible polymer blend systems, the component polymer T_g 's would shift toward one another. So, important information about the compatibility of LCP with PAN in semi-ILCPNs would be obtained by the DSC measurements. Table I lists the glass transition temperatures of the blend and semi-ILCPNs with different contents of the crosslinking agent, along with PAN homopolymers. The typical DSC thermograms of corresponding samples are also shown in Figure 2. It can be seen that the blend exhibited two distinct T_g 's, at 64 and 101°C, corresponding to those of pure LCP and PAN, which indicated a

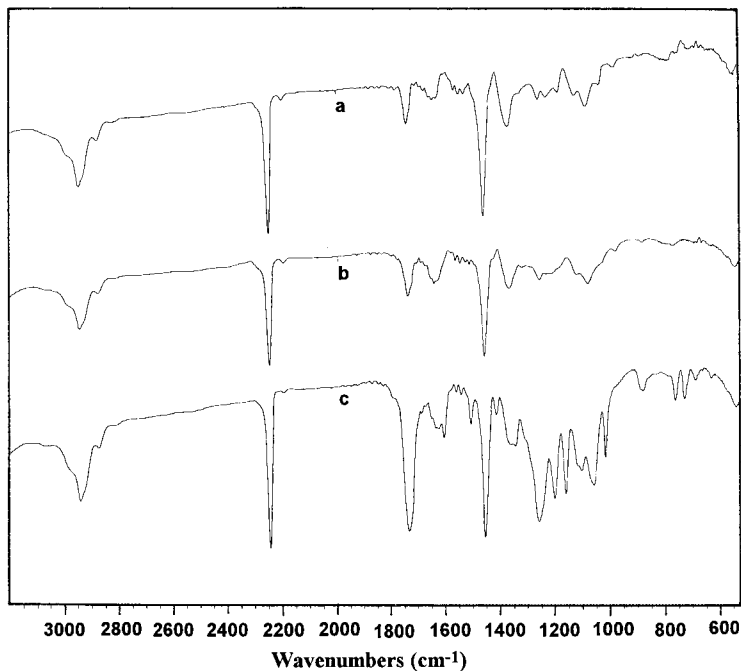


Figure 1 FTIR spectra of (a) PAN 1, (b) difference spectrum of blend minus LCP, and (c) difference spectrum of semi-ILCPN 1 minus LCP. The compositions of the samples are listed in Table I.

complete immiscibility between the two components.

The semi-ILCPNs containing different contents of EGDMA showed an obvious inward shift

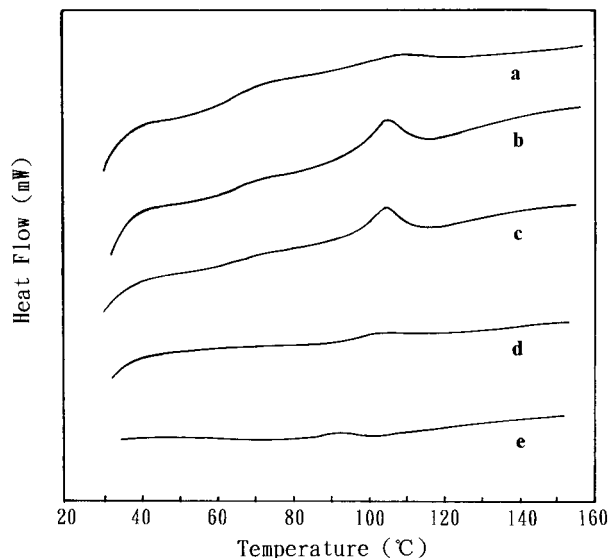


Figure 2 DSC thermograms of (a) LCP, (b) blend, (c) semi-ILCPN 1, (d) semi-ILCPN 2, and (e) semi-ILCPN 3. The compositions of samples are listed in Table I.

of the T_g 's (in the case of semi-ILCPN 3, the T_g 's of the LCP phase were not observed) and the greater the amount of EGDMA added, the more the T_g 's of the component polymers shifted toward each other, obviously revealing that the compatibility between LCP and PAN was improved by the forming of semi-ILCPNs in which enforced compatibility has taken place due to forming a "snake-cage" structure,²⁷ where the linear LCP phases and crosslinked PAN networks were interlocked toward each other.

Furthermore, to determine the thermal stability of the samples, thermogravimetric analysis of semi-ILCPNs, and also of the blend and the PAN homopolymers, was carried under a N_2 atmosphere at a scanning rate of $20^\circ\text{C}/\text{min}$; the results are collected in Table I. It is obvious that the initial thermal decomposition temperatures of all the semi-ILCPNs were considerably higher than that of the pure crosslinked PAN and its blend. It means that the heat resistance of PAN could be enhanced by forming semi-ILCPNs with LCP. In addition, the experimental results also show that the initial thermal decomposition temperature increases with increasing the content of EGDMA of PAN; this is because the content of EGDMA affects directly the effective phase mixing

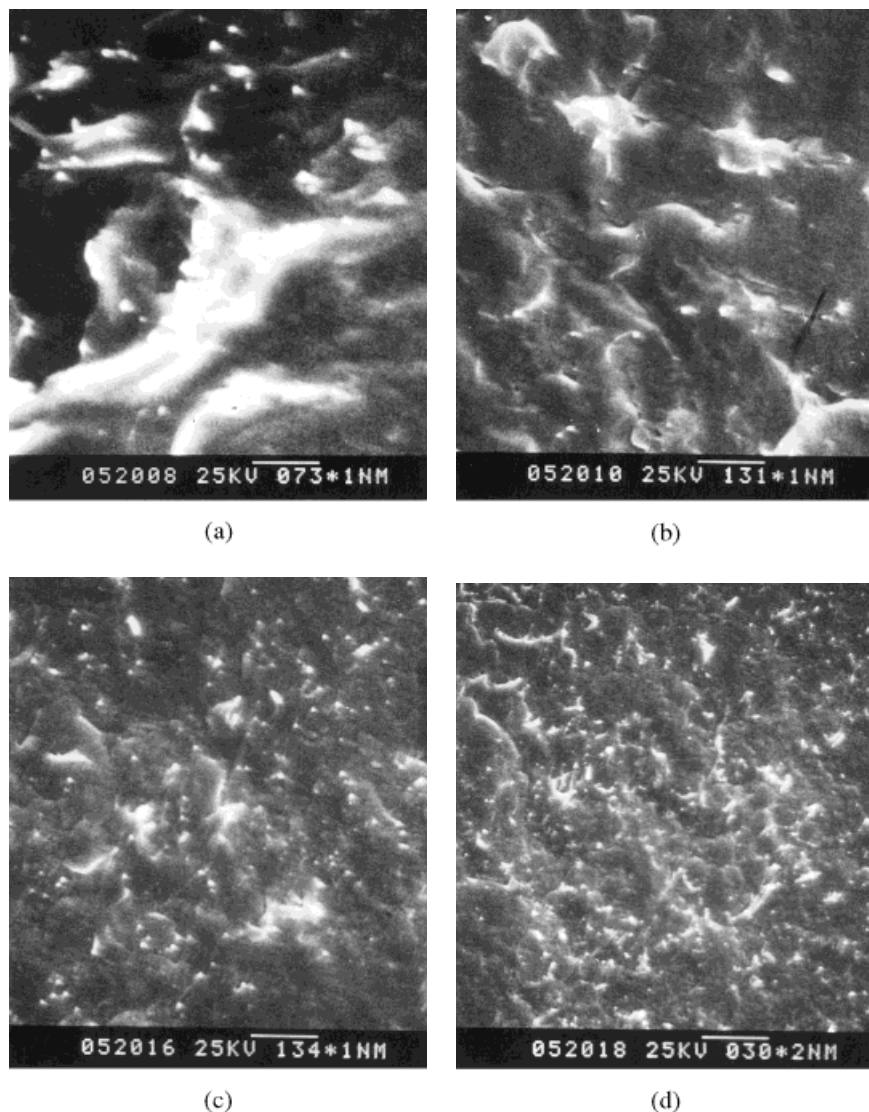


Figure 3 SEMs of fractured surfaces of (a) blend, (b) semi-ILCPN 1, (c) semi-ILCPN 2, and (d) semi-ILCPN 3. The compositions of samples are listed in Table I.

and synergistic effect²⁸ of PAN with LCP, and the morphology of the final products is different with varying contents of EGDMA, which could be also confirmed by SEM for the fractured surface of the semi-ILCPNs.

The fractured surface of the semi-ILCPNs with different contents of the crosslinking agent, as well as of blend, were obtained using SEM, which can give direct information concerning the morphology of these materials. The SEM micrographs in Figure 3 clearly show that the morphology of the blend [Fig. 3(a)] is typical for a phase-separated system characterized by the rough dispersion of the LCP phase in the continuous PAN matrix. In the case of semi-ILCPNs, however, the

compatibility of PAN with LCP was improved considerably and the LCPs were well dispersed in the matrix [Fig. 3(c,d)], which suggests that semi-ILCPNs have been formed between LCP and PAN during the polymerization of AN in the presence of LCP. This is in good agreement with the results obtained by the DSC measurements.

CONCLUSIONS

In this article, a new approach for enhancing the compatibility between LCP and the thermoplastic matrix was introduced, by which well-dispersed composite semi-ILCPNs consisting of LCP and

crosslinked PAN were obtained, which show better thermal stability than that of the corresponding blend. With the increase of the amount of the crosslinking agent, the compatibility between LCP and PAN would be improved, which resulted in obvious enhancement of the initial thermal decomposition temperature of the materials. In addition, we confirm that the potential of semi-ILCPNs as a new system of an LCP combination with thermoplastics needs to be explored extensively in search of the ways of making new, special high-performance polymer materials. More detailed studies about this system are being undertaken in our laboratory, including (1) the effects of the semi-ILCPN compositions on the liquid crystalline phase transition behavior and the investigation of morphology control and (2) the practical application of semi-ILCPNs as a compatibilizer in polymer blend systems.

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