

Mechanical Performance of Blends of Thermotropic Liquid Crystalline Polymer Spheres-Dispersed Polycarbonate

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ABSTRACT: Liquid crystalline polymer (LCP) blends with a thermotropic LCP dispersed in the form of microspheres is studied to show the role of LCP spheres. Polycarbonate (PC), p-hydroxybenzoic acid-poly(ethylene terephthalate) copolyester, and random styrene-maleic anhydride copolymer are used as the matrix, the dispersed phase, and the compatibilizer, respectively. A scanning electron microscopy observation shows the formation of LCP spheres with improved interfacial adhesion in the injection-molded samples via compatibilization. The mechanical tests show in-

creased modulus, elongation at break, and fracture-absorbed energy of blends of LCP spheres-dispersed PC. This shows an optimistic potential for the dispersed LCP phase, in spite of its morphology in the form of fibrils for reinforcing the matrix or in the form of microspheres for toughening the matrix. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1493–1499, 2003

Key words: polycarbonates; liquid-crystalline polymers; morphology; mechanical properties; compatibilization

INTRODUCTION

Thermotropic liquid crystalline polymers (LCPs) are a group of polymers that are composed of rigid or semi-rigid rodlike molecules, and they can be readily deformed and oriented through a flow field in blending with conventional thermoplastic polymers. The fibrillation of LCPs is usually maintained by cooling after processing, so that the resulting so-called *in situ* polymer composite has attracted considerable attention.^{1–5} One of the features of *in situ* composites is their skin-core structure.

The dispersed LCP phase in the skin region readily deforms into long fibrils whereas that in the core region usually forms a microsphere structure, because of a smaller velocity gradient and slower cooling. The study on the fibrillation of LCPs has revealed that it depends on the characteristics of the LCPs themselves⁶ and their processing conditions, such as the shear rate,⁷ melt drawing,⁸ LCP concentration,⁹ and viscosity ratio of the LCP to the matrix.¹⁰ The LCP fibrils can act as a reinforcing agent, like carbon fibers and glass fibers in fiber-reinforced plastics. However, the role of LCP microspheres in the core section of *in situ* composite has been studied less. One purpose of the present work is to reveal on what and how the LCP microspheres act.

There are studies demonstrating an increase in toughness with rigid-particle fillers in certain systems.^{11,12} Such systems toughened by rigid-particle fillers would result in substantial improvement of the stiffness of the blend and overcome the decrease of the rigidity that commonly occurs in rubber-toughened blends. If LCP particles can improve the toughness of *in situ* composites, then it is possible to design an optimal skin-core structure with particles in the core region improving the toughness and fibrils in the skin region increasing the modulus and strength. Such a structure is expected to be similar to the ideal structure of natural materials such as bamboo.

A system with a uniformly dispersed microsphere structure but without any fibrils is considered first in order to learn the role of LCP microspheres. He and Zhang⁶ found that a wholly aromatic copolyester LCP only formed uniformly distributed spherical droplets in the matrix of polycarbonate (PC). In the present work, blends of PC with two LCPs were considered: one is p-hydroxybenzoic acid-poly(ethylene terephthalate) copolyester (PHB-PET), a random liquid crystalline copolyester, and the other is Vectra A950. However, two evidently different morphologies were observed: the LCP phase in PC/Vectra A950 blends formed long fibrils even under a very small shear rate, but the LCP phase in PC/PHB-PET had a small deformation. Thus, blends of PC/PHB-PET were eventually chosen.

Interfacial interaction is a very important factor in multiphase polymer systems. Strong interactions result in good adhesion and efficient stress transfer from the matrix to the dispersed phase. PC is partially

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miscible with the PET portion of LCP, whereas PC is immiscible with the PHB portion of the LCP.^{13,14} Therefore, the compatibility between PC and PHB-PET with a PHB ratio higher than 70% is predicted to not be good. Transesterification is an interesting method to improve the compatibility of PC/PHB-PET blends.^{15,16} However, during conventional processing conditions, such as extrusion and injection, the extent of transesterification is so low that the compatibility of the PC/PHB-PET blend is evidently not improved. Thus, adding a third component to improve the compatibility of this system is meaningful. Furthermore, the improvement of the compatibility between the matrix and the LCP tends to shift the fibrous LCP morphology of the uncompatibilized blends into the droplet domains in the compatibilized blend.¹⁷ A copolymer is often used as a compatibilizer, based on the compatibility or reactivity of its segments with at least one of the blend components. Copolymers can be generated *in situ* during processing^{18,19} or added separately.^{20–22}

The reactive monomer maleic anhydride (MA) can be copolymerized with other monomers or grafted to other polymers. Such copolymers, which contain the reactive anhydride functional group, can be used to improve the compatibility of some immiscible blends containing hydroxyl or amino groups such as polyamides, polyesters, and so on. Baird et al.^{23–25} reported that MA-grafted polypropylene (PP-g-MA) effectively improved the compatibility of PP/Vectra B950, PP/Vectra A950, and PP/LC-3000, causing higher modulus and higher strength and homogenizing the dispersed phase unlike that without PP-g-MA. Seo et al.^{26–28} used MA-grafted ethylene-propylene-diene monomer to improve the compatibility of blends of PA46/Vectra B950, PA6/Vectra B950, and PBT/Vectra B950.

Random styrene-MA copolymer (SMA) containing about 5–33 mol % MA has the potential of being an excellent modifier and compatibilizer for thermoplastics and polymer alloys.²⁹ In the present work, SMA was used as the third component in PC/LCP blends. The PC and LCP were fixed at a weight ratio of 80:20, but the content of SMA was varied at 2, 4, 6, and 8 wt %. The compatibility and mechanical properties were studied. The binary blend of PC/PHB-PET was also studied as a reference.

EXPERIMENTAL

Materials

The materials used in this study were PC, PHB-PET (LCP), and SMA. The PC (T1260, Shanghai Zhonglian Chemical Plant, Shanghai) has a number-average molecular weight of 26,000. The thermotropic LCP was a copolyester of PHB/PET with 75 mol % PHB and 25

mol % PET (Chengdu Silicone Research Center, Chengdu, China), hereafter simply referred to as LCP. The third component, SMA, which was the compatibilizer, was a random copolymer (Shanghai Petrochemical Institute, Shanghai) with 18 wt % MA.

Blending and injection molding

The polymers were premixed to give PC/LCP/SMA composition ratios of 80/20/0, 80/20/2, 80/20/4, 80/20/6, and 80/20/8. All the materials were carefully dried at 90°C under a vacuum for at least 24 h before melt blending and molding.

Blending was completed in a CS-194 Mini-Max Extruder (CSI Co.). The rotor temperature and the head temperature were set at 300°C. The voltage of the drive motor on the indicator was set at 50%. The extrudates were cooled by air and pelletized.

Cylindrical dumbbell samples with an overall length of 22 mm and a narrow section diameter of 1.58 mm were injection molded by using a CS-183 Mini-Max Molder (CSI Co.).

Extraction experiment

The solvent 1,2-dichloroethane was used to dissolve the matrix PC and SMA from these injection-molded bars. After the sample was dissolved for 6 h, the LCP phase was separated by centrifuging the solution and decanting the supernatant liquid. The centrifuged LCP phase was immersed in fresh solvent and separated 4 more times. Finally, a drop of the residue was thoroughly dried.

Morphology observations

The morphological observation with a scanning electron microscopy (SEM) microscope (Hitachi S530) was carried out with injection-molded samples frozen and broken in liquid nitrogen. In order to obtain the average LCP particle size, the LCP particles were also observed and measured after the PC matrix and SMA were extracted with a selective solvent (1,2-dichloroethane). The statistical analysis of the size of the LCP particles was conducted on more than 200 particles.

Differential scanning calorimetry (DSC) analysis

The DSC measurements were conducted on a Perkin-Elmer DSC 7. The samples were heated from 25 to 280°C at a heating rate of 20°C/min and maintained for 5 min to eliminate any thermal history. Then the samples were quenched to 25°C and reheated from 25 to 280°C at a heating rate of 20°C/min. The DSC curves of the samples were taken during the second heating.

TABLE I
Glass-Transition Temperatures (T_g) of Component
Polymers and Their Blends

Composition	T_g (°C)
PC	150.0
PC/LCP 80/20	147.0
PC/LCP 80/20 (blending for 20 min)	144.5
PC/LCP/SMA 80/20/2	145.4
PC/LCP/SMA 80/20/4	141.2
PC/LCP/SMA 80/20/6	145.7
PC/LCP/SMA 80/20/8	145.7
LCP	111.0
SMA/LCP 70/30 (30-min blending)	135.0
SMA	140.0

Mechanical tests

The tensile strength and modulus of the dumbbell samples were measured with an Instron 1122 Universal tensile tester. The tests were carried out at a cross-head speed of 5 mm/min. The average of at least five tests was reported. The relative humidity at the test was about 36%.

RESULTS AND DISCUSSION

Formation of LCP spheres in PC blends via compatibilization

Interfacial interaction improved by addition of SMA

The DSC method has been extensively used for the analysis of the phase behavior of polymer blends. The glass-transition temperatures (T_g) of the starting materials and their blends are summarized in Table I. The T_g values of PC and LCP are about 150.0 and 111.0°C, respectively. Pure LCP shows a much lower heat flow in the glass-transition zone than pure PC. The glass transition of LCP is not evident enough to be detected in their blends. The T_g of PC in the binary blend of PC/LCP is 147.0°C. The small shift of the T_g indicates that PC and LCP have poor compatibility and phase separation in these blends. Ternary blends of PC/LCP with SMAs of different compositions are studied to show the shift of the T_g values of the PC-rich phase toward the T_g of LCP. The T_g shift is up to 8.8°C in 80/20/4 PC/LCP/SMA, compared with that of pure PC. This indicates that PC and LCP become more compatible in the ternary blend containing SMA. Note that when over 4 wt % SMA is added, the shift of the T_g is restrained.

The increase in compatibility and the improvement in interfacial adhesion caused by the addition of SMA can be ascribed to the occurrence of a chemical reaction or an interaction such as hydrogen bonding. After blending 80/20 PC/LCP for 20 min, the T_g becomes 144.5°C, which is shifted by 2.5°C compared to that of the binary blend with the usual blending time (~2 min as other samples). This indicates that transesterification has po-

tential for improving the compatibility of the PC/LCP blend by increasing the blending time. In addition, 70/30 SMA/PHB-PET was blended under the preservation of N_2 in a Haake mixer at 280°C for 30 min. The T_g of SMA shifts to 135.0°C, compared to that of pure SMA at 140°C. Yoon et al.³⁰ studied the reaction effect of PET and SMA blends by DSC measurements and drew the conclusion that the reaction between ester groups and MA occurred during melt mixing at 280°C for 30 min. These results show that it is possible to compatibilize PC/LCP blends with the addition of SMA.

The SEM micrograph in Figure 1(a) shows the fracture microstructure of the PC/LCP blend in the core section. This sample has a distinct two-phase morphology (i.e., a continuous PC phase and a dispersed LCP phase). The LCP particles are severely pulled out during the fracture of the samples. All the spheres and holes have smooth surfaces, and microvoids are found around the LCP particles. All these phenomena indicate poor interfacial adhesion between the LCP and PC phases. SEM micrographs in the core section of PC/LCP/SMA ternary blends are shown in Figure 1(b–e). Compared with that of the PC/LCP shown in Figure 1(a), the morphology of the ternary blends changes dramatically. Less LCP spheres were pulled out and less cavities were seen. The interfacial adhesion between PC and LCP is tight without microvoids around them. Thus, it is evident that the interfacial adhesion between PC and LCP is improved.

Morphology of dispersed LCP phase

Figure 2(a,b) shows the fracture microstructure of the injection-molded 80/20 PC/LCP blend in the core and skin sections, respectively. The LCP phase in the core region appears as microspheres, while that in the skin layer is partially deformed into ellipsoids. Figure 3(a,b) shows the fracture microstructure of the injection-molded 80/20/4 PC/LCP/SMA blend in the core and skin, respectively. The addition of SMA to the blend influences the morphology of the skin–core structure. The LCP phase in the skin layer is less deformed and appears as microspheres. Hence, the trend of the formation of a skin–core structure in the *in situ* blends is weakened.

After the PC matrix and the third component SMA were extracted, the LCP particles were photographed by the SEM method. The change of the average size of the LCP particles with increasing SMA is plotted in Figure 4. The average size of the dispersed phase is reduced from 0.73 μm in the binary blend to 0.56 μm in the ternary blend with 4 wt % SMA. However, after there is over 4 wt % SMA, the average size of the LCP particles increases to a small extent. When SMA content is up to 8 wt %, the average size is nearly equal to that without SMA. This may have two causes: one is that excessive added SMA forms a new phase itself and does

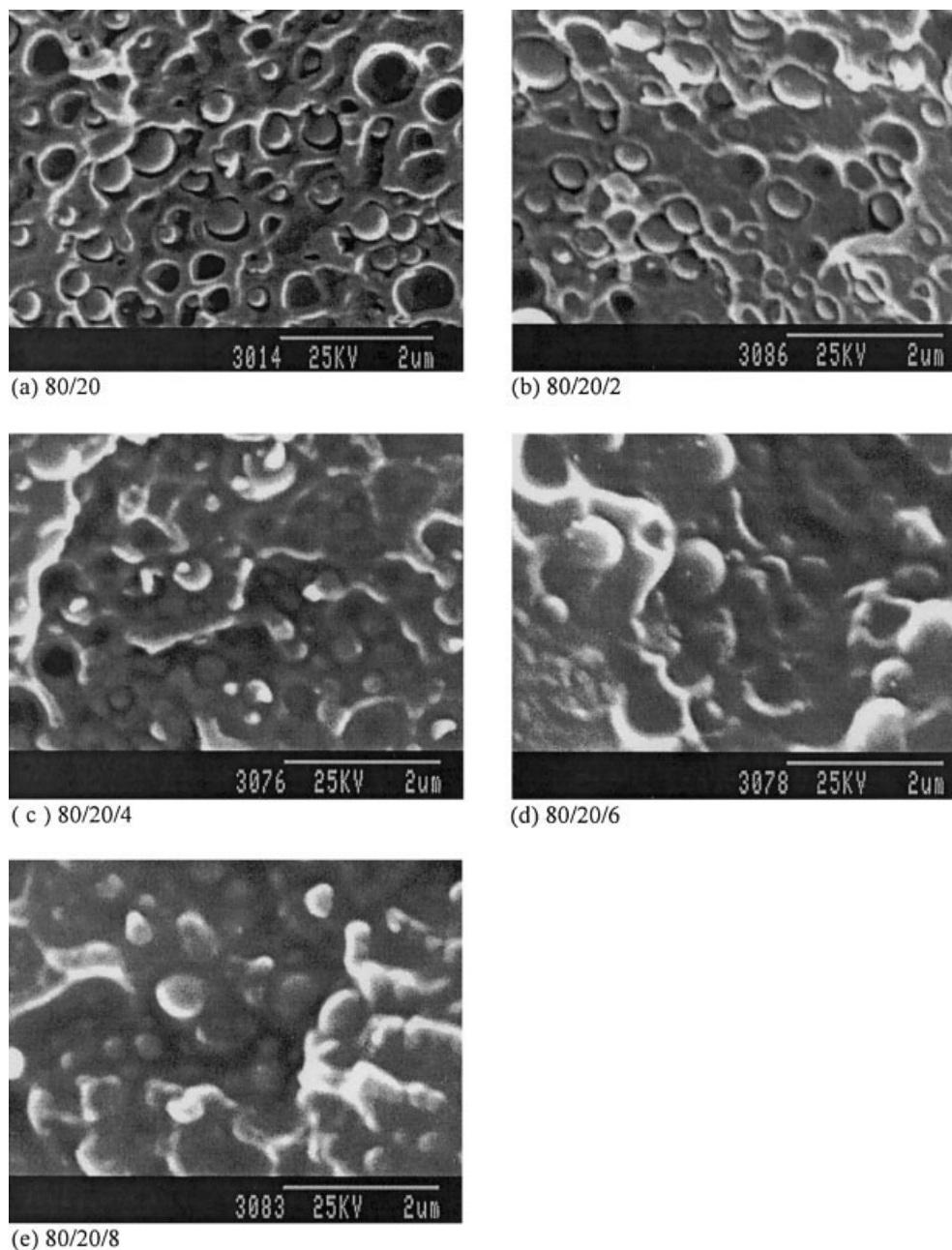


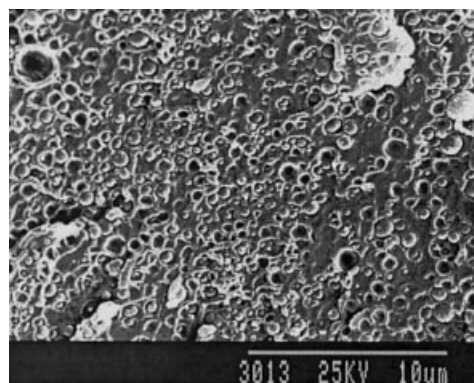
Figure 1 SEM photographs of fractured surfaces of PC/LCP/SMA at the core region with weight ratios of (a) 80/20, (b) 80/20/2, (c) 80/20/4, (d) 80/20/6, and (e) 80/20/8.

not play its role as a compatibilizer, and the other is that excess levels of SMA induce coagulation or flocculation of the dispersed LCP phase. The second explanation was also assumed by Seo et al.³¹ Nevertheless, the existence of only dispersed LCP spheres ensures the accuracy of the present investigation of the mechanical role of the dispersed LCP spheres in PC blends.

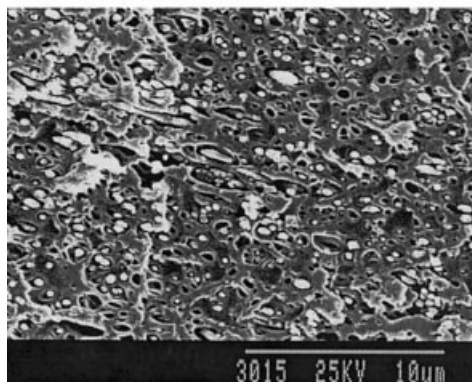
Mechanical properties

A material with a different structure and morphology has different physical properties. Table II lists the tensile performance of blends with and without SMA.

The tensile modulus of the PC/LCP blend is 2.93 GPa, which is increased by 31% compared to that of PC, because of the high modulus of LCP. When SMA is added, the tensile modulus of PC/LCP/SMA blends increases continually with increasing SMA content. The tensile modulus of 80/20/8 PC/LCP/SMA is 3.82 GPa, which is a 71% increase compared to that of PC. The tensile strength of the binary blend increases by 21% more than that of the pure PC. The tensile strength of the ternary blends with 2, 4, and 6 wt % SMA has only a small improvement over than that of the binary blend. When the SMA content is up to 8 wt



(a) core

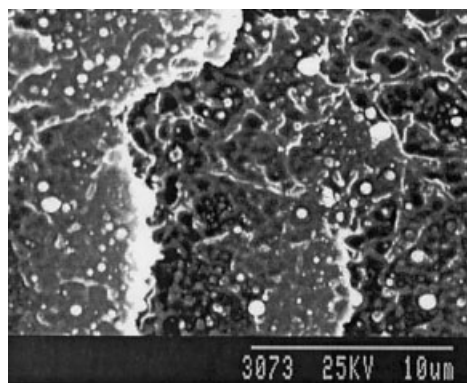


(b) skin

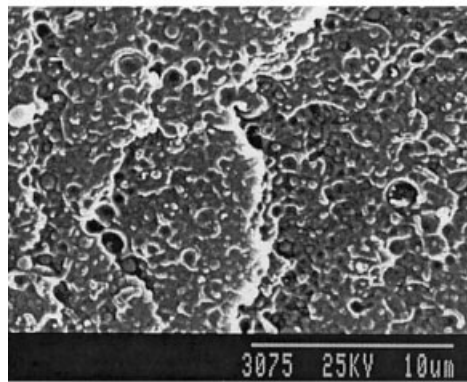
Figure 2 SEM photographs of fractured surfaces of injection-molded 80/20 PC/LCP (a) at the core and (b) at the skin.

%, the tensile strength decreases drastically, which indicates excess SMA impairs the performance of this system, similar to sulfonated polystyrene in PC/LCP blends.³² The elongation at break of the binary blend decreases from 73.1 to 17.2%, compared to that of pure PC, which exhibits the typical behavior of the short fiber reinforced composites. However, the elongation at break of PC/LCP/SMA blends with 2 or 4 wt % SMA is continually increased. The elongation at break of the blend increases by 77% to a value of 30.5% when the amount of SMA is up to 4 wt %. When up to 6 wt % SMA is added, the elongation at break begins to decrease. Thus, it is indicated that the PC/LCP/SMA blend with 4 wt % SMA has an evident improvement in the tensile strength, modulus, and elongation at break, although the LCP phase is in the form of microspheres.

Representative stress-strain curves for the PC/LCP blends with and without SMA are plotted in Figure 5. The binary blend and ternary blends with 2, 4, and 6 wt % SMA exhibit a yield point and some plastic deformation. The yield strengths are almost the same and are not as high as that usually expected in an *in situ* composite. However, the elongation at break in the ternary blends with 2 or 4 wt % SMA has an



(a) core



(b) skin

Figure 3 SEM photographs of fractured surfaces of injection-molded 80/20/4 PC/LCP/SMA (a) at the core and (b) at the skin.

evident improvement over that of the binary blend. This is because two factors, the morphology of LCP and the interfacial adhesion, should contribute to the mechanical performances of the *in situ* composites. For the ternary blend with 2, 4, or 6 wt % SMA, the improved interfacial adhesion favors the stress trans-

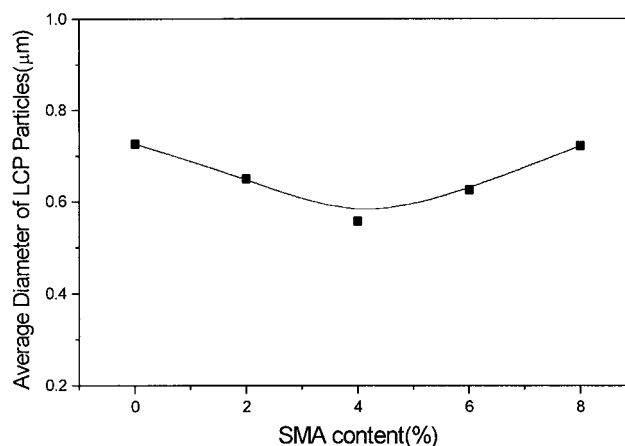


Figure 4 The average diameter of LCP particles versus the SMA content for injection-molded 80/20 PC/LCP and PC/LCP/SMA blends.

TABLE II
Tensile Performance of PC, PC/LCP, and Their Ternary Blends with SMA

Composition	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation at Break (%)
PC	75.8 ± 3.2	2.23 ± 0.12	73.1 ± 5.9
PC/LCP	80/20	92.0 ± 2.8	17.2 ± 2.6
PC/LCP/SMA	80/20/2	94.6 ± 1.9	26.5 ± 3.2
PC/LCP/SMA	80/20/4	93.9 ± 2.3	30.5 ± 5.1
PC/LCP/SMA	80/20/6	94.7 ± 4.5	17.5 ± 2.5
PC/LCP/SMA	80/20/8	78.1 ± 2.6	12.0 ± 3.5

fer at the interface but the dispersed LCP spheres cannot reinforce the matrix. Thus, the tensile strength has little change. However, the improvement in the interfacial adhesion and the formation of spheres-dispersed LCP both benefit the tensile elongation. This is ascribed to the following reason: proper SMA enhances the interfacial interaction between PC and LCP, which prevents fast fracture at the interface and benefits the plastic flow of PC.

The absorbed energy determined from the area under the tensile stress-strain curves of the blends is shown in Figure 6. The 80/20/4 PC/LCP/SMA possesses the highest energy-absorbing capability with a value of 318 mJ. The absorbed energy of the ternary blends with 2 and 4 wt % SMA is increased continually by 55 and 87%, respectively, compared with that of the binary blend at 170 mJ. This indicates that the dispersed LCP microspheres can absorb fracture energy and toughen the materials, except that the LCP fibrils benefit the reinforcing of the matrix. Therefore, it is possible to design an optimal structure of the *in situ* composite with a partial fibril morphology for reinforcing and a partial microsphere morphology for toughening. Such a structure with good strength and

good energy-absorbing capability is expected to have a similarity to the ideal structure of natural composite materials such as bamboo. The result in the present work only shows the possibility of the positive role of dispersed LCP microspheres in enhancing the mechanical performance of LCP blends. However, for practical purposes, the composition and processing conditions should be optimized.

CONCLUSIONS

PC/LCP blends with wholly dispersed LCP spheres were studied. By using a small amount of SMA, the LCP phase was uniformly dispersed as spheres and the interfacial interaction was improved. Dispersed LCP spheres with good interfacial interaction benefit the improvement of the tensile mechanical performance of the system, including the rigidity, elongation at break, and absorbed fracture energy. This shows good potential for the dispersed LCP phase, in spite of its morphology in fibril form for reinforcing the matrix or microsphere form for toughening the matrix. A balance of portions of the spherical and fibrous LCP

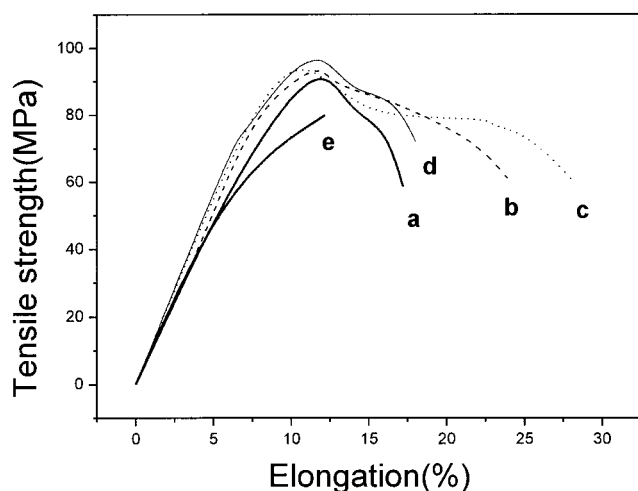


Figure 5 The tensile stress-strain curves of the typical blends with and without SMA: (a) 80/20 PC/LCP, (b) 80/20/2 PC/LCP/SMA, (c) 80/20/4 PC/LCP/SMA (d) 80/20/6 PC/LCP/SMA, and (e) 80/20/8 PC/LCP/SMA.

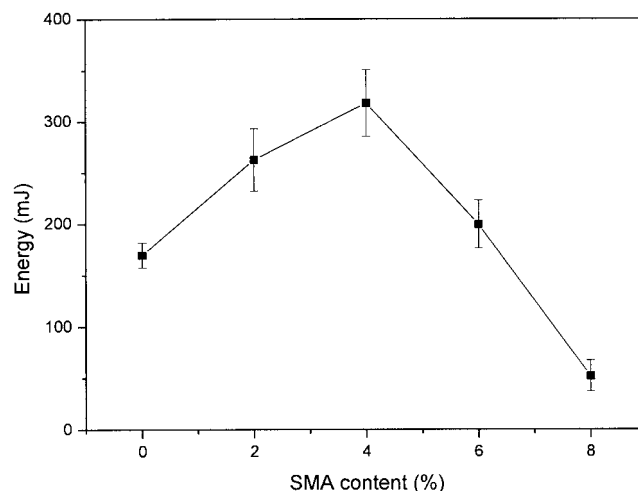


Figure 6 The absorbed energy determined from the tensile stress-strain curves of the typical blends with and without SMA: (a) 80/20 PC/LCP, (b) 80/20/2, PC/LCP/SMA, (c) 80/20/4 PC/LCP/SMA, (d) 80/20/6 PC/LCP/SMA, and (e) 80/20/8 PC/LCP/SMA.

morphologies will be a task for the design and control of optimized mechanical performance of LCP blends or *in situ* composites.

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