Improved Thermal and Mechanical Properties of Poly(butylene succinate) by Polymer Blending with a Thermotropic Liquid Crystalline Polyester

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ABSTRACT: A novel polymer blending system consisting of poly(butylene succinate) (PBS) and a thermotropic liquid crystalline polyester [LCP: a poly(4-hydroxybenzoate)-based polymer] was investigated in the presence and absence of a polycarbodiimide (PCD) and/or 1,1′-carbonyl biscaprolactam (CBC) as chain extenders. Although the LCP was immiscible with PBS, it formed elongated fibrous domains having an orientation in the flowing direction when an extensional flow was applied during the processing. Scanning electron micrograph (SEM) of the injection-molded polymer blends supported the distribution of micro fibrils of LCP in the PBS matrix by which the efficient toughening was provided. These blend specimens showed highly improved mechanical properties along with retaining high dynamic storage-moduli (E') up to the melting temperature of PBS. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39952.

INTRODUCTION

The increasing demand for light-weight, high-performance materials has been stimulating our current research and development for reinforced polymeric systems. While thermoset polymer composites showing high modulus and high strength are now widely used, the alternative thermoplastic polymer composites have acquired a rather limited application because of their difficult processing and structural control. However, the potential significance of the latter composites has continuously driven us to develop new systems by utilizing newly emerging polymer systems such as bio-based polymers that can be derived from non-petroleum biomass resources.[1–6] Since bio-based polymers are originated from biomass feedstock, they are considered to be composed of atmospheric carbon dioxide via photo-synthesis of plants. Incineration of the bio-based polymers, therefore, does not give any additional load of carbon dioxide to the atmosphere. In the last decade, much effort has been paid to develop such polymers in order to reduce the use of the conventional petroleum-based polymers that is believed to be a factor to cause environmental pollution. Among the biobased polymers thus developed, poly-L-lactides (PLLA), poly(3-hydroxyalkanoate)s (PHA), poly(butylene succinate)

(PBS), etc. have already been accepted as biodegradable polymers and utilized in a considerable amount by industries.[7,8]

PBS is a typical diol–diacid aliphatic polyester which was first synthesized by Carothers about 80 years ago.[9] Its industrial production, however, started in late 1990s, when its excellent biodegradability was recognized. Since then, it has been applied to packaging and mulching as temporary-use materials in spite of limited market size at present. The weakness of this polymer is originated from its poor thermal stability or low melting temperature (T_m: below 120°C), hindering its application to the ordinary plastic materials. Therefore, many studies have previously been conducted to improve the properties of PBS materials by polymer blending and copolymerization.[10–12] Typical examples are polymer blends of PBS/poly(ethylene oxide) (PEO) and diblock copolymers of poly(butylene carbonate)-*b*-poly(butylene succinate) (PBCBS) and poly(butylene succinate-*co*-propylene succinate) (PBSPS). None of these trials, however, have succeeded in preventing melt-down of PBS materials around 80°C which is considerably lower than the T_m of PBS.

On the other hand, liquid crystalline polymers (LCPs) have been utilized as blending modifiers of various polymers. They show higher stiffness, higher use temperature, and better
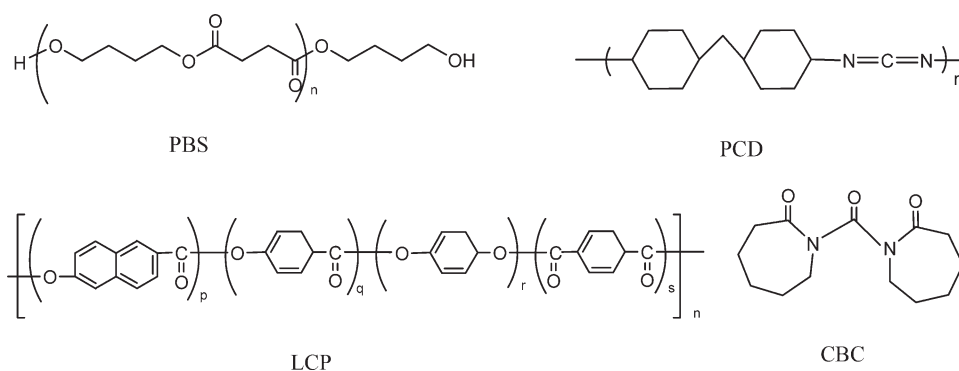
Scheme 1. Chemical structures of PBS, LCP, PCD, and CBC.

chemical resistance than the ordinary polymers. Particularly, thermotropic LCPs are versatile modifiers because of their easy processability. An important characteristic of thermotropic LCPs is that molecular orientation and ordering can be induced by application of shear on their melt. In particular, injection-molded or melt-extruded LCPs can readily acquire a molecular orientation state to exhibit anisotropic physical properties leading to exceptionally high mechanical properties that may correspond to those of fiber-reinforced plastics or even metals. This nature is often referred to as "self-reinforcing."[13] In fact, polymeric materials blended with LCPs exhibit improved properties due to this self-reinforcing structure where LCPs are arranged in fibrous forms in the polymer matrices.[14,15] There are, however, some cases that the polymer blends show poorer properties because the component polymers are thermodynamically immiscible in many combinations. For enhancing the compatibility of the component polymers, one can add another component that is miscible with both component polymers,[7] or induce chemical reaction to modify the polymer interface.[16]

Very recently, we demonstrated that PLLA polymers can effectively be reinforced by melt-blending of a relatively small amount of an LCP polymer composed of poly(4-hydroxybenzoate) (PHB) as the main segments.[15] In this blend system, the LCP was found to effectively form micro-fibrils in the PLLA matrix and orient in the direction of melt-injection, enhancing the melt-down temperature of PLLA polymers and making their mechanical properties almost comparable with those of the conventional engineering plastics. Furthermore, addition of a chain extender, polycarbodiimide (PCD), was found to be effective for improving the compatibility of the PLLA and LCP because of the formation of block and graft copolymers by the cross-coupling of the carboxyl-terminated PLLA and LCP with PCD.

Based on this finding, we intend to modify PBS by the similar polymer blending of a thermotropic LCP. Since the melt-down temperature of the PBS polymers is much lower than that of PLLA, the enhanced thermal resistivity of PBS is essential for its wider application. Here, the LCP polymer examined is the PHB-based polyester that was utilized for reinforcing PLLA. Two types of chain extenders, PCD and 1,1′-carbonyl biscaprolactam (CBC), are also utilized for ensuring the increased compatibility of the PBS and LCP. The resultant polymer blends, exhibiting well controlled blend morphologies, can be used as heat-resistive PBS materials. Although both PBS and LCP are

now petrochemically synthesized, most of their component monomers such as succinic acid and 4-hydroxybenzoic acid are considered to be bio-originated, making the present polymer blends partly or even wholly bio-based in the near future.

EXPERIMENTAL

Materials
A PBS sample (BIONOLLE: $M_n = 53,000$, $M_w = 166,000$, $T_m = 106°C$) and an LCP sample (Ueno LCP A-8000: $M_n = 10,000$, $M_w = 31,000$) were provided by Showa Polymer Co. (Tokyo, Japan) and Ueno Fine Chemicals Industry (Osaka, Japan), respectively. The LCP showed an amorphous-to-liquid crystalline transition temperature (T_{ac}) at 220°C. A PCD sample (HMV-8CA: $M_n = $ ca. 1,000, $T_m = 65°C$) was provided by Nisshinbo Industries (Tokushima, Japan). CBC (ALLINCO[R] –CBC: $M_n = 252$, $T_m = 113°C$) was provided by DSM Japan (Tokyo, Japan). The chemical structures of these polymers are shown in Scheme 1.

### Sample Preparation by Injection Molding
Predetermined amounts of PBS and LCP in pellet form were mixed and dried at 100°C for 10 h. The mixture (2.0 g in total) was then subjected to melt-blending using a handy melt-blend/injection-mold machine IMC-18D6 (Imoto Machinery Co., Kyoto, Japan). The furnace of the machine was maintained at 230°C, and the polymer mixture was melt-kneaded with a rotor speed of 100 rpm for 2 min. The resultant polymer melt was subsequently injected manually into a metal mold which had primarily been heated at 230°C in an oven. Then, the mold was cooled to room temperature in 15 min, and the thin plastic plate formed was taken out from the mold. The size of the molded plate (rectangular shape) was $1 \times 2 \times 20$ mm in thickness $\times$ width $\times$ length, respectively.

Preparation of Sample Films of LCP
A certain amount of the LCP sample was first dried in vacuum at 100°C for 10 h and hot-pressed at 230°C for 3 min by using a hot-pressing machine (TOYOSEIKI MINI TEST PRESS-10). The resultant film was quenched in an ice/water to obtain a white film specimen of 0.2 mm in thickness.

Measurements
The number-[M_n (gpc)] and weight-average [M_w (gpc)] molecular weights were determined by gel permeation chromatography (GPC) with a Shimadzu analyzer system comprising LC-
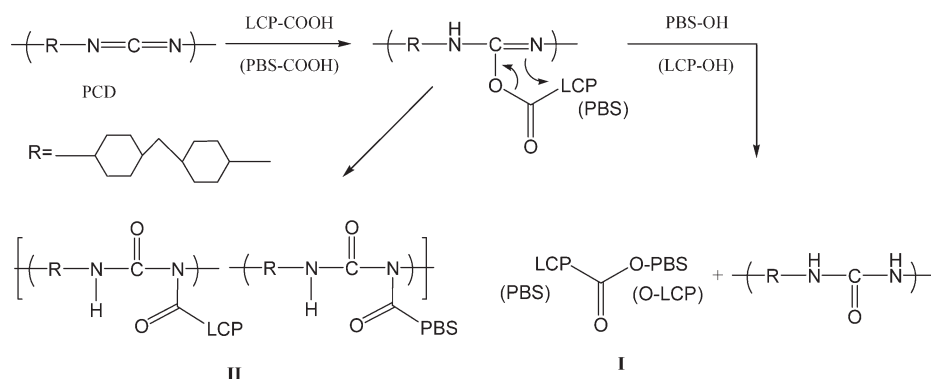
Scheme 2. Reactions of PCD with the carboxyl tails of polyesters.

10ADvp pump, a RID-10A refractive index detector, and a C-R7A Chromatopac data processor. A Tosoh GMHHR-M gel column (7.8 mm ID. × 300 mm: Tosoh, Tokyo, Japan) was used with chloroform as eluent at a flow rate of 0.25 mL/min. A sample was injected at a concentration of 5.0 mg/mL. The molecular weights were calibrated as relative values to polystyrene standards. Wide-angle X-ray scattering (WAXS) was recorded on a system combining a CN4037A1 X-ray generator, an R-AXISDS3 imaging detector (Rigaku Co., Japan) and a CCD camera with a monochromatized Ni-filtered Cu Kα radiation (wave length, 0.154 nm). The generator was operated at 40 kV and 20 mA. The camera length was 73.645 mm, and the exposure time was 15 min. Differential scanning calorimetry (DSC) was performed on a Diamond DSC thermal analyzer (Perkin-Elmer) with an alumina as the reference under a nitrogen flow. The samples were heated from −50 to 240°C at a heating rate of 10°C /min. Dynamic mechanical analysis (DMA) was conducted on a DMS6100 analyzer (SEIKO, Japan) manipulated on the tension mode. The temperature dependences of dynamic storage modulus (E'), loss modulus (E''), and their ratio (tan δ) were measured at a constant frequency (ω) of 33.3 Hz in a temperature range from −80°C to 240°C at a heating rate of 3°C/min. Scanning electron microscopy (SEM) was conducted on a Hitachi S-3400N SEM microscope (Hitachi High-tech, Japan) at 10 kV in accelerating voltage (Tungsten filament). The specimens were fractured in liquid nitrogen and

subjected to Pt coating on a Hitachi E1010 ion sputter (Hitachi High-Tech, Japan).

RESULTS AND DISCUSSION

Each of the two-component (PBS–LCP), three-component (PBS–LCP–PCD and PBS–LCP–CBC), and four-component (PBS–LCP–PCD–CBC) polymer mixtures was subjected to melt-blending with a small kneader at 230°C which was slightly higher than the T_{ac} (220°C) of LCP. Here, the LCP content was changed from 10 to 30 wt % because the modification of PBS materials was intended with as a smaller amount of LCP as possible. The resultant melt-blend was injected into a hot mould to prepare a specimen of rectangular shape. The chain extenders PCD and/or CBC were added because they can react with carboxyl and hydroxyl tails of polyesters as shown in Schemes 2 and 3, respectively. In Scheme 2, —N=C=N— can react with carboxyl to form intermediate product O-acylisourea. The O-acylisourea will react with hydroxyl to give the desired compound I. The reaction of path II involves the rearrangement of the O-acylisourea to the stable N-acylurea.[17,18] In Scheme 3, carboxyl and hydroxyl can react with CBC to give a ring opening reaction.[19]

Table I. DSC Data of the PBS–LCP, PBS–LCP–PCD, PBS–LCP–CBC, and PBS–LCP–PCD–CBC (In the first Heating from −50°C to 240°C at a Heating Rate of 10°C/min)

PBS–LCP–PCD–CBC	T_m (°C)	ΔH_m (J/g)	χ_c (%)
100-0-0-0 (control)	105.9	71.7	64.9
90-10-0-0	105.4	15.7	15.7
80-20-0-0	105.6	21.7	24.5
70-30-0-0	105.5	27.8	35.9
90-10-1-0	106.2	15.9	16.1
80-20-1-0	105.5	17.7	20.1
70-30-1-0	105.3	36.7	47.6
90-10-0-1	105.4	14.8	14.9
80-20-0-1	105.8	24.1	27.4
70-30-0-1	105.9	21.4	27.9
90-10-0.5-0.5	106.4	15.0	15.2
80-20-0.5-0.5	106.6	16.2	18.5
70-30-0.5-0.5	106.3	18.9	24.7
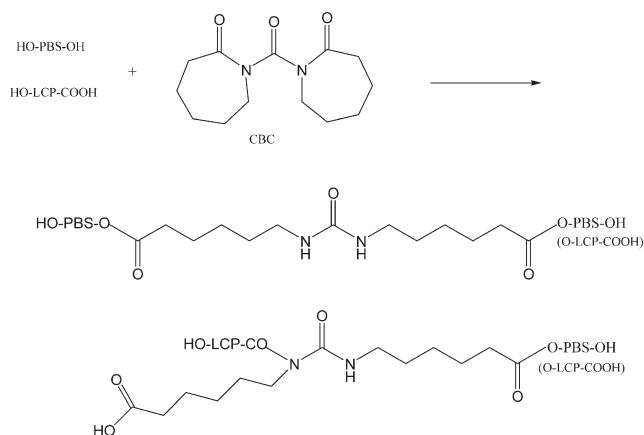
Scheme 3. Reactions of CBC with the hydroxyl and carboxyl tails of polyesters.
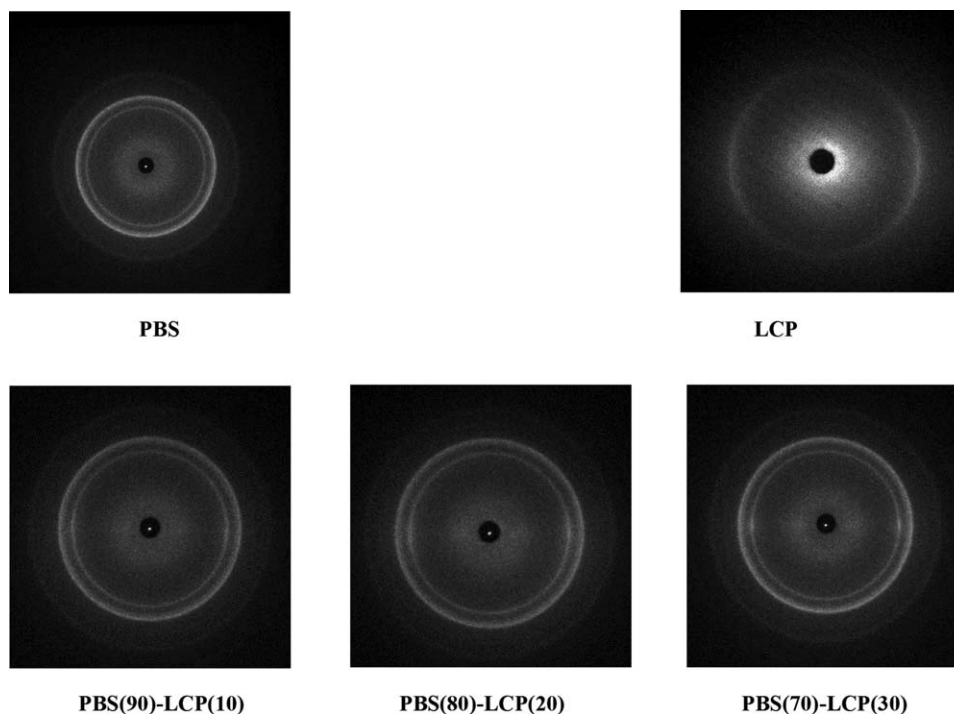
Figure 1. Typical WAXS photos of the PBS–LCP blend specimens compared with those of LCP and PBS.

Their amount was set at 1 wt % relative to the total weight of polymer (part), which was almost correspondent to the stoichiometric amount of terminal groups of the whole polymers (*ca.* 5–9 mmol per 100 g of polymer depending on the LCP-to-PBS compositions). Cross-coupling of PBS and LCP can therefore undergo *in situ* with formation of their block copolymers, and by which the both polymers can be compatibilized.

For assuring the cross-coupling of the LCP and PBS, a small amount of the sample of LCP–PBS–PCD blend was extracted with chloroform to separate free PBS. The insoluble residue was then dissolved in a concentrated D_2SO_4 and analyzed by ^{1}H NMR spectroscopy. The obtained spectrum showed small signals due to the PBS at δ 1.71 (C—C$\underline{H}_2$C$\underline{H}_2$—C), 2.63 (—OC(O)C$\underline{H}_2$—), and 4.12 (—C(O)O—C$\underline{H}_2$—) ppm, together with large multiplet signals attributed to LCP at δ 6.7–8.0 ppm. The same experiment for the bicomponent LCP–PBS blend was

also done, but no PBS signal was detected in the ^{1}H NMR spectrum of the insoluble part consisting only of LCP. These results strongly indicate that the PBS and LCP were conjugated in the presence of PCD. Similar results were obtained in the case of LCP–PBS–CBC. Therefore, the cross-coupling products between LCP and PBS are responsible for increasing the compatibility of the two polymers.

Thermal Properties of the PBS–LCP Blends

Table I summarizes the DSC data of the as-prepared PBS–LCP, PBS–LCP–PCD, PBS–LCP–CBC, and PBS–LCP–PCD–CBC blend specimens as compared with those of a PBS specimen (control) in the first heating scan. Each specimen shows a melting peak of PBS at almost identical temperature of about 105°C irrespectively of presence or absence of PCD or CBC. The crystallinity (χ_c) of PBS of each specimen was therefore estimated from the heat of fusion (ΔH_m) of the melting peak in reference
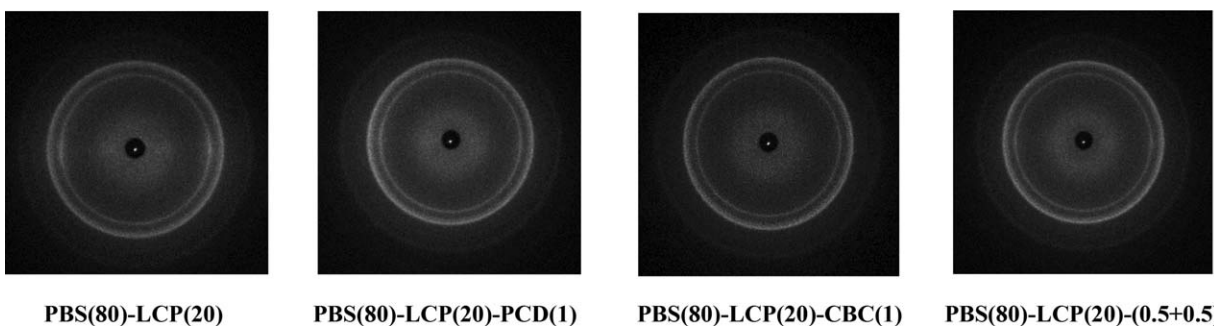

Figure 2. Comparison of the WAXS photos of the PBS–LCP, PBS–LCP–PCD, PBS–LCP–CBC, and PBS–LCP–PCD–CBC specimens having an identical PBS–LCP composition (80–20).

to the specific heat of fusion (ΔH^*_m) reported as 110.5 J/g[20] for the 100% crystalline PBS as follows:

$$\chi_c = \frac{\Delta H_m}{\varphi \Delta H^*_m} \times 100\% \qquad (1)$$

where φ denotes the weight fraction of PBS. As noted in Table I, the ΔH_m and χ_c values of all the specimens added with LCP are much lower than those of the control PBS. It is therefore suggested that the LCP interferes with the crystallization of PBS which easily takes place at ambient temperature in the control PBS specimen. On the other hand, the χ_c value increases with increasing the LCP content both in the two-component (PBS–LCP) and three-component systems (PBS–LCP–PCD and PBS–

Figure 3. SEM micrographs of the fractured surfaces of PBS–LCP, PBS–LCP–PCD, PBS–LCP–CBC, and PBS–LCP–PCD–CBC.

LCP–CBC). This increased crystallization of PBS may be related to the orientational arrangement of PBS existing in between the LCP domains (vide infra). While the χ_c values of the three-component systems are comparable with those of the two-component systems at identical PBS-to-LCP compositions, those of the four-component (PBS–LCP–PCD–CBC) system containing both chain-extenders (0.5 part each) are slightly lower at high LCP contents, suggesting that the interaction between the PBS and LCP may be changed under the co-existence of the two chain extenders.

Figure 1 shows the WAXS photos of the PBS–LCP having different LCP contents as compared with those of the LCP and PBS (control). All the blend samples exhibit two strong scatterings around $2\theta = 19.7°$ and $22.6°$. When compared with the WAXS photos of PBS and LCP showing broad scatterings at $2\theta = 19.6$ and $22.6°$ and at $2\theta = 19.7°$, respectively, it is known that the former arc at $2\theta = 19.7°$ is mainly attributed to the scattering from the LCP crystals whereas the latter circle at $2\theta = 22.6°$ is attributed to that from the PBS crystals. Around $2\theta = 19.7°$, the arc scattering from LCP, being stronger than that from PBS regardless of the LCP content, indicates that LCP has self-oriented in the injection direction. (Note that the control specimen of LCP alone was prepared by hot pressing, showing decreased orientation.) The scatterings from PBS crystals are only slightly stronger around the equatorial region in each blend specimen, indicating a partial orientation of the PBS molecules. Since the relative scattering intensities of PBS crystals are similar to each other among the specimens, the decreased crystallinity with addition of more LCP ought to be compensated by the opposite increase in crystallinity of PBS. These data are compatible with the DSC data.

Figure 2 compares the WAXS photos of the PBS–LCP, PBS–LCP–PCD, PBS–LCP–CBC, and PBS–LCP–PCD–CBC specimens having an identical blend ratio of PBS(80)–LCP(20). It is evident that the scattering from LCP ($2\theta = 19.7°$) is significantly weaker in PBS–LCP–PCD than in PBS–LCP and even undetectable in PBS–LCP–CBC and PBS–LCP–PCD–CBC. Similar results were obtained for other specimen series having different PBS-to-LCP compositions. These results indicate that the reaction with CBC gives a profound effect on the crystallization LCP. Probably, LCP may have lost its crystallization character by the increased compatibility of LCP and PBS in the presence of their cross-coupling products formed with CBC.

Blend Morphology of the PBS–LCP Blends

For analyzing the blend morphology of PBS and LCP, some of the specimens were broken in liquid nitrogen, and their fracture surfaces were observed by SEM. Figure 3 shows the representative SEM images of the two-, three-, and four-component specimens as compared with the control specimens of PBS and LCP. While no specific feature is noted in the PBS and LCP (control), many LCP fibrils are detected in the PBS matrices of the PBS–LCP, PBS–LCP–PCD, and PBS–LCP–CBC specimens. These LCP fibrils are known to orient perpendicularly to the fractured surface or parallel to the injection direction, being responsible for the increased mechanical properties. It is evident that the fibrils are much thicker at higher LCP content (20%), thinner in the
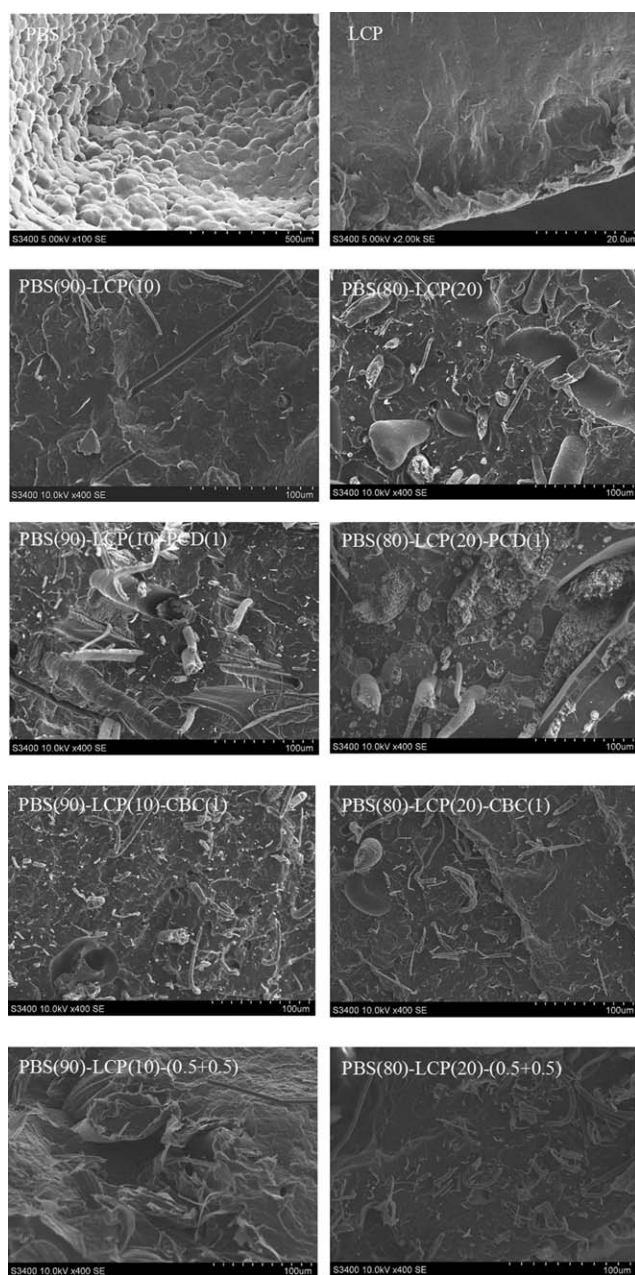
Table II. Tensile Properties of the PBS–LCP, PBS–LCP–PCD, PBS–LCP–CBC, and PBS–LCP–PCD–CBC

PBS-LCP-PCD-CBC	Modulus (GPa)	Strength (MPa)	Elongation at break (%)
100-0-0-0 (control)	1.9 ± 0.28	32 ± 0.87	6.7 ± 0.47
0-100-0-0 (control)	3.1 ± 0.36	84 ± 1.01	7.4 ± 0.52
90-10-0-0	2.6 ± 0.30	40 ± 0.68	4.6 ± 0.65
80-20-0-0	4.0 ± 0.56	56 ± 0.76	3.2 ± 0.33
70-30-0-0	5.6 ± 0.42	72 ± 0.58	2.0 ± 0.42
90-10-1-0	4.0 ± 0.37	48 ± 0.62	3.6 ± 0.53
80-20-1-0	5.5 ± 0.59	65 ± 0.43	2.8 ± 0.66
70-30-1-0	6.0 ± 0.48	86 ± 1.32	1.6 ± 0.34
90-10-0-1	3.0 ± 0.34	43 ± 0.88	4.1 ± 0.28
80-20-0-1	4.5 ± 0.48	61 ± 1.24	3.0 ± 0.43
70-30-0-1	5.8 ± 0.41	80 ± 0.98	1.9 ± 0.16
90-10-0.5-0.5	4.1 ± 0.46	50 ± 0.86	3.4 ± 0.48
80-20-0.5-0.5	5.6 ± 0.68	67 ± 1.34	2.7 ± 0.32
70-30-0.5-0.5	6.1 ± 0.49	86 ± 1.22	1.7 ± 0.24

PBS–LCP–CBC specimens, and the thinnest PBS–LCP–PCD–CBC specimens. The thinning of the LCP fibrils is a clear support for the increased affinity of LCP and PBS in the presence of CBC that can react with the hydroxyl tails of the both polymers.

Mechanical and Thermomechanical Properties of the PBS–LCP Blends

Table II summarizes the tensile properties of the two-, three-, and four-component specimens as compared with the control speci-

mens of PBS and LCP. In all blend systems, the tensile modulus and strength increased with increasing the LCP content, whereas the elongation at break showed a decreasing tendency with it. In particular, the specimens containing 30 wt % of LCP showed the highest moduli that were much higher than that of LCP itself while showing strengths comparable to that of LCP. The lower modulus of the pure LCP specimen is attributed to the difference in processing method; hot-pressing, applying low shear to the melt, was used instead of injection-molding that can give high
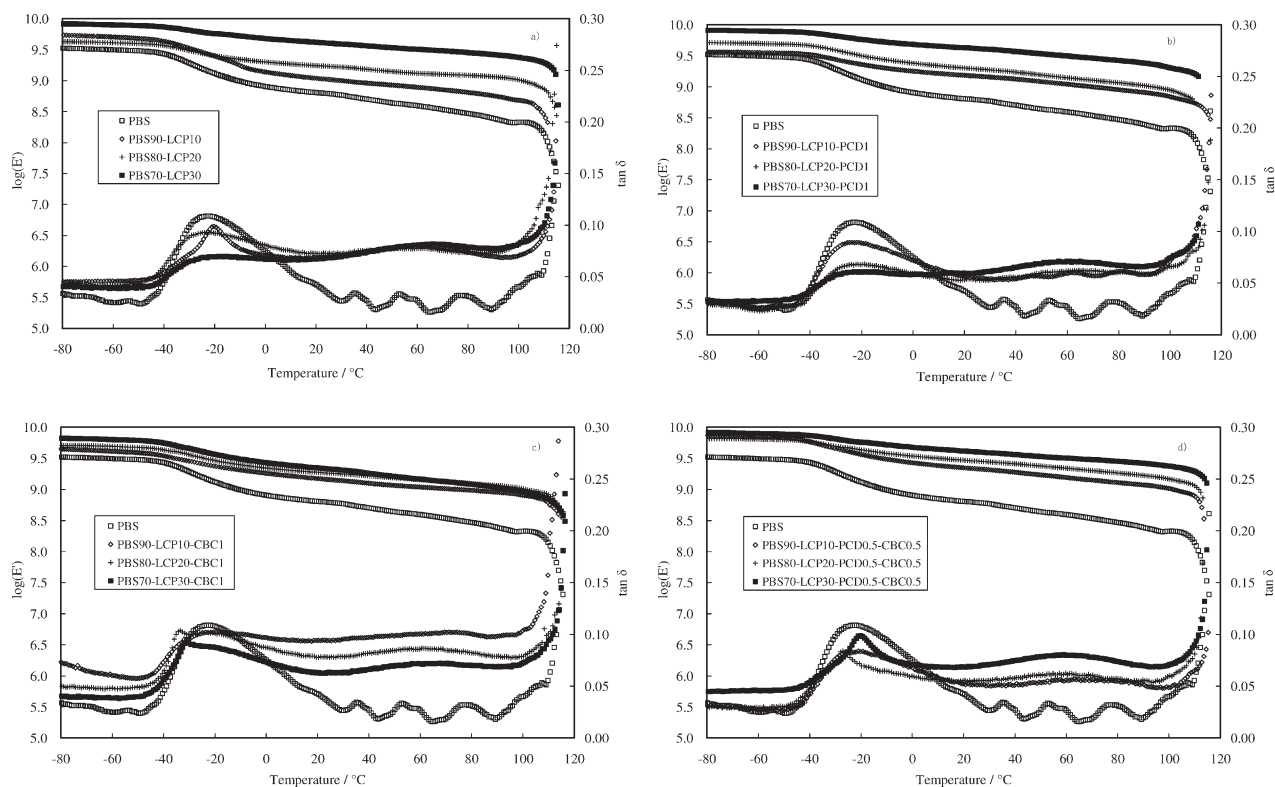

Figure 4. Temperature-dependent changes in storage modulus (E') and tan δ of (a) PBS–LCP, (b) PBS–LCP–PCD, (c) PBS–LCP–CBC, and (d) PBS–LCP–PCD–CBC as compared with PBS (from $-80°C$ to $230°C$ at $3°C/min$).

shear in the injecting direction of the melt. The three- and four-component specimens showed slightly higher tensile modulus and strength than the two-component system at the identical LCP contents. This result suggests that the two chain-extenders (Schemes 2 and 3) can improve the compatibility of PBS and LCP to enhance the mechanical properties. These data clearly demonstrated that the PBS blended with LCP can acquire excellent mechanical properties depending on the LCP content and that co-addition of PCD and CBC is quite effective for improving the tensile properties of the polymer blends of PBS–LCP.

Figure 4 shows the temperature dependences of storage modulus (E') and tan δ of the (a) PBS–LCP, (b) PBS–LCP–PCD, (c) PBS–LCP–CBC, and (d) PBS–LCP–PCD–CBC specimens (injection-molded in rectangular shape) as compared with those of PBS (control).

In Figure 4(a), PBS (control) shows a large drop in E' above its α-relaxation temperature (or $T_g \sim -40°C$) followed by continuous decrease in E' up to the melt-down temperature around 110°C. Both drops of E' are successfully hindered in the PBS–LCP specimens, and the drop becomes lower with the LCP composition increasing. In particular, PBS(70)–LCP(30) maintains E' higher than 10^9 Pa with least change in tan δ in the whole range of temperature. The maximum value of tan δ also decreases with increasing the LCP content up to 30 wt %. These behaviors are definitely due to the mechanical reinforcement by the fibril orientation of LCP in the blend.[15] Similar thermomechanical changes are also shown by the three component system of PBS–LCP–PCD [Figure 4(b)] where only PBS(90)–LCP(10)–PCD(1) exhibits rather improved mechanical properties compared to the PCD-free PBS(90)–LCP(10). This small addition effect of PCD may be because PBS, mainly dihydroxyl-terminated, contains a small amount of terminal carboxyl groups and is not very much involved in the cross-coupling with LCP shown in Scheme 2. On the other hand, the PBS–LCP–CBC specimens shows different thermomechanical changes [Figure 4(c)] where the E' changes are comparable among the three specimens having different LCP contents. This result indicates that CBC has reacted with the hydroxyl terminals of both PBS and LCP to form the cross-coupling products shown in Scheme 3 in higher amount. In consequence, both LCP and PBS acquire increased compatibility, and the LCP domain is more finely distributed in the PBS matrix to make the specimens rather softer. Figure 4(d) shows the thermomechanical behaviors of the four-component system of PBS–LCP–PCD–CBC. It is evident that the E' values of this system are significantly higher than those of the above PBS–LCP–CBC specimens. Co-addition of PCD and CBC allows both the reactions of Schemes 2 and 3 to form the cross-coupling products in appropriate degree, and with which a homogeneous phase separation with fibril formation is possible. The increased E' may be attributed to the reduced mobility of the amorphous PBS that should be flanked by the LCP and PBS crystalline phases. In conclusion, blending of PBS and LCP with the aid of two chain-extenders having different reactivity can improve the thermo-mechanical properties of PBS to enable wider application of the PBS-based materials.

CONCLUSIONS

The novel polymer blend systems of PBS–LCP were prepared by simple melt-blending technique in the presence and absence of PCD and/or CBC as chain extenders that allowed cross-coupling of PBS and LCP to increase their compatibility. It was revealed that the tensile strength and modulus of the PBS–LCP blend specimens increase with increasing the LCP content whereas their tensile elongation showed an opposite tendency. Their DMA analysis revealed that addition of LCP to PBS is very effective for retaining high E' for the injection molds over the temperature range up to T_m of PBS. This behavior was attributed to the self-reinforcing effect of the LCP that had been distributed in the PBS matrix in a form of micro fibrils having an orientation in the direction of melt-injection. The addition effect of CBC that easily reacts with hydroxyl terminals of LCP and PBS was very high for enhancing the thermomechanical and mechanical properties because of the homogeneous phase separation of LCP fibrils in the PBS matrix. Since the present PBS-LCP polymer blends show an improved thermal stability, they ought to be applicable as ordinary plastic materials for which PBS polymers have not been used before.

ACKNOWLEDGMENTS

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