Mechanical Properties and Morphological Changes of Poly(lactic acid)/Polycarbonate/Poly(butylene adipate-*co*-terephthalate) Blend Through Reactive Processing

Takeshi Kanzawa,[1,2] **Katsuhisa Tokumitsu**[2]

[1]*Northeastern Industrial Research Center of Shiga Prefecture, 27-39 Mitsuyamoto-cho, Nagahama-city, Shiga 526-0024, Japan*
[2]*Department of Materials and Science School of Engineering, The University of Shiga Prefecture, Hikone-city, Shiga 522-8533, Japan*

Received 29 July 2010; accepted 10 December 2010
DOI 10.1002/app.33916

ABSTRACT: The mechanical properties and morphological changes of poly(lactic acid) (PLA), polycarbonate (PC), and poly(butylene adipate-*co*-terephthalate) (PBAT) polymer blends were investigated. Several types of blend samples were prepared by reactive processing (RP) with a twin-screw extruder using dicumyl peroxide (DCP) as a radical initiator. Dynamic mechanical analyses (DMA) of binary polymer blends of PC/PBAT indicated that each component was miscible over a wide range of PC/PBAT mixing ratios. DMA of PLA/PBAT/PC ternary blends revealed that PBAT is miscible with PC even in the case of ternary blend system and the miscibility of PLA and PBAT can also be modified through RP. As a result, the tensile strain and impact strength of the ternary blends was increased considerably through RP, especially for PLA/PBAT/PC = 42/18/40 (wt/wt/wt) with DCP (0.3 phr). Scanning electron microscopy (SEM) analysis of the PLA/PBAT/PC blends revealed many small spherical island phases with a domain size of approximately 0.05–1 μm for RP, whereas it was approximately 10 μm without RP. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 2908–2918, 2011

Key words: polymer blends; reactive processing; polycarbonate; morphology; polyesters

INTRODUCTION

Recently, poly(lactic acid) (PLA) has attracted much attention as a biodegradable polymer, because it can be produced from several carbon neutral resources. However, PLA has some disadvantages such as low thermal stability, low impact resistance, and brittleness, but it has some advantages such as high elastic modulus and good transparency.[1]

Polycarbonate (PC) has been widely used as an engineering plastic that has high thermal stability, impact resistance, and also compatibility with poly (butylene terephthalate) (PBT). To improve the properties of PLA, several PLA/PC blends have been investigated.[2–4] Although the thermal stability and impact resistance of PLA could be improved by the addition of over 45 wt % PC to PLA, the elongation at break and/or the brittleness of PLA was not improved.[3,4]

On the other hand, poly(butylene adipate-*co*-terephthalate) (PBAT) is a soft biodegradable plastic containing PBT units in the main chain. It has been reported that PBAT is incompatible with PLA; however, it could improve the brittleness and slow the crystallization behavior of PLA.[5–7] Therefore, there is a possibility that the poor mechanical properties of PLA could be enhanced by the addition of PC and PBAT, and this ternary blend could also be a new environmentally-benign material consisting of over 50 wt % biodegradable polymers.

Reactive processing (RP) is a promising cost effective production technique used to introduce a variety of functional groups into polymeric materials with outstanding physical and chemical properties.[8,9] Functionalization of PLA with maleic anhydride and radical initiators (POs) has been achieved by melt blending using a twin-screw extruder[10] and by solution reactions with solvents such as toluene.[11] Multiphase polymeric materials using maleated PLA have been attained in PLA/starch[12–15] and PLA/poly(ethylene glycol) (PEG) blends.[16] Another successful application of RP is the addition of POs to several PLA blends, such as PLA/poly(ε-caprolactone) (PCL),[17–20] PLA/poly(butylene succinate) (PBS),[19] PLA/poly(butylene succinate-*co*-adipate),[20] PLA/PBAT,[21] PLA/polyurethane,[22] PLA/ PEG glycidyl ether[23] by simultaneous melt blending. Addition of POs to those polymer blends forms cross-linked and/or branched structures by hetero- and/or homogeneous radical coupling reactions. Heterogeneous reactions improve the compatibility of the

---

Correspondence to: T. Kanzawa (kanzawa.takeshi@shiga-irc.go.jp).

Journal of Applied Polymer Science, Vol. 121, 2908–2918 (2011)

polymer blends, the melt tensions and the extrusion stability. Lysine triisocyanate is also a useful RP agent to increase the compatibility of PLA/PBS[24] or PLA/PCL[25] blends to increase the impact strength of PLA.

In this work, we investigated improvement of the elongation at break and/or the brittleness of PLA/PC blends by (1) optimizing the fundamental thermal and mechanical properties of PLA/PC, PBAT/PC, and PLA/PBAT blends for use in ternary polymer blends, (2) examining the morphological changes of the ternary polymer blends, PLA/PBAT/PC, and (3) elucidating the mechanism for improvement of the mechanical properties of the blends.

EXPERIMENTAL

Materials

Commercially obtained PLA with a weight average molecular weight of 155,000 (determined by size-exclusion chromatography (SEC) based on calibration with polystyrene (PS) standards), a polydispersity index [PDI; weight-average molecular weight (M_w)/number average molecular weight (M_n)] of 1.92, and a melt flow rate (MFR) of 12.3 (at 200°C and 2.16 kg load), was dried in a hot air oven at 80°C for 5 h before use.

Commercially obtained PC (Calibre 301-30, Sumitomo Dow, Tokyo, Japan) with a weight average molecular weight of 42,200 (SEC, PS standards), a PDI of 2.14, and a MFR of 0.3 (at 200°C and 2.16 kg load), was dried in hot air oven at 80°C for 5 h before use.

Commercially obtained PBAT (Ecoflex, BASF Japan) with a weight average molecular weight of 153,000 (SEC, PS standards), a PDI of 2.34, and a MFR of 2.9 (at 200°C and 2.16 kg load), was dried in hot air oven at 80°C for 5 h before use.

Dicumyl peroxide (DCP) (Percumyl D, NOF, Tokyo, Japan; half life of 1 min at 175°C) was used as a radical initiator.

Polymer Blends

Several types of blend materials were prepared in a twin-screw extruder (KZW15–45HG, Ø15 mm, L/D = 45, Technovel) equipped with both a top and a side feeder at a rotation speed of 250 rpm. The extruder consists of six heating zones; the first zone was kept constant at 100°C and the second to sixth zones and die were changed from 180 to 230°C to obtain the desired polymers, as specified below. These temperatures are represented as X°C, which denotes the temperature of the second to sixth zones and the die. After the die, the blend samples were cooled with water and pelletized. For example, pristine polymers of PLA, PBAT, and PC with/without DCP were introduced into the extruder from a top feeder at 180, 180, and 230°C, respectively.

For the PLA/PBAT/PC ternary blend, three preparation processes were investigated as follows;

The "top-feed method" was prepared by feeding the mixtures of PLA, PBAT, PC, and DCP into the extruder from a top feeder at 200°C. It should be noted that the binary blends, such as PLA/PBAT, PLA/PC and PC/PBAT, were also prepared by this method at 180, 230, and 230°C, respectively.

The "two-steps method" was performed as follows; (1) first, the binary polymer blend of PLA/PBAT (70/30) (wt/wt) with DCP (0.0, 0.5 phr) was prepared at 180°C and pelletized, (2) second, the binary blend (preblend) of PLA/PBAT was mixed with PC, and the mixing ratio of the preblend and PC was kept at 60/40 (wt/wt), and (3) lastly, the blend was introduced into the extruder at 200°C from a top feeder. As a result, 60 wt % of preblended PLA/PBAT (70/30) (wt/wt) with DCP (0.0, 0.5 phr) and 40 wt % of PC gave a PLA/PBAT/PC (42/18/40) (wt/wt/wt) blend with DCP (0.0, 0.3 phr) to produce ternary blends of PLA/PBAT/PC.

The "side-feed method", which is a one-step method, was performed as follows; (1) firstly, the preblend of PLA/PBAT (70/30) (wt/wt) with DCP (0.0, 0.5 phr) was prepared through the first heating zone at 100°C and the second to fourth zones at 180°C, (2) secondly, without taking the preblend out of the extruder, PC was continuously added from the fifth zone of the extruder through a side feeder and blended in the fifth to sixth zones and the die set at 200°C. The feed ratio of the preblend at the top feeder and PC at the side feeder was controlled by keeping a ratio of 60/40 (wt/wt). Finally, a ternary polymer blend of PLA/PBAT/PC (42/18/40) (wt/wt/wt) with DCP (0.0, 0.3 phr) was obtained.

Preparation of molded films

The blend samples were molded into films by hot pressing with a desk press (G−12, Techno supply). The samples were placed between a pair of polyimide sheets with a 0.3 mm thick spacer and then hot pressed at 210°C under a pressure of 60 MPa for 1 min. The pressed samples were then quenched in ice water. Before hot pressing, all of the samples were dried in a hot air oven at 80°C for 5 h.

Preparation of injection moldings

The samples for impact tests were prepared by injection molding (ES1000, Nissei Plastic Industrial) with the nozzle at 210°C. The injection speed was 10 mm/s and the holding pressure was 60 MPa for 30 s. The dimensions of the samples were 80 × 4 × 10 mm^3, in accordance with JIS K 7111/ISO 179.

Measurements

Size exclusion chromatography (SEC)

The PDI and M_w of the polymers were determined using SEC apparatus (LaChrom D-7000, Hitachi High-Technologies) equipped with a SEC column (K-805L, Shodex). Chloroform was used as the mobile phase solvent at a flow rate of 1.0 mL/min, and the measurement temperature was kept constant at 40°C. The SEC chromatograms were calibrated using several standard (monodispersed) PS samples of different molecular weight.

MFR

Values of MFR were measured using a melt indexer (F−F01, Toyo Seiki Seisakusho) with a load of 2.16 kg. All samples were dried in a hot air oven at 80°C for 5 h prior to measurement.

Tensile test

Tensile tests were carried out using a tensile tester (5569, Instron) under tensile mode at 20°C and a relative humidity of 65%, with a head speed at 10 mm/min and a span length of 20 mm. The samples were 0.3 mm thick and 4 mm wide. Tensile tests were carried out with at least five repetitions for each sample type.

Dynamic mechanical analyses (DMA)

DMA were carried out using a dynamic viscoelastometer (Rheogel E−4000, UBM) under tensile mode with a span length of 20 mm at a frequency of 30 Hz and a heating rate of 2°C /min using 0.3 mm thick and 5 mm wide samples.

Impact strength

Charpy impact tests were carried out at 20°C according to JIS K 7111/ISO 179 using 2 J (notched samples) and 4 J (unnotched samples) impact hammers with an impact tester (258-L-PC, Yasuda Seiki Seisakusho).

SEM observations for the fractured samples

Scanning electron microscopy (SEM) observations were carried out for the binary blends of PLA/PBAT, PLA/PC, and the ternary blends of PLA/PBAT/PC. The PLA/PBAT samples were prepared by freeze fracturing of the molded film in liquid nitrogen, and PLA/PC and PLA/PBAT/PC samples were prepared by fracturing of both tensile stress test and charpy impact test samples with notches.

SEM (S−3000N, Hitachi) observations were performed at an accelerating voltage of 10 kV to examine the phase structure on the surface of fractured samples sputter-coated (E−1010 Ion Sputter, Hitachi) with a thin layer of gold. It should be noted that in terms of the fractured samples for the charpy impact test, PBAT and PC were extracted with a solvent before SEM observation as follows: (1) first, the fractured samples were placed in a hot air oven at 120°C for 1 h to perfectly crystallize the PLA phase in the blend, (2) second, PBAT was extracted with a mixed solvent of chloroform/acetone (75/25) (v/v), and (3) finally, PC was extracted with a mixed solvent of tetrahydrofuran/acetone (95/5) (v/v).

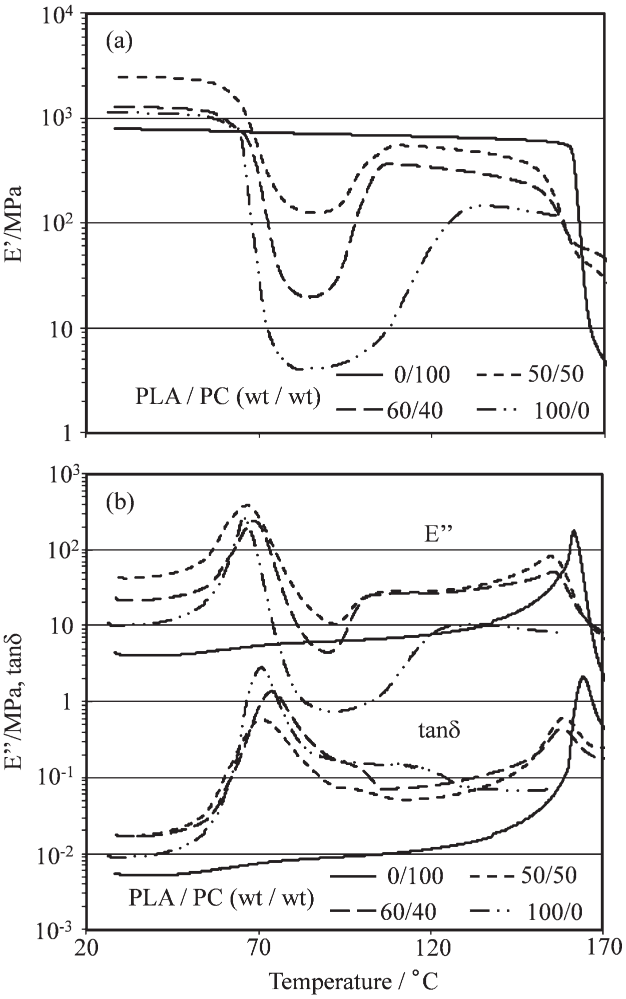


Figure 1 The temperature dependence of (a) E′ and (b) E" and tanδ for PLA/PC blends.

RESULTS AND DISCUSSION

DMA results

Figure 1 shows the temperature dependence of the storage modulus [E′: Fig. 1(a)], loss modulus (E") and tanδ [Fig. 1(b)] for binary blends of PLA/PC (100/0), (60/40), (50/50), (0/100) (wt/wt) determined by DMA. The E′ values of the PLA blends

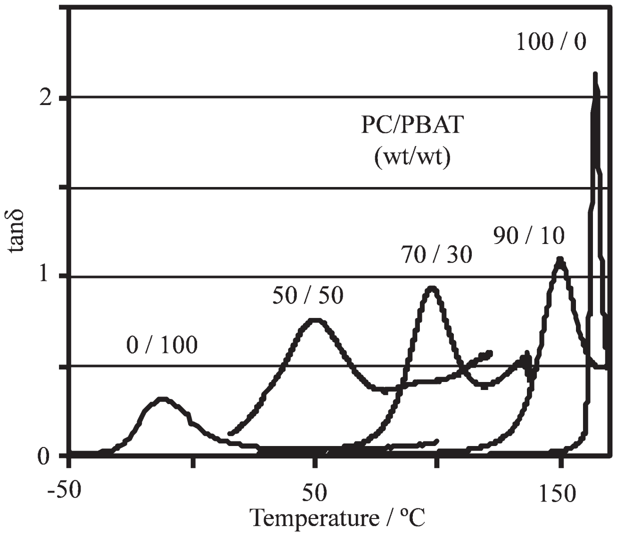


Figure 2 The temperature dependence of tanδ for PC/PBAT blends.

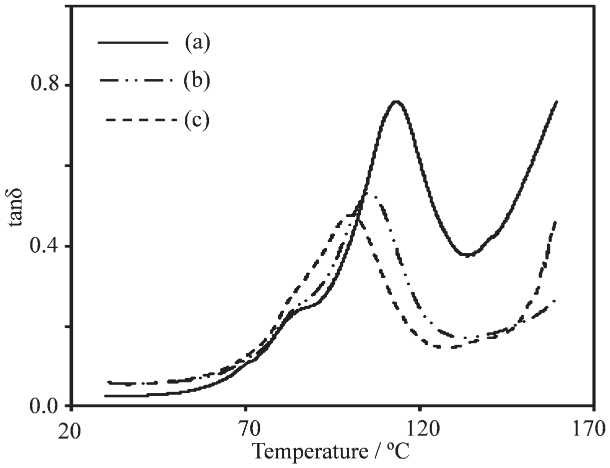


Figure 4 The temperature dependence of tanδ for several PLA/PBAT/PC blends: PBAT/PC ratios (wt/wt) for the ternary blends are (a) Run 1: 22/77, (b) Run 2: 27/73 and (c) Run 3: 31/69.

were decreased and the E'' values increased at ~ 70°C, which corresponds to the glass transition of PLA, and the E′ values increased again at about 100–130°C. These results suggest that the PLA phase is crystallized in this range.

In Figure 1(b), two large tanδ peaks were observed with smaller ones. The larger peaks around 160 and 70°C are due to PC and PLA, respectively, and the smaller peaks at around 100 to 130°C are due to the crystallization of PLA. The values of PLA tanδ max were increased slightly by addition of PC, and those of PC were also decreased, which indicates that PLA and PC are not miscible; however, some interactions occur between these two materials.

Figure 2 shows the temperature dependence of tanδ for binary blends of PC/PBAT (100/0), (90/10), (70/30), (50/50), and (0/100) (wt/wt). Unlike the case for PLA/PC, only a single peak was observed for all the PC/PBAT samples, and the peak shifted to lower temperature with increase in the PBAT content. Figure 3 shows the variation of the peak temperature of tanδ for the PC/PBAT blends against the PBAT content. The tanδ peaks of the PC/PBAT blends changed linearly with the PBAT content, which confirms that PC and PBAT are totally miscible for the variety of PC/PBAT mixing ratios examined.

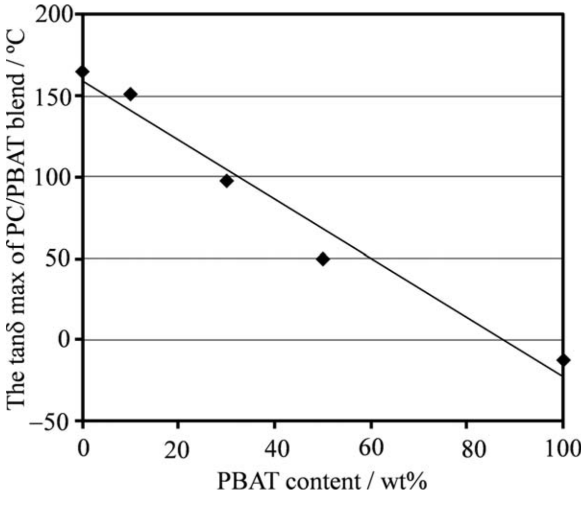


Figure 3 The change of tanδ max for the PC/PBAT blends against the amount of PBAT.

Figure 4 shows the temperature dependence of tanδ for ternary blends of PLA/PBAT/PC (35/15/50: Run 1), (39/17/45: Run 2) and (42/18/40: Run 3) (wt/wt/wt) determined by DMA. The recalculated PBAT/PC ratios of these blends were 22/77 (wt/wt) (Run 1), 27/73 (wt/wt) (Run 2) and 31/69 (wt/wt) (Run 3), respectively. The tanδ derived from the PBAT/PC components of these samples should appear at 100 to 120°C, because these components were miscible for a wide range of PC/PBAT mixing ratios (see Fig. 3). However, they could be difficult to detect if the tanδ peak due to crystallization of the PLA phase was also observed in this range. Therefore, it should be noted that these samples were annealed at 120°C for 1 h prior to measurement to ensure the complete crystallize of the PLA phase. Clearly, some tanδ peaks were evident in Figure 4; the small peaks at ~ 80°C were derived from PLA, which showed smaller tanδ at a higher temperature than those of samples containing no crystallized PLA phase [see Fig. 1(b)]. These results suggest that the mobility of the amorphous PLA phase is decreased by crystallization. The large peaks of tanδ around 100−120°C derived from PBAT/PC components were found to decrease with increase in the PBAT content. Interestingly, plots of the peaks around 100−120°C from Figure 3 indicated a linear

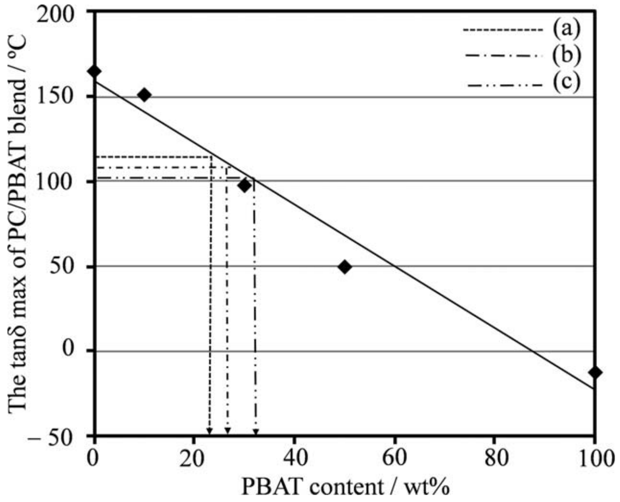


Figure 5 The change of tanδ max for the PC/PBAT content in several PLA/PBAT/PC blends against the amount of PBAT: PBAT/PC ratios (wt/wt) for the ternary blends are (a) Run 1: 22/77, (b) Run 2: 27/73, (c) Run 3: 31/69.

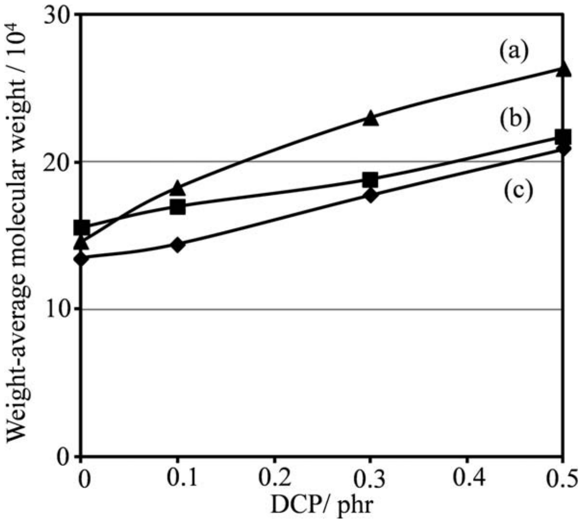


Figure 7 Weight-average molecular weight of dissolve part in chloroform of (a) PLA/PBAT (70/30) (wt/wt), (b) PLA and (c) PBAT with DCP calculated from SEC curves.

change of these peaks with the PBAT content (Fig. 5), therefore, each component was miscible, even in the ternary blend.

MFR and SEC results

To optimize the amount of the DCP radical initiator for PLA/PBAT blends, several blends of PLA/PBAT (70/30) (wt/wt) with DCP (0.0, 0.1, 0.3, 0.5, 0.7, and 1.0 phr) were prepared at 180°C; however, gel-like components of PLA/PBAT were generated for addition of more than 0.7 phr of DCP and they caused instability of the extrusion. Therefore, addition of more than 0.7 phr of DCP was not suitable for these blends.

To clarify the meltdown properties of PLA/PBAT blends with DCP, MFR measurements of PLA/PBAT (70/30) (wt/wt) blends with DCP (0.0, 0.1, 0.3, 0.5 phr) and pure PC were carried out, and the results are shown in Figure 6. The MFR values for PLA/PBAT decreased gradually with the amount of DCP at the same temperature, and the values for PC were lower than those for PLA/PBAT at all measurement temperatures. Wu reported that the diameter of the dispersion phase was smaller when the viscosity of the matrix (η_m) was closer to that of a droplet (η_d), and attained a minimum value when the ratio of η_d/η_m was 1.[26] For ternary blends of PLA/PBAT/PC prepared by the two-steps method and/or the side-feed method (see Experimental), it could be assumed that the PLA/PBAT and PC phases behave as a matrix and droplet, respectively. With respect to the melt viscosity of the matrix and droplet, the MFR results, which are associated with viscosity, indicated that the optimum amount of DCP in PLA/PBAT for PLA/PBAT/PC ternary blends was 0.5 phr, because this amount of DCP resulted in the closest value of η_m to η_d.

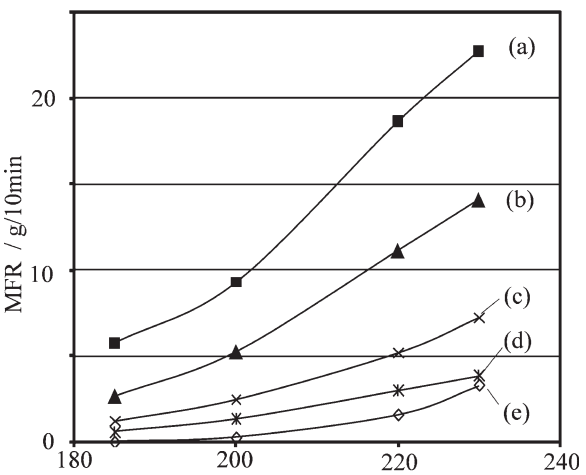


Figure 6 The MFR results of the PLA/PBAT (70/30) (wt/wt) with (a) 0.0 phr, (b) 0.1 phr, (c) 0.3 phr, (d) 0.5 phr, and (e) neat PC measured at several temperatures.

Figure 7 shows the M_w of the chloroform-soluble part of PLA, PBAT and PLA/PBAT (70/30) (wt/wt) with DCP (0.0, 0.1, 0.3, and 0.5 phr) calculated from SEC curves. The values of M_w of all samples were increased with the amount of DCP, which suggests that some chemical bonds between PLA and PLA, PBAT and PBAT, and PLA and PBAT would be formed by hetero- and/or homogeneous radical coupling reactions by the addition of DCP as a reaction initiator.

Mechanical properties

The mechanical properties of PLA/PC and PC/PBAT are summarized in Table I. Although the

TABLE I
The Mechanical Properties of PLA/PC and PC/PBAT Prepared at 230°C

PLA/PC (wt/wt)	PC/PBAT (wt/wt)	Tensile modulus /MPa	σ[a]	Tensile strength /MPa	σ[a]	Elongation at break /%	σ[a]
100/0	–	1940	50	61	5	9	3
60/40	–	1730	64	61	3	5	0.04
0/100	100/0	1330	38	57	1	68	28
–	90/10	1280	69	61	5	50	22
–	70/30	1410	110	57	4	62	20
–	50/50	480	143	38	4	203	22

[a] Standard deviation.

modulus for PLA/PC (60/40) (wt/wt) was an intermediate value of that for PLA and PC, the elongation at break was still low. These results also support that the simple blending of PC with PLA is not efficient for improvement of the elongation of PLA.

The tensile modulus, strength, and elongation at break of PC/PBAT blends with 10 to 30 wt % PBAT were the same as that for pure PC. On the other hand, those for the blend with 50 wt % PBAT were significantly changed, which suggests that phase inversion of the PC/PBAT blend occurred at around 50 wt % PBAT.

The mechanical properties of PLA/PBAT (70/30) (wt/wt) with DCP (0.0, 0.1, 0.3, 0.5, and 1.0 phr) are summarized in Table II, and indicate that the brittle properties of PLA can be modified by the addition of PBAT. In particular, the elongation at break of PLA/PBAT (70/30) (wt/wt) with at 0.1–0.5 phr DCP attained 280−290%, which was much higher than that for pure PLA (ca. 9%), whereas the modulus and the strength did not change. However, addition of over 0.5 phr DCP into PLA/PBAT resulted in a significant decrease of the elongation at break, the modulus and the strength of the blend, which suggests that the mechanical properties of PLA lowered by the addition of PBAT and excess DCP. This result suggests that excess amount of DCP induced the negative effect for improving the mechanical properties of PLA. In the case of PLA/PCL, Semba et al. also reported similar results, in that the elongation at break of PLA/PCL increased with an increase of DCP up to the optimum point, and gradually decreased with increasing DCP.[17]

The mechanical properties of PLA/PBAT/PC (42/18/40) (wt/wt/wt) with DCP (0.0 and 0.3 phr) prepared by several feed methods are summarized in Table III. It should be noted that the blend of 60 wt % PLA/PBAT (70/30) (wt/wt) with 0.5 phr DCP, which was the optimum amount for PLA/PBAT, and 40 wt % of PC gave PLA/PBAT/PC (42/18/40) (wt/wt/wt) blend with 0.3 phr DCP.

For the top-feed method, the elongation at break of the ternary reactive blend with DCP (0.3 phr) increased up to 21%, and it was slightly better than that of DCP (0.0 phr). However, the standard deviation (σ) of the elongation at break of the reactive blend was quite large, which suggests that the top-feed method was not sufficient to produce a PLA/PBAT/PC ternary blend for improving its mechanical properties.

To investigate an effective method to enhance the mechanical properties of PLA/PBAT/PC ternary blends, the two-steps method was used. Figure 8 shows tensile stress−strain curves of PLA/PBAT/PC (42/18/40) (wt/wt/wt) ternary reactive blends prepared using the two-steps method, and their mechanical properties are summarized in Table III. The elongation at break of the ternary reactive blend increased up to 121%, which was much better than that of DCP (0.0 phr). Moreover, the value of σ for the ternary reactive blend was also improved. These results suggest that preparation of a pre-blend of PLA/PBAT with DCP before blending PC is important to improve the mechanical properties of the ternary blend, especially for the elongation at break; therefore, the preparation of PBAT-grafted PLA

TABLE II
The Mechanical Properties of PLA/PBAT (70/30) (wt/wt) With/Without DCP Prepared at 180°C

DCP /phr	Tensile modulus /MPa	σ[a]	Tensile strength /MPa	σ[a]	Elongation at break /%	σ[a]
0.0	1270	42	35	1	220	80
0.1	1210	51	38	2	280	36
0.3	1270	69	36	2	290	19
0.5	1240	72	36	2	280	16
1.0	1080	63	32	2	10	2

[a] Standard deviation.

TABLE III
The Mechanical Properties of PLA/PBAT/PC (42/18/40) (wt/wt/wt) With/Without DCP Prepared by Several Feeding Methods

		Tensile modulus		Tensile strength		Elongation at break	
Method	DCP /phr	/MPa	σ^a	/MPa	σ^a	/%	σ^a
Top-feed	0.0	1790	101	63	7	5	1
	0.3	1770	80	60	6	21	45
Two-steps	0.0	1650	55	56	2	5	0.7
	0.3	1610	68	59	2	121	34
Side-feed	0.0	1660	81	53	3	4	0.5
	0.3	1490	111	44	6	101	31

[a] Standard deviation.

and/or PBAT-branched PLA (see following section) is necessary before only PBAT can be mixed with PC into a monophase.

The two-steps method was found to be effective for improvement of the elongation at break of PLA/PC. However, this method was not sufficient for extrusion productivity; therefore, the side-feed method was investigated for improvement of the extrusion productivity of ternary polymer blends (Table III).

The elongation at break of the PLA/PBAT/PC ternary reactive blend (DCP 0.3 phr) prepared by the side-feed method was almost the same as that prepared by the two-steps method, whereas the elongation at break of the PLA/PBAT/PC ternary mechanical blend (DCP 0.0 phr) was still very low (<5%). These results suggest that preparation of a ternary reactive blend by the side-feed method is also effective to improve the elongation at break.

Table IV shows the charpy impact strength of PLA, PLA/PC (60/40) (wt/wt) and PLA/PBAT/PC (42/18/40) (wt/wt/wt) with/without DCP prepared by the side-feed method. Although the notched impact strength of PLA, the PLA/PC binary blend and the PLA/PBAT/PC ternary polymer blend (DCP 0.0 phr) were comparable (ca. 2.0 kJ/m^2), the strength of the PLA/PBAT/PC ternary reactive blend (DCP 0.3 phr) was 1.5 times that of the others. On the other hand, in the case of unnotched samples, these tendencies were remarkable. The unnotched impact strength of PLA/PBAT/PC (42/18/40) (wt/wt/wt) with DCP became quite large, resulting in a not-breakable result. Therefore, it should be noted that addition of DCP into the PLA/PBAT/PC ternary system is also important for enhancement of the impact properties.

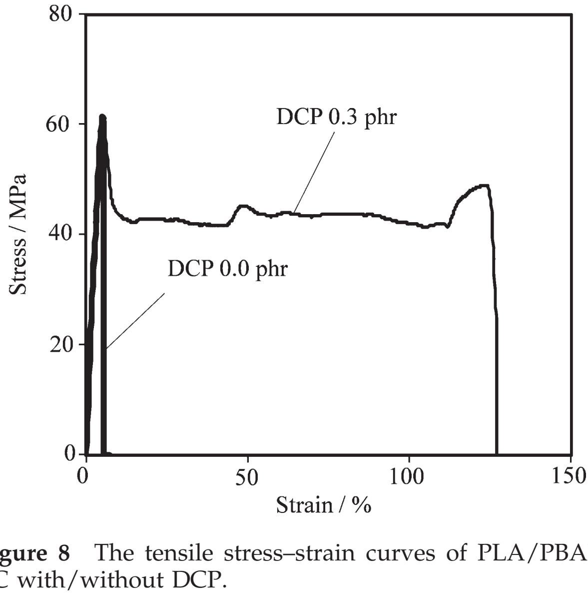


Figure 8 The tensile stress–strain curves of PLA/PBAT/PC with/without DCP.

Therefore, compatibility of both the extrusion productivity and the improvement of mechanical properties such as the elongation at break and the impact strength were achieved. In the following sections, the PLA/PBAT/PC ternary system was used to investigate prereactive blending of PLA/PBAT with DCP before blending with PC by the two-steps method or the side-feed method.

SEM observation

Figure 9 shows the SEM micrographs of fractured frozen PLA/PBAT (70/30) (wt/wt) with DCP (0.0, 0.1,

TABLE IV
The Charpy Impact Strength of PLA, PLA/PC (60/40) (wt/wt) and PLA/PBAT/PC (42/18/40) (wt/wt/wt) With/Without DCP Prepared by a Side-Feed Method

			Impact strength	
Notch type	Polymers	DCP/phr	/kJ/m^2	σ^c
Notched	PLA[a]	0.0	2.1	0.2
	PLA/PC	0.0	1.9	0.2
	PLA/PBAT/PC	0.0	2.1	0.9
		0.3	3.0	0.2
Unnotched	PLA[a]	0.0	18	0.2
	PLA/PC	0.0	56	27
	PLA/PBAT/PC	0.0	41	12
		0.3	NB[b]	–

[a] Prepared at 180°C.
[b] Not-breakable.
[c] Standard deviation.

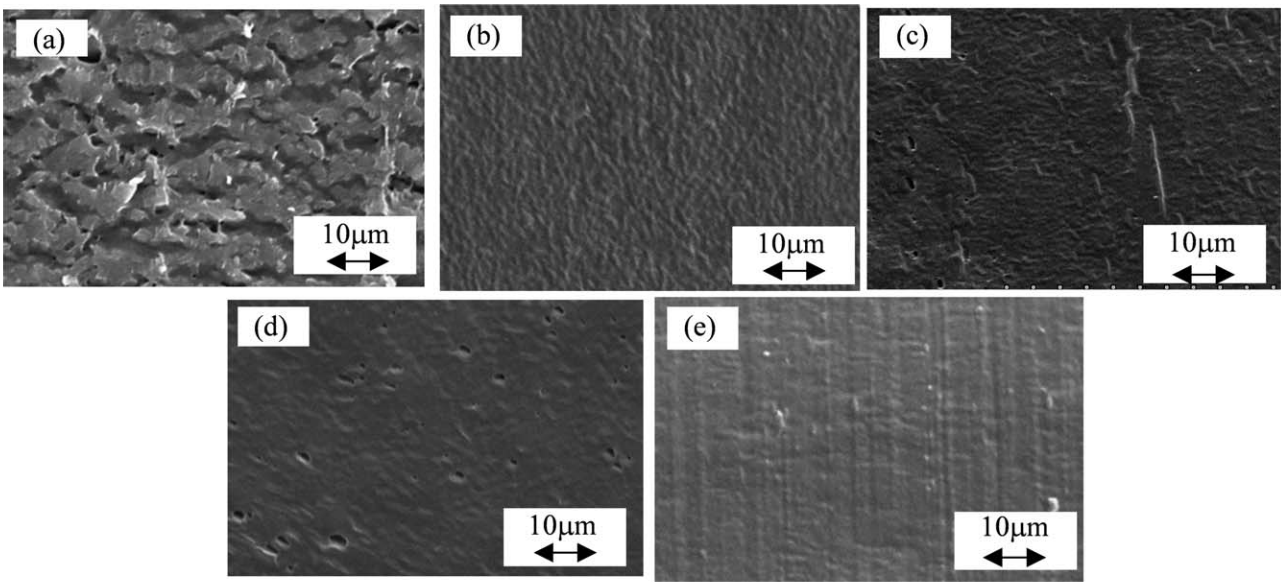
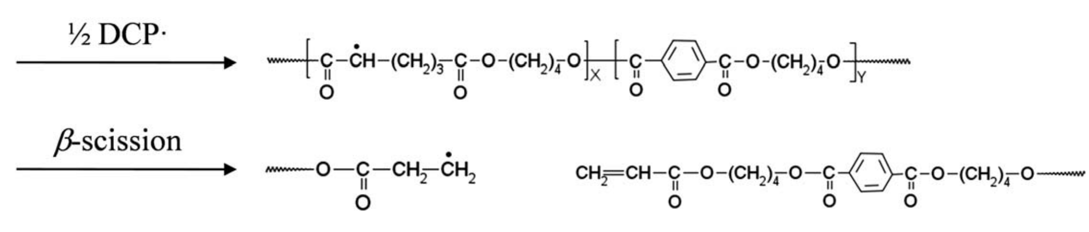


Figure 9 The SEM observation results of PLA/PBAT(70/30) (wt/wt) with DCP (a) 0.0, (b) 0.1, (c) 0.3, (d) 0.5 and (e)1.0 phr prepared by fracturing the frozen samples.

0.3, 0.5, and 1.0 phr) samples. Phase separation was clearly observed for the PLA/PBAT blend without DCP in Figure 9(a), which indicates that PLA and PBAT are immiscible. However, in the reactive blend of PLA/PBAT with DCP in Figures 9(b− e), such phase separation was not evident, because the compatibility of PLA and PBAT was improved by addition of the DCP reaction initiator. After the scission of organic peroxide occurs, the free radical can easily extracts a secondary hydrogen from the α-carbon atom of PBAT, and then β-scission occurs to yield a primary radical and the α, β-unsaturated carbonyl chain, as illustrated in Scheme 1.[11] On the other hand, PLA has tertiary carbon atoms of which the generated radical is stabilized even under melt conditions, which resulted in crosslinking,[16] so that β-scission of PLA does not occur by the addition of DCP. When taking these results into consideration, we proposed the most probable structures derived from the reaction of the PLA/PBAT blend and DCP as follows: (1) branched structures of PLA via homogeneous radical coupling reactions, (2) PBAT-grafted PLA via radical coupling between primary radicals of PBAT and tertiary radicals of PLA, (3) branched structures of PLA and PBAT via heterogeneous radical coupling reactions between ternary radicals of PLA and secondary radicals of PBAT, (4) branched structures of PBAT via homogeneous radical coupling reactions on the α, β-unsaturated carbonyl chain ends. Considering the significant morphology change of the PLA/PBAT blend with/without DCP, the reaction of PBAT-grafted PLA and PBAT-branched PLA would be most probable, and would lead to a finely dispersed phase of PBAT within the PLA phase.

Figure 10 shows SEM micrographs of tensile tests fracture samples of PLA/PC (60/40) (wt/wt) and PLA/PBAT/PC (42/18/40) (wt/wt/wt) blends prepared by the top-feed method. At the fractured surfaces of the binary blend [PLA/PC; Fig. 10(a)] and the ternary blend without DCP [Fig. 10(b)], many small particles (spherical island phases) are observed, and the domain size was about 5−10 μm. In contrast, the ternary reactive blend [DCP 0.3 phr; Fig. 10(c)] of which the elongation at break was higher than that



Scheme 1 The probable mechanism for radical reaction of PBAT.

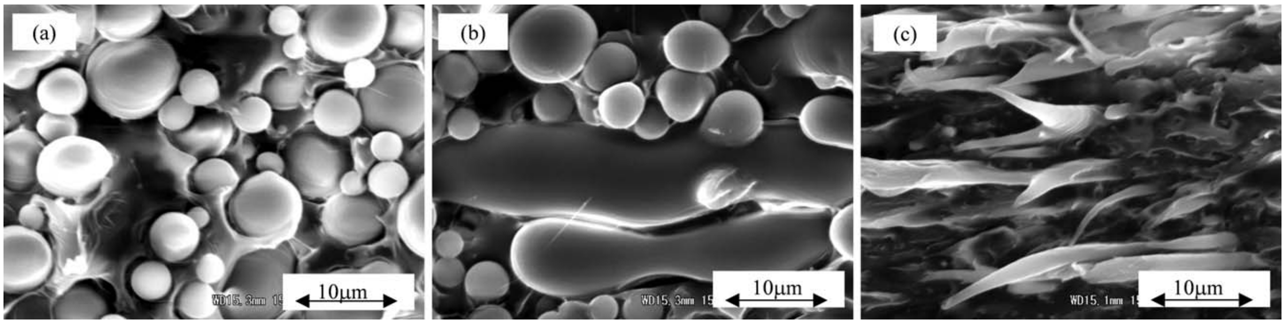


Figure 10 The SEM observation results of PLA/PC (60/40) (wt/wt) and PLA/PBAT/PC (42/18/40) (wt/wt/wt) blends fractured by tensile tests: (a) PLA/PC, (b) PLA/PBAT/PC with DCP 0.0 phr and (c) PLA/PBAT/PC with DCP 0.3 phr.

prepared by other methods, had many fibril-like structures, which indicates that the interfacial adhesion among each dispersed phase was improved by the addition of DCP.

Figure 11 shows the SEM micrographs of fractured charpy impact (notched) samples of PLA/PC (60/40) (wt/wt) and PLA/PBAT/PC (42/18/40) (wt/wt/wt) blends prepared by the side-feed method. It should be noted that PBAT and PC were removed from the fractured samples by solvent etching. Figure 11(c) shows many small spherical phases and the domain size of the island phases was about 0.05−1 μm [Fig. 11(c), magnified inset]. The domain size was much smaller than that for the mechanical blend [Fig. 11(b)] and PLA/PC blend [Fig. 11(a)]. It has already been determined that (1) the mechanical properties of PLA/PBAT/PC blends were improved by prereactive blending of PLA/PBAT with DCP prior to blending with PC and (2) PLA and PBAT can react to yield grafted- and/or branched-PLA by the addition of DCP, which lead to a finely dispersed phase of PBAT within the PLA phase. When taking these results into consideration, the SEM observations indicate that DCP could cause PBAT to easily react with PLA in the first to fifth zone of the extruder, and as a result, it also assisted in reducing the surface energy of

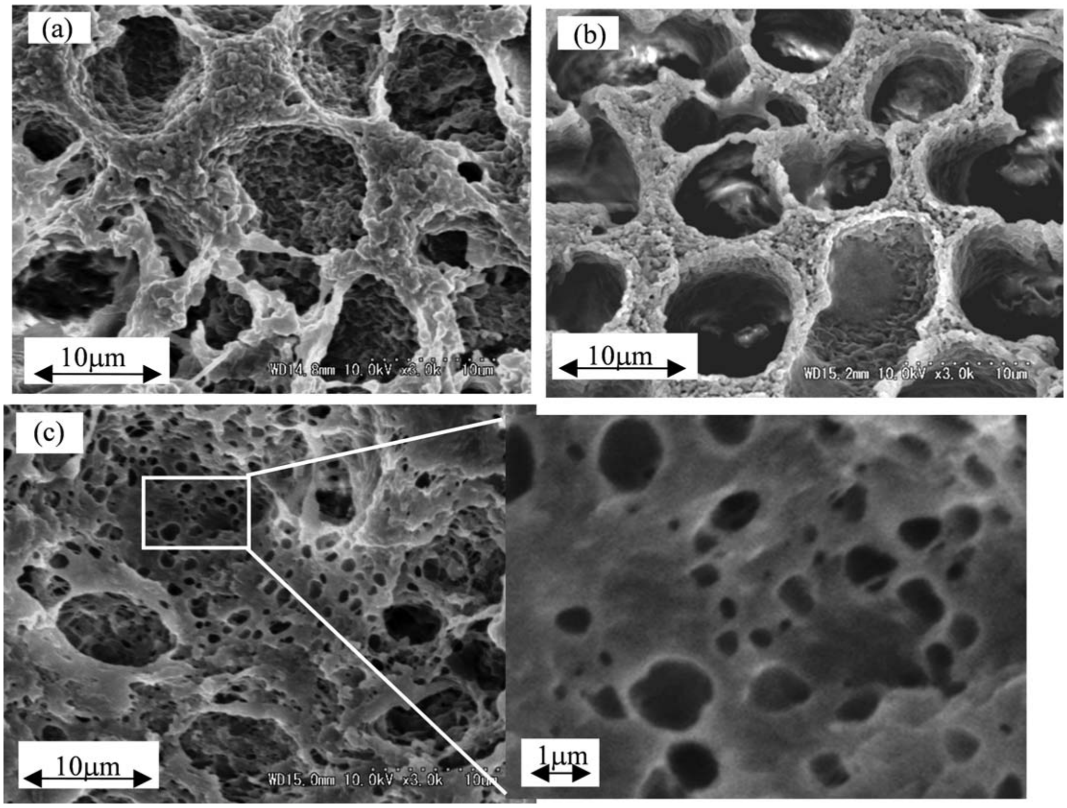


Figure 11 The SEM observation results of PLA/PC (60/40) (wt/wt) and PLA/PBAT/PC (42/18/40) (wt/wt/wt) fractured by charpy impact tests with notch: (a) PLA/PC, (b) PLA/PBAT/PC without DCP and (c) PLA/PBAT/PC with DCP (0.3phr).

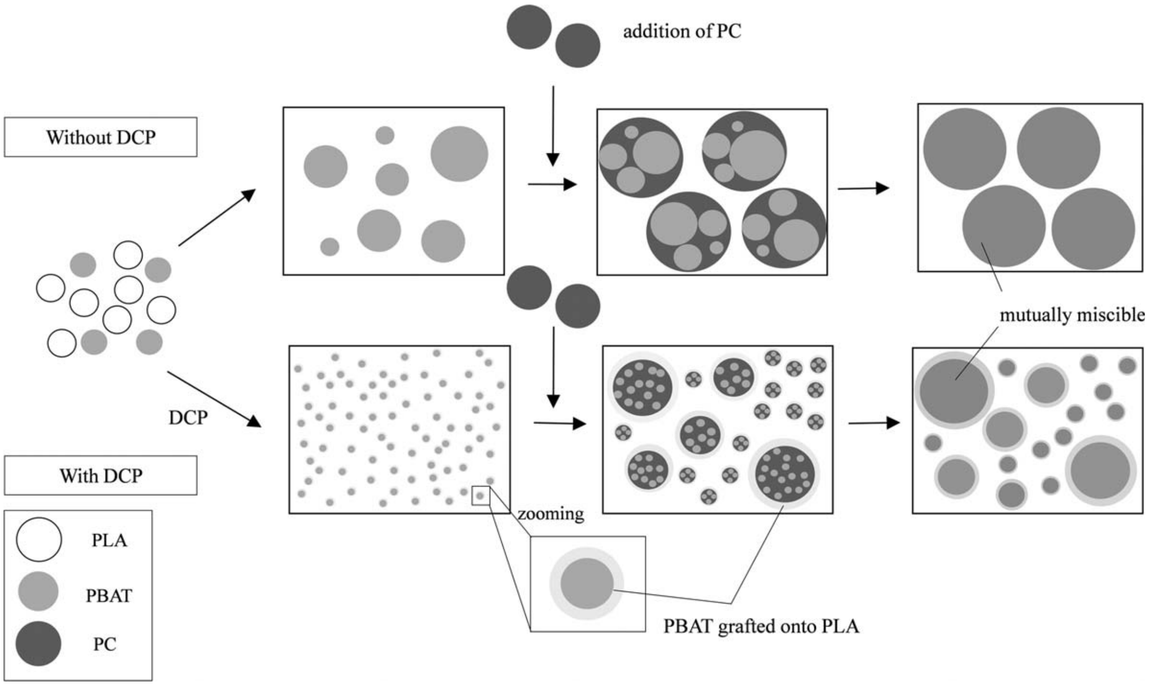


Figure 12 The proposed mechanism of the morphological change in PLA/PBAT/PC blends.

PLA/PBAT to incorporate with the PC phase through RP when added from the fifth zone of the extruder through a side feeder. This morphological change had an influence on the improvement of the mechanical properties, such as the elongation at break and the impact strength of the PLA/PBAT/PC blends.

On the basis of above results, we propose a morphological change mechanism for this system in Figure 12, as follows:

Without DCP, (1) first, large islands of PBAT are dispersed into the PLA phase, because they are immiscible, (2) then the PC phase tends to locate near the PBAT phase due to their good miscibility, and (3) finally, a two-dispersed phase of PLA/PBAT/PC with large islands could be formed.

With DCP, (1) first, PBAT can react with PLA through RP and result in a dispersion of small islands in PLA, (2) then the PC phase tends to locate near the PBAT phase due to their good miscibility, and (3) finally, a multidispersed phase of PLA/PBAT/PC could be formed of which the morphology contributes to an enhancement of the mechanical properties.

CONCLUSIONS

1. It has been shown that PC and PBAT were miscible for a wide blend range of PC/PBAT mixing ratios based on DMA results.
2. The compatibility of PLA/PBAT (70/30) (wt/wt) was improved by addition of DCP based on the results of SEM observations, and the optimum amount of DCP in PLA/PBAT for PLA/PBAT/PC ternary blends was 0.5 phr based on MFR results.
3. The ternary reactive blend (PLA/PBAT/PC) using a prereactive blending of PLA and PBAT prepared by the two-steps method and side-feed method was sufficient to improve the mechanical properties.
4. SEM observations of PLA/PBAT/PC blends revealed many small spherical island phases and a domain size of about 0.05–1 μm for the blends prepared by RP, although the domain size was ∼ 10 μm without RP.

References

1. Tsuji, H. Poly (lactic acid); Yoneda Shuppan: Chiba, Japan, 2008.
2. Kido, T.; Yoshimura, M.; Yoda, K. Japan, Published patent application 1995, 109413.
3. Takehara, A.; Onoki, T.; Kageyama, F. Japan, Published patent application 2007, 131795.
4. Kitamura, A.; Tokumitsu, K.; Tanaka, A. Polym Prepr Jpn 2007, 56, 3897.
5. Jiang, L.; Wolcott, M. P.; Zhang, J. W. Biomacromol 2006, 7, 199.
6. Gu, S. Y.; Ren, J.; Zhang, K.; Zhan, H. Carbohydr Polym 2008, 74, 79.
7. Xiao, H.; Lu, W.; Yeh, J. T. J Appl Polym Sci 2009, 112, 3754.
8. Ide, F.; Hasegawa, A. J Appl Polym Sci 1974, 18, 963.
9. Menges, G.; Bartilla, T. Polym Eng Sci 1987, 27, 1216.
10. Carlson, D.; Nie, L.; Narayan, R.; Dubois, P. J Appl Polym Sci 1999, 72, 477.
11. Mani, R.; Bhattacharya, M.; Tang, J. J Polym Sci Part A 1999, 37, 1693.
12. Huneault, M.; Li, H. Polymer 2007, 48, 270.
13. Zhang, J.; Sun, X. J Appl Polym Sci 2004, 94, 1697.

14. Zhang, J.; Sun, X. Biomacromol 2004, 5, 1446.
15. Dubois, P.; Narayan, R. Macromol Symp 2003, 198, 233.
16. Kanzawa, T.; Tokumitsu, K. J Mat Sci Jpn 2009, 58, 16.
17. Semba, T.; Kitagawa, K.; Ishiaku, U. S.; Hamada, H. J Appl Polym Sci 2006, 101, 1816.
18. Semba, T.; Kitagawa, K.; Ishiaku, U. S.; Kotaki, M.; Hamada, H. J Appl Polym Sci 2007, 103, 1066.
19. Yoshida, I.; Obuchi, S.; Kitahara, Y.; Watanabe, T.; Aihara, H.; Nakata, T. Japan, Published patent application 2001, 26658.
20. Kanamori, K.; Horibe, Y. Japan, Published patent application 2001, 64379.
21. Ueda, K.; Matsuoka, F.; Fujita, M. Japan, Published patent application 2004, 67894.
22. Kanamori, K.; Horibe, Y. Japan, Published patent application 2002, 37995.
23. Horibe, Y. Kokai Japan, Published patent application 2002, 69192.
24. Harada, M.; Ohya, T.; Iida, K.; Hayashi, H.; Hirano, K.; Fukuda, H. J Appl Polym Sci 2007, 106, 1813.
25. Harada, M.; Iida, K.; Okamoto, K.; Hayashi, H.; Hirano, K. Polym Eng Sci 2008, 48, 1359.
26. Wu, S. Polym Eng Sci 1987, 27, 335.