

Effect of Compounding Procedure on Mechanical Properties and Dispersed Phase Morphology of Poly(lactic acid)/Polycaprolactone Blends Containing Peroxide

Takeshi Semba,¹ Kazuo Kitagawa,¹ Umaru S. Ishiaku,² Masaya Kotaki,² Hiroyuki Hamada²

¹Organic Materials Laboratory, Kyoto Municipal Industrial Research Institute, Industrial Research Center, Shimogyo-ku, Kyoto 600-8813, Japan

²Division of Advanced Fibro-science, Kyoto Institute of Technology, Gosityokaido-cho, Matsugasaki, Sakyo-ku, Kyoto 606-5858, Japan

Received 16 May 2006; accepted 9 August 2006

DOI 10.1002/app.25311

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Side feeding technique was applied to poly(lactic acid) (PLA)/polycaprolactone (PCL) blends containing peroxide. Feeding procedures attempted were blanket and split feeding. In the former procedure, all the materials were fed into the main hopper at once. On the other hand, the feeding of materials was split by using main hopper and side feeder in the later procedure. The results indicated that static tensile properties were not dependent on feeding procedure, but the impact strength was superior in the case of the split feeding samples. It is noteworthy that the impact strength of the split feeding sample was considerably affected as it was four times better.

Coarse dispersions such as continuous filament and layer dispersions were formed in the blend specimens without peroxide. On the other hand, fine dispersions were formed in the blend specimens containing peroxide which served as compatibilizer in this blend system. Peroxide addition through the side feeder brought about fine dispersions, promoted adhesion at the interface, and increased viscous nature of the PCL phase. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1066–1074, 2007

Key words: poly lactic acid; poly caprolactone; blend; peroxide

INTRODUCTION

Side feeding technique is often used in polymer/filler composites systems because filler fragmentation easily occurs when it is fed into molten polymers. Therefore many related studies have been published or commercialized.^{1–4} In the case of fiber-reinforced composites, glass or carbon fibers used as reinforcing fibers break easily during the compounding process, and this often results in reduction of mechanical properties, and so on. Side feeding method resolves this issue as fiber addition is delayed, which decreases excessive fiber breakage.⁵ A recent development is the compounding of organoclay used as nanofiller with various polymers. This employs such techniques that are capable of yielding nanosize dispersions.^{6–9} The high modulus and strength are notable features of these nanocomposites in which the distance of each nanofiller is several dozens of nanometer.

However, studies of polymer/polymer composites systems using side feeding techniques are rather lim-

ited. St-Pierre et al.¹⁰ investigated the thermoplastic starch/polyethylene blends, in which the thermoplastic starch was fed into a twin-screw extruder by using a single-screw extruder. The fine dispersed morphology of the starch was constructed in polyethylene matrix. Huneault et al.¹¹ examined polyethylene/polypropylene blends with similar compound process which takes into account feeding states such as solid or melt, and feeding positions. These attempts may open up epoch-making polymer compounding methods for polymer blend materials.

Poly(lactic acid) (PLA) resin as a biobased polymer is expected to become a “green substitute” for petroleum-based polymers in commodity and perhaps engineering applications. But it has defects such as brittle properties, low heat resistance, and poor processing properties. Recently, the authors improved this brittle nature by blending with polycaprolactone (PCL) and dicumyl peroxide (DCP).^{12–14} The ductile nature of PCL gets imparted to the PLA matrix because of improve interfacial adhesion resulting from cocrosslink formation by the DCP. This yields a ductile material with five times better elongation at break than the corresponding blend without peroxide.

In this study, the side feeding method was applied to the PLA/PCL blend containing peroxide, to

Correspondence to: T. Semba (sentake@city.kyoto.jp).

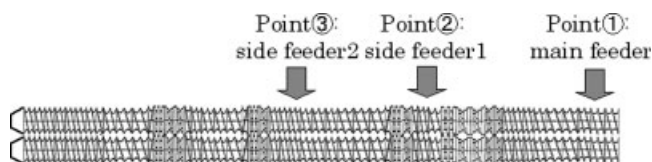


Figure 1 Schematic diagram of screw configuration and feeding positions.

enhance efficiency of interfacial adhesion and dispersion properties.

EXPERIMENTAL

Materials and polymer processing

The materials used in this study were PLA (Lacea, H100, $M_w = 150,000$, melt index = 8.0 g/10 min, $T_m = 164^\circ\text{C}$; Mitsui Chemicals, Tokyo, Japan), PCL (Cel green PH7, $M_w = 160,000$, melt index = 2.3 g/10 min, $T_m = 56^\circ\text{C}$; Daicel Chemical Industries, Osaka, Japan), and DCP (half-life at 175°C is 1 min; NOF Corp., Tokyo, Japan).

The materials were blended with a twin-screw extruder ($\phi = 15$, $L/D = 60$, Technovel Corp.). The blend ratio of PLA/PCL was 70/30 by weight. The DCP content investigated was 0.3 phr which was determined as optimum concentration in previous investigations.^{12–14} Compounding was done at a cylinder temperature of 180°C and screw revolution of 80 rpm. Three feeding positions were employed to investigate the effect of feeding procedure on mechanical properties and dispersed morphology. The screw configuration and sample details are shown in Figure 1 and Table I, respectively. The screw configuration consisted of four kneading and other full-flight zones. The side feeder could be set up at full-flight zone just after the first kneading zone or between second and third kneading zones. The feature of sample Nos. 1 and 3 is that all materials were fed at once through the main hopper (point ①). While the other samples (Nos. 2, 4, 5, and 6) employed split feeding method by using the side feeder which was set up at points ② or ③. The blends without DCP were Nos. 1 and 2. The final composition of all the blends containing DCP was PLA/PCL + DCP = 70/30 wt % + 0.3 phr. The compounded materials were fabricated into dumbbell- and bar-shaped injection moldings.

Dynamic mechanical properties

Dynamic mechanical analysis (DMA) (ARES; TA Instruments, Delaware) yields useful information on interfacial profile, such as the characteristics of the interface, compatibility, etc. The dynamic temperature ramp test was employed for rectangular samples fabricated by injection machine. Measurement was done at temperatures ranging from -100°C to 200°C with $3^\circ\text{C}/\text{min}$ of ramp speed, 0.1% of strain, and frequency of 6.28 rad/s.

Tensile and Izod impact test

Tensile test for dumbbell-type specimen was carried out by using a Universal testing machine at 50 mm/min while specimen gauge length was 25 mm at room temperature.

Two types of Izod impact tests were carried out for bar-shaped injection moldings. One was normal Izod impact test in which the crack propagated from the tip of the notch. The second was reverse Izod impact test in which the crack propagated from the opposite side against the notch. The former method can evaluate the impact strength taking into account notch sensitivity, while the later method takes into account products in use without crack. The hammer capacities used were 2.75 and 5.5 J.

The fracture surfaces of tensile and Izod impact test were studied with scanning electron microscope (SEM) (JSM5900LV; JEOL, Tokyo, Japan).

Observation of dispersed size and morphology

The cross section of injection moldings were observed by using atomic force microscopy (AFM) (Nanoscope IIIa; Digital instruments Co., California) that is capable of distinguishing each component. The cross-sectional area was adjusted to a flat surface by using a microtome equipped with a glass knife. The tapping mode which is a commonly used observation method in AFM was applied to the cross-sectional area, and the phase images were taken. The size and aspect ratio of dispersions were measured by image analysis.

TABLE I
Sample Details and Feeding Positions During Extrusion

No.	Feeding point			Final composition	Feeding method
	①	②	③		
1	PLA/PCL = 70/30	–	–	PLA/PCL = 70/30	Blanket
2	PCL	PLA	–	PLA/PCL = 70/30	Split
3	PLA/PCL = 70/30 + DCP	–	–	PLA/PCL = 70/30 + DCP 0.3 phr	Blanket
4	PCL	PLA + DCP	–	PLA/PCL = 70/30 + DCP 0.3 phr	Split
5	PLA/PCL = 40/60	–	PLA + DCP	PLA/PCL = 70/30 + DCP 0.3 phr	Split
6	PLA/PCL = 40/60 + DCP	–	PLA + DCP	PLA/PCL = 70/30 + DCP 0.3 phr	Split

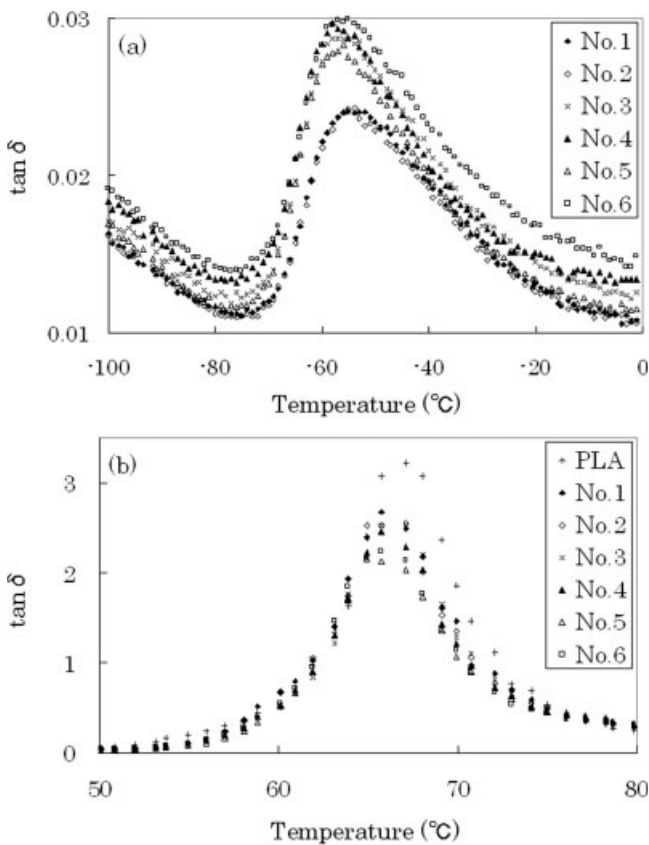


Figure 2 Tan δ curve of DMA (a) around -55°C and (b) around 60°C .

RESULTS AND DISCUSSION

Effect of compounding procedure on viscoelastic property

The storage modulus and loss modulus of all the blends containing DCP were similar, and their differences with the blends without DCP have been reported previously.^{12,13} Differences could be seen in the two tan δ peaks that appear around -55°C and 65°C , which could be associated to the glass-transition temperatures

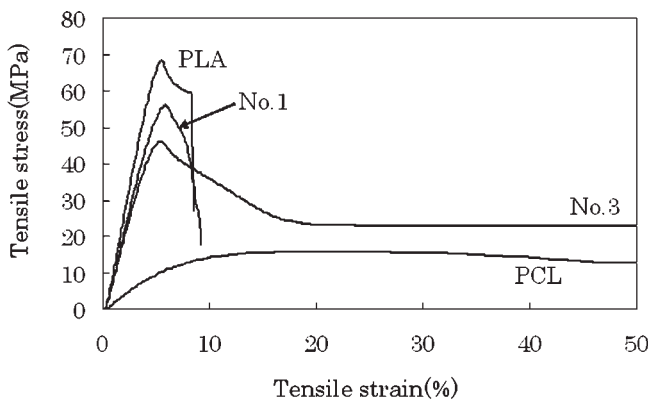


Figure 3 Typical stress-strain curve of neat resins, PLA/PCL blend, and PLA/PCL blend containing DCP.

(T_g) of PCL and PLA. The peak height was changed according to composition and feeding procedure, respectively [Fig. 2(a)]. The peaks of sample Nos. 1 and 2 containing no DCP around -55°C were lower than those of the blends containing DCP. The increased height indicates an increase in the viscous nature of PCL phase, which could have implication on tensile ductility and impact strength. The viscous nature is attributed to crosslinking and decomposition in the PCL phase, in which hydrogen abstraction is easy to

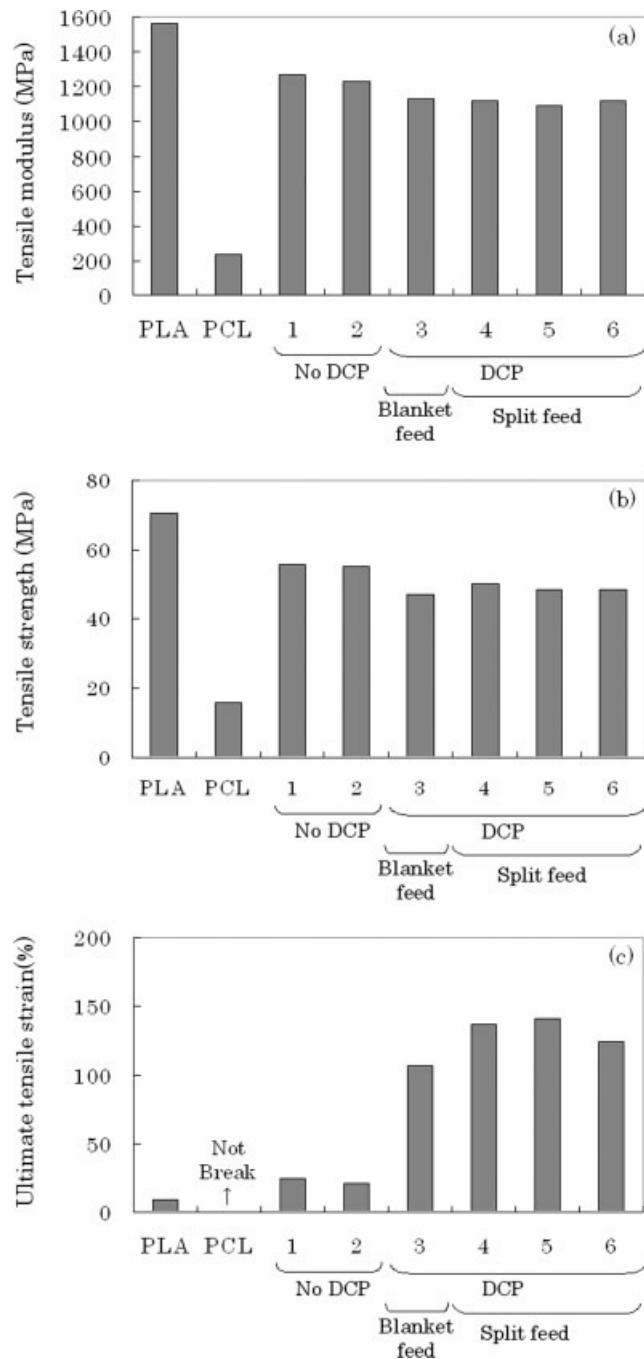


Figure 4 Tensile properties of PLA/PCL blend. (a) Tensile modulus, (b) tensile strength, and (c) tensile strain at break.

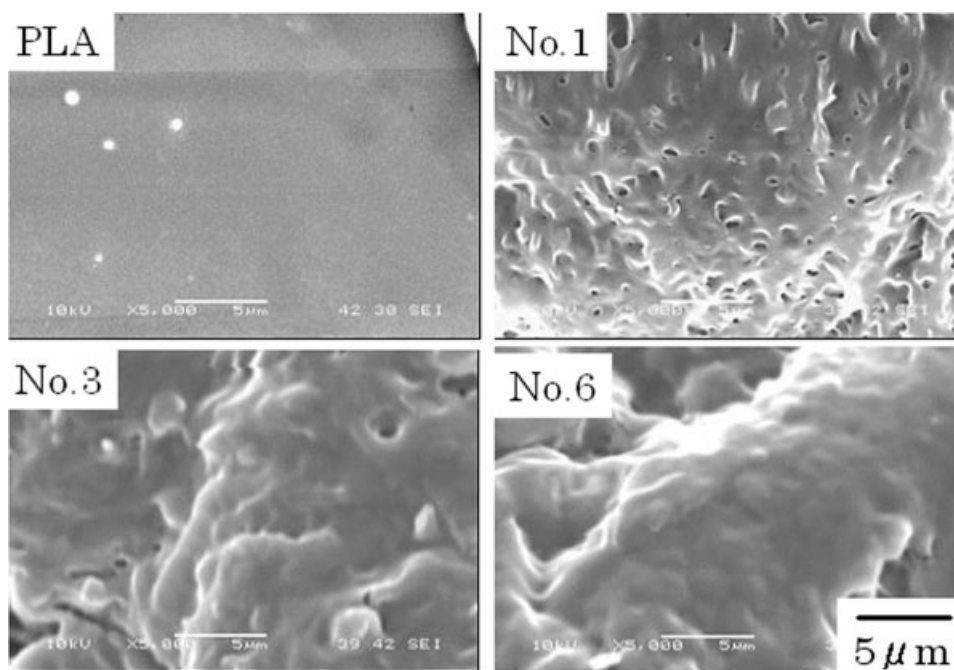


Figure 5 Tensile fracture surface of PLA/PCL blends.

occur, resulting in inclusion of many secondary hydrogen atoms in PCL. The free radicals generated are next to the carbonyl groups, and so β -scission of PCL occurs.¹⁵ Thus, the crosslinking process of PCL phase involves decomposition which should enhance viscosity. The peak height seems to correlate with time for which free radicals generated are active. For example, in the case of sample No. 6, the reaction time for PCL melt was the longest of all blends containing DCP, because free radicals were kept activated by DCP throughout the extrusion process as the DCP was added into main feeder (point ①) and side feeder (point ③). On the other hand, the peak of sample No. 5 was the lowest of all the blends containing DCP, because DCP was fed only at side feeder 2 (point ③) positioned far downstream from the main feeder; therefore, the DCP could not sufficiently work because of the short time available. All the peaks derived from T_g of PLA around 65°C were shifted to lower temperatures from that of neat PLA [Fig. 2(b)], and this indicates a certain degree of compatibility between PLA and PCL phases whether in the presence of DCP or not. DCP facilitates the increase of PCL viscosity, and therefore the preservation of active DCP free radicals would be of importance to have good mechanical properties.

Mechanical property

Mechanical properties were evaluated via tensile test and presented in Figures 3 and 4. Figure 3 shows the typical stress–strain curves of neat samples, the blend without DCP, and that containing DCP. The initial slope and maximum stress of PLA was the highest,

but the strain at break was the smallest. On the other hand, PCL shows low initial slope, indicating the softness of the material and low maximum stress, but the ultimate strain was very high. The PLA/PCL blend without DCP showed similar brittleness as neat PLA; thus PCL on its own does not impart sufficient ductility on PLA. With the addition of DCP, the product showed yield stress and necking. There were no definite differences in the stress–strain curves based on the feeding sequence of DCP. The detailed tensile properties are elaborated in Figure 4. The tensile properties of Nos. 1 and 2 were similar even though the feeding position was different. The modulus and strength decreased slightly in the case of the blend containing DCP, but ultimate strain increased five times. Somehow the tensile properties of the all the blends containing DCP were similar. The differences become obvious by observing the tensile fracture surfaces as shown in Figure 5. The fracture surface of PLA was smooth which indicates occurrence of brittle fracture. PCL was blended with PLA to improve this brittle property of PLA, but the desired ductile nature was not imparted to the PLA matrix in sample Nos. 1 and 2. There were many dropout traces in the tensile fracture surface of the blends without DCP (Nos. 1 and 2). It is inferred that these dropout traces at the fracture surface arise from the weak interfacial adhesion of PLA/PCL. On the other hand, the same aspects in which there were no dropout traces were observed in all the PLA/PCL blends containing DCP in accordance with the tensile results. This indicates that the interfacial adhesion was improved as a result of interaction brought about by DCP addition.

Figure 6(a) shows the result of normal Izod impact test done with a hammer of 2.75 J capacity. The impact strength of the blend specimens could be classified into two groups which were low value samples without DCP and high value samples containing DCP. Sample No. 6 belonging to latter group showed the highest impact strength of all. Further differences became obvious in the reverse Izod impact test with hammer capacity of 2.75 J as shown in Figure 6(b).

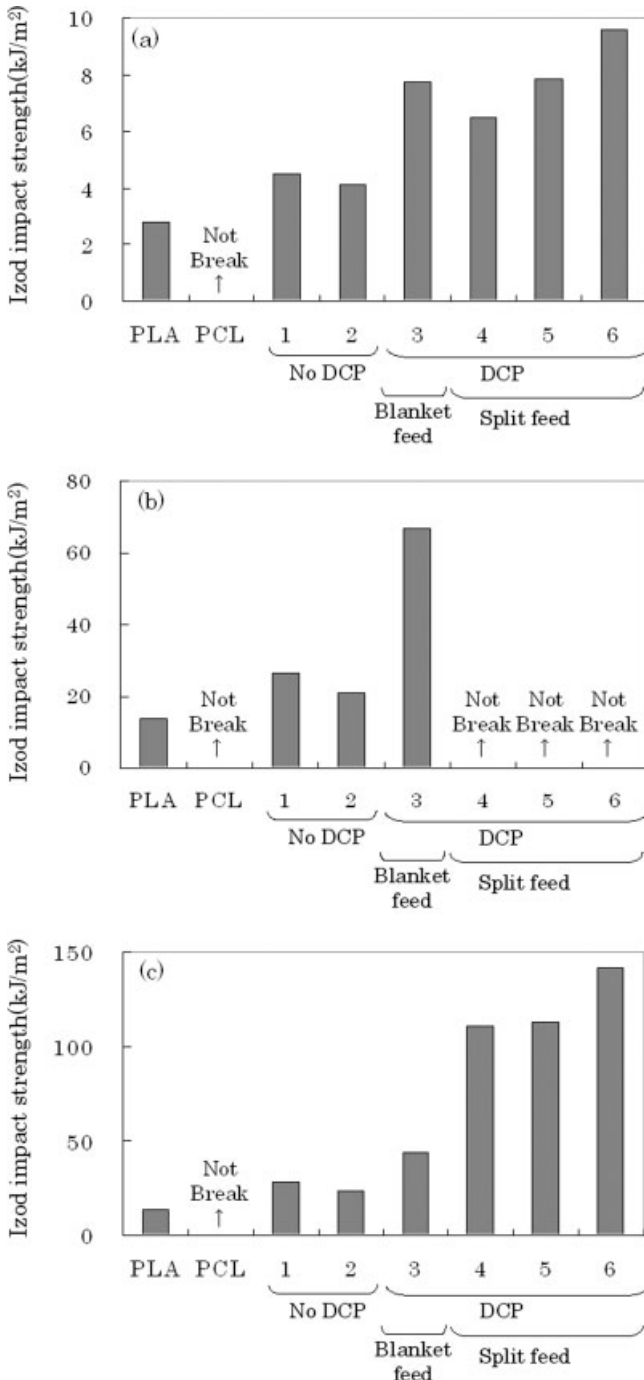


Figure 6 Izod impact strength of PLA/PCL blend. (a) Normal test with 2.75 J, (b) reverse test with 2.75 J, and (c) reverse test with 5.5 J.

The impact strength of the blanket feed sample No. 3 was about 3.5 times better than the blend without DCP. Furthermore, samples Nos. 4, 5, and 6 with split feeding were not broken in this test. Therefore, higher impact energy from a bigger hammer with capacity 5.5 J was applied to the samples as shown in Figure 6(c). The impact strength value of sample No. 6 was nine times higher than that of pure PLA, and this phenomenon indicates the effect of split feeding in this study. The impact strength of sample No. 6 is four times higher than that of No. 3 (blanket feeding) even though both have the same composition.

The Izod fracture surfaces at two areas obtained by using the hammer of 5.5 J, i.e., the initiation area of crack and center of specimen, are shown in Figure 7. There were some differences depending on the composition and feeding procedure. The dropout traces of sample Nos. 1 and 2 were observed at both areas. The dropout traces at the center area of No. 3 was similar to Nos. 1 and 2 on one hand, and that at initiation area was not too conspicuous on the other. Furthermore, the fracture aspects of samples Nos. 4 and 5 are similar to that of 6, in which there were no dropout traces. These fracture aspects also agree with the impact strength values.

The ultimate tensile strain of sample No. 3 (Blanket feed) was almost the same as those of the other blends containing DCP, but the impact strength was smaller, i.e., the ductility of sample No. 3 differs between static and dynamic tests. This may be attributed to the interfacial adhesion of sample No. 3 being insufficient. The tensile static stress is conducted slowly through all the dispersed particles via the interface with stress relaxation, and so the interfacial adhesion would be capable of showing resistance against breakage. It is evident that there were no exposed particles in the tensile fracture surface of sample No. 3 (Fig. 5). However, the adhesive forces in sample No. 3 could not bear against the impact (dynamic) stress which concentrated on a limited part without stress relaxation. The presence of dropout traces on impact fracture surface of sample No. 3 (Fig. 7) is an evidence of this phenomenon. The addition of DCP at the middle of the extruder, where the dispersed phase would be more stable than that at the upstream, was more effective in promoting interfacial adhesion. This method is efficient, because the peroxide is concentrated on the interfacial area. In the case of the addition of DCP only at the main hopper, the adhered interfaces are broken up at upstream to midstream areas in the extruder, and the active DCP free radicals would have been depleted beyond the midpoint or downstream. Accordingly, insufficient interfacial adhesion would be formed.

Internal structure of injection moldings

The dispersed state and size have direct relationship with mechanical properties of polymer blend materi-

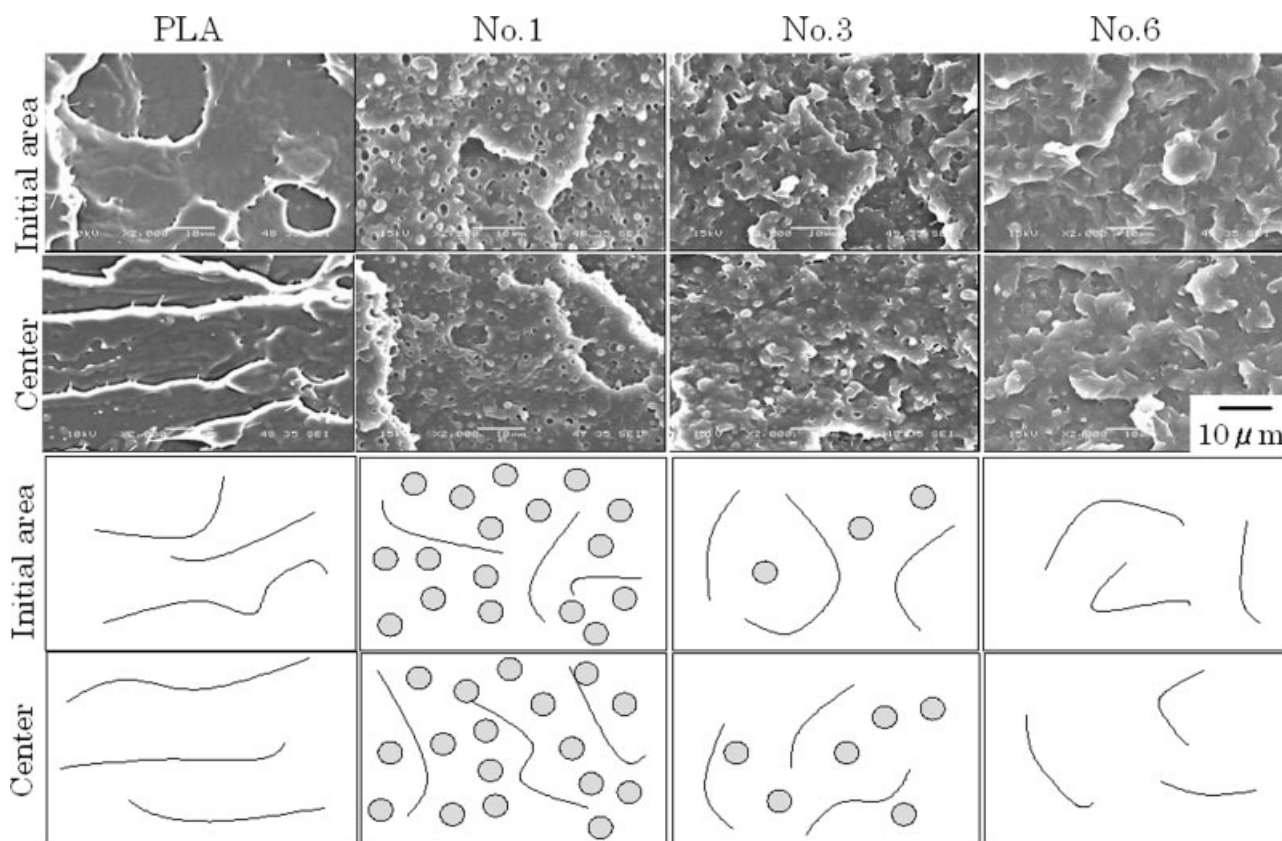


Figure 7 Izod impact fracture surface and schematic diagram of PLA/PCL blends.

als. Therefore, these were observed and measured by using AFM and image analysis. The phase-separated images from AFM were traced and converted to binary

images, and the size and aspect ratios were calculated. The AFM images of the skin layer of injection moldings are shown in Figure 8. The interesting morphology, in

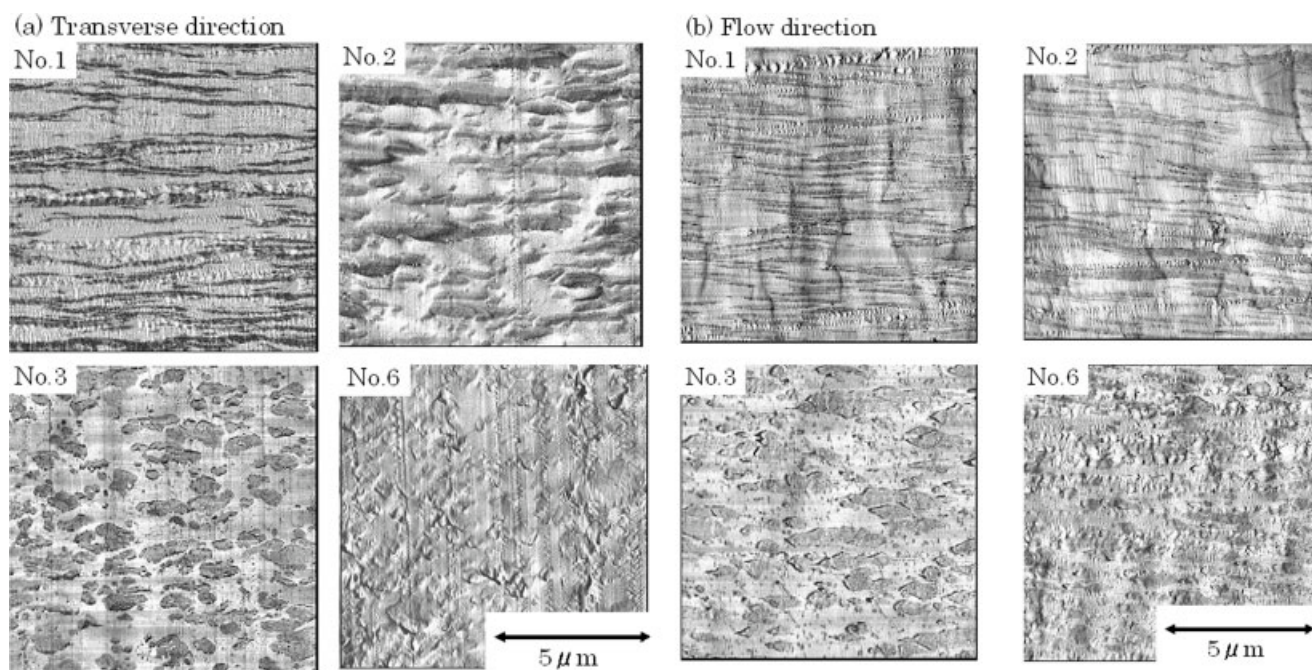


Figure 8 AFM phase image of injection moldings at skin area. (a) Transverse direction and (b) flow direction.

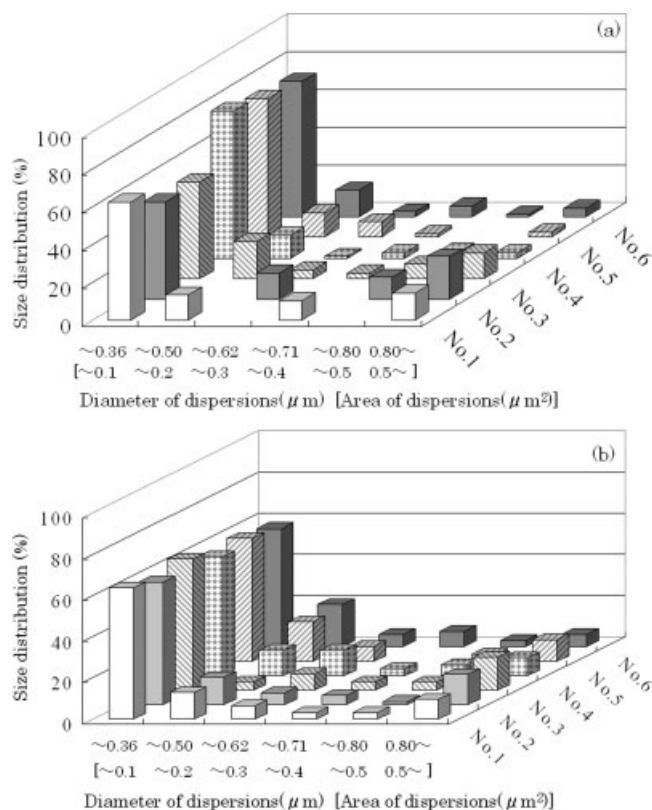


Figure 9 Size distribution of dispersed phase at skin area in injection moldings. (a) Transverse direction and (b) flow direction.

which the dispersions of both transverse and flow directions are stretched, was observed in the blend without DCP (samples Nos. 1 and 2). The average layer size of sample No. 1 was $1.13 \mu\text{m}$ wide and $2.00 \mu\text{m}$ long while that of sample No. 2 was $1.43 \mu\text{m}$ wide and $19.0 \mu\text{m}$ long. The dispersions of all blends containing DCP exhibit a similar morphology in which the shape was either spherical or spheroidal. The average dispersed diameters along transverse direction of sample Nos. 3, 4, 5, and 6 were 0.523 , 0.379 , 0.371 , and $0.424 \mu\text{m}$, respectively. The average dispersed size is an often useful data, but it sometimes leads to prejudiced conclusion because it describes only a limited profile. Therefore, to verify further the detailed dispersed state, the size distribution of the dispersions was measured. The distribution size was shown in Figure 9. The finest dispersed class under $0.36 \mu\text{m}$ of diameter along transverse direction of samples Nos. 1, 2, and 3 was less than that of the split feed blend containing DCP, while coarse dispersions frequently existed [Fig. 9(a)]. On the contrary, the sum of the finest ($\sim 0.36 \mu\text{m}$) and second ($\sim 0.50 \mu\text{m}$) finer dispersed class of samples No. 4, 5, and 6 were more than 90%. The size distribution of sample No. 3 was quite different from that of sample Nos. 4, 5, and 6, even though it contains DCP. The fine dispersions were less at skin layer, and its distribution was similar to those of samples Nos. 1 and 2. The

dispersed particles at skin layer were stirred by strong shear flow during the injection process, and so it is considered that the interface of sample No. 3 with insufficient adhesion would be broken and newly generated particles without cocrosslinking would be coalesced. Similar results along flow direction were obtained in all blend systems [Fig. 9(b)]. Among all the samples, the dispersions of sample Nos. 4, 5, and 6 were of relatively finer distribution. The aspect ratio values and schematic diagram of dispersions in injection moldings at skin layer are shown in Table II and Figure 10. The dispersions at skin layer of sample Nos. 1 and 2 formed broad layer structure. The dispersions become finer gradually and spherical in shape with DCP addition while taking full advantage of optimum feeding procedures.

Figure 11(a) shows the AFM images of the injection moldings at the core layer along the transverse direction. It seemed that the morphology was quite different from that of the skin layer. The morphology was such that the size was increased, and the shape was close to spherical due to low shear stress, stress relaxation, and coalescence. The size distributions of the dispersed phase in injection moldings along transverse direction were measured as shown in Figure 12(a). The distribution of sample Nos. 1 and 2 were similar in which the dispersed size under $0.36 \mu\text{m}$ was only 20%, and other coarser dispersed classes were major. On the other hand, the blend containing DCP consisted of finer dispersions in comparison with the blend without DCP. Especially, the dispersed state of sample No. 6 had the finest structure.

Figure 11(b) shows the AFM images of the injection moldings at the core layer along the flow direction. The continuous filaments lay along the whole length of the image frame, which was $10 \mu\text{m}$, in sample Nos. 1 and 2, and hence their actual size could not be measured. The morphology of the blends containing DCP seemed to attain fine spherical and spheroidal shapes. The size distribution is shown in Figure 12(b). The dispersed state of sample No. 6 was also the finest of all along flow direction at core layer. The aspect ratios of the dispersed phase in the injection moldings at the core layer are shown in Table III. The aspect ratios except for the flow direction of sample Nos. 1 and 2 were below 1.0

TABLE II
Aspect Ratio of Dispersed Phases in Injection Moldings at Skin Area

No.	TD cross section aspect ratio (–)	FD cross section aspect ratio (–)
1	9.13	12.5
2	3.48	7.18
3	1.95	2.73
4	1.46	1.14
5	1.31	1.95
6	0.873	2.06

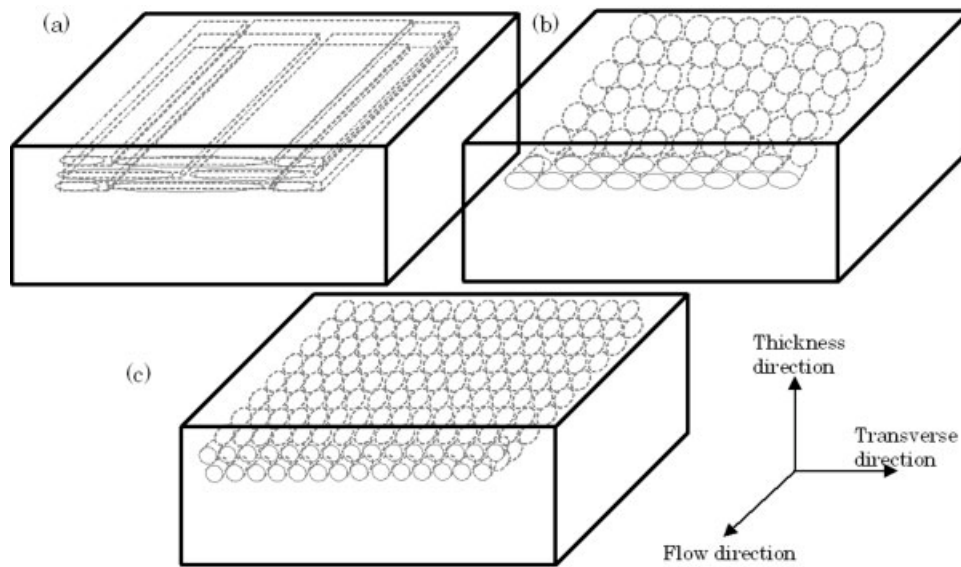


Figure 10 Schematic diagram of dispersed morphology in injection moldings at skin layer. (a) No DCP, (b) blanket feed, and (c) split feed.

which describes the dispersed phase as spheroidal along the thickness direction. Two typical schematic diagrams for the injection moldings at the core layer could be drawn as shown in Figure 13. The dispersions of the blend without DCP were stretched and became coarse continuous filaments. On the other hand, there were no differences between the blanket and split feed blend containing DCP. The dispersions were spheroidal in shape along thickness direction.

Thus, the dispersed size of the blends containing DCP was entirely fine. It is considered that the DCP fixed the interface between both phases by cocrosslinking. Accordingly, the dispersed state could be retained while the materials were re-melted for fabrication during injection molding. This could suppress the reduction of fine dispersions. Furthermore, it was

clarified that the feeding method also affected the dispersed state of injection moldings. The addition of DCP at midstream of the extruder brought about beneficial effect as the concentration of DCP at the interface was stimulated, and the viscous nature of PCL also increased. The dispersed morphologies of all the blends containing DCP at core layer were similar; however, the skin layers were different. The blanket feed blend containing DCP was coarser than that of split feed blend. The dispersed size could account for the superior impact properties of the split feed blend. The impact strength of split feed blend was far superior to that of the blanket feed blend. It is noteworthy that the impact strength of sample No. 6 was superior to the other split feed blend containing DCP as well. Several reasons could be proposed to account for this

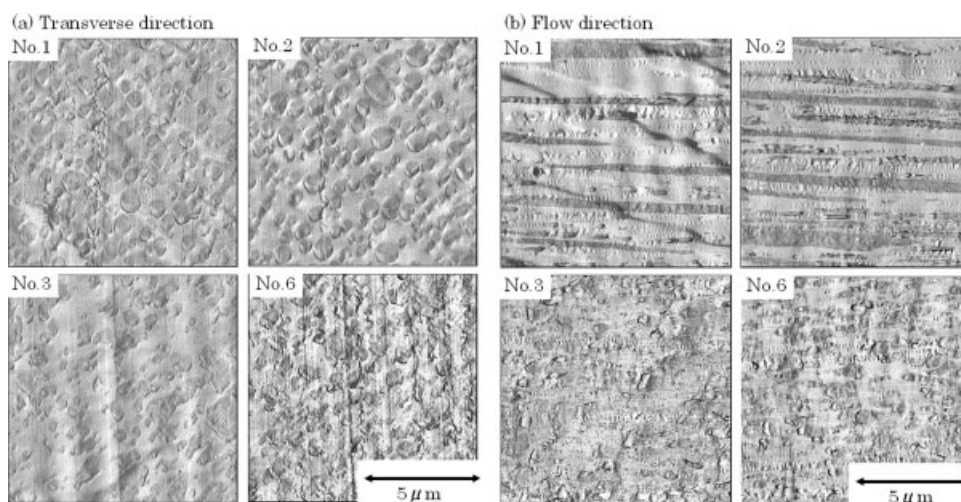


Figure 11 AFM phase image of injection moldings at core area. (a) Transverse direction and (b) flow direction.

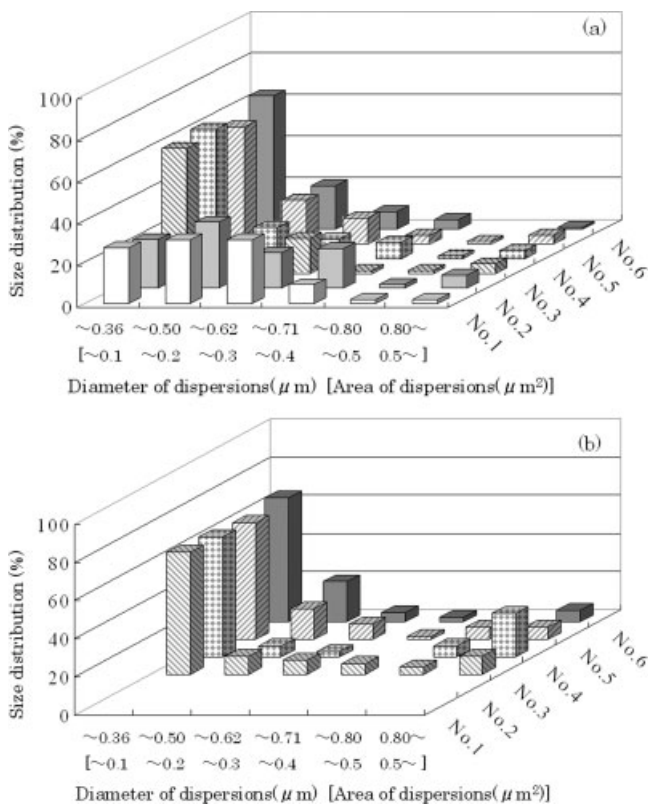


Figure 12 Size distribution of dispersed phase at core area in injection moldings. (a) Transverse direction and (b) flow direction.

observation as follows; first, DCP free radicals were kept active for the longest period by DCP addition at main and side feeders. Second, the finest dispersed size is developed during split feed method, and the addition of a little DCP at the main hopper may have affected the viscosity ratio of the two phases that led to fine dispersions.

CONCLUSIONS

The effect of compounding procedure by means of side feeder on the mechanical properties and disperse phase morphology was investigated in this study. The addition of DCP at the middle of the extruder was more effective because the DCP works as cocrosslink-

TABLE III
Aspect Ratio of Dispersed Phases in Injection Moldings at Core Area

No.	TD cross section aspect ratio (–)	FD cross section aspect ratio (–)
1	0.876	Large
2	0.762	Large
3	0.764	0.280
4	0.849	0.745
5	0.823	0.422
6	0.758	0.367

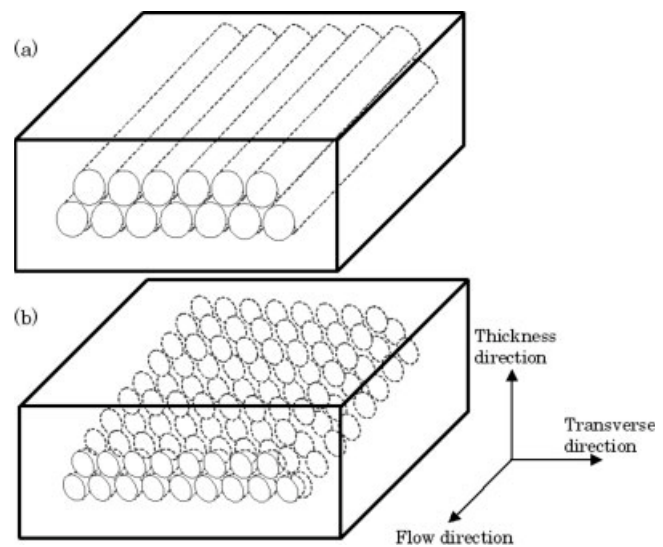


Figure 13 Schematic diagram of dispersed morphology in injection moldings at core layer. (a) No DCP and (b) containing DCP.

ing agent against a stable dispersed phase. Furthermore, when the DCP addition was split, i.e., the DCP was added at main and side feeders, the high viscous nature of PCL phase, adhesion of interface, and a fine dispersed state were attained. Consequently, the high impact strength could be attained. It was concluded that the side feeding method was valuable to the PLA/PCL blend containing DCP.

References

- Todd, D. *Adv Polym Technol* 2000, 19, 54.
- Mobley, G.; Boutelle, T.; Garrett, S.; Joiner, L.; Calhoun, A. *J Vinyl Additive Technol* 2004, 8, 271.
- Huneault, M.; Godfroy, P.; Lafleur, P. *Polym Eng Sci* 2004, 39, 1130.
- Schrauwen, B. A. G.; Govaert, L. E.; Meijer, H. E. H. *Macromol Symp* 2002, 185, 89.
- Roberts, D.; Constable, R.; Thiruvengada, S. *Polym Eng Sci* 2004, 37, 1421.
- Tanoue, S.; Utracki, L.; Garcia-Rejon, A.; Tatibouet, J.; Cole, K.; Kamel, M. *Polym Eng Sci* 2004, 44, 1046.
- Ton-That, M.; Perrin-Sarazin, F.; Cole, K.; Bureau, M.; Denault, J. *Polym Eng Sci* 2004, 44, 1212.
- García-López, D.; Merino, J.; Gobernado-Mitre, I.; Pastor, J. *J Appl Polym Sci* 2005, 96, 2377.
- Garcia, M.; Vliet, G.; Jain, S.; Schrauwen, B.; Sarkissov, A.; Zyl, W.; Boukamp, B. *Rev Adv Mater Sci* 2004, 6, 169.
- St-Pierre, N.; Favis, B.; Ramsay, B.; Ramsay, J.; Verhoogt, H. *Polymer* 1997, 38, 647.
- Huneault, M.; Mighri, F. *Polym Eng Sci* 2001, 41, 672.
- Semba, T.; Kitagawa, K.; Ishiaku, U. S.; Hamada, H. *J Appl Polym Sci* 2006, 101, 1816.
- Semba, T.; Kitagawa, K.; Ishiaku, U. S.; Hamada, H. *Society of Plastic Engineers, Annual Technical Conference, Boston, MA, 2005, 2423.*
- Semba, T.; Kitagawa, K.; Hamada, H. In *Proceedings of the Japan Society of Polymer Processing 15th Annual meeting, 2004*; p 481.
- John, J.; Tang, J.; Yang, Z.; Bhattacharya, M. *J Polym Sci Part A: Polym Chem* 2000, 35, 1139.