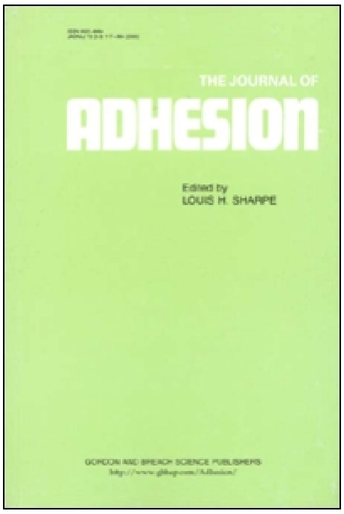


The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Application of Poly(acetic Acid)-Based Graft Copolymer as a Compatibilizer for Poly(L-lactic Acid)/Poly(butylenesuccinate) Blend System

Naohisa Tamura[a]; Kazuhiro Ban[a]; Shinya Takahashi[a]; Tomoyuki Kasemura[a]; Shoji Obuchi[a]
[a] Department of Applied Chemistry, Faculty of Engineering, Gifu University, Gifu-City, Japan

To cite this Article Tamura, Naohisa , Ban, Kazuhiro , Takahashi, Shinya , Kasemura, Tomoyuki and Obuchi, Shoji(2006) 'Application of Poly(acetic Acid)-Based Graft Copolymer as a Compatibilizer for Poly(L-lactic Acid)/Poly(butylenesuccinate) Blend System', The Journal of Adhesion, 82: 4, 355 — 373
To link to this Article: DOI: 10.1080/00218460600683787
URL: http://dx.doi.org/10.1080/00218460600683787

The Journal of Adhesion, 82:355–373, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460600683787

Application of Poly(acetic Acid)–Based Graft Copolymer as a Compatibilizer for Poly(L-lactic Acid)/ Poly(butylenesuccinate) Blend System

Naohisa Tamura
Kazuhiro Ban
Shinya Takahashi
Tomoyuki Kasemura
Department of Applied Chemistry, Faculty of Engineering,
Gifu University, Gifu-City, Japan

Shoji Obuchi
Mitsui Chemicals, Ichihara-City Chiba, Japan

Poly(L-lactic acid) (PLLA) was blended with poly(butylenesuccinate) (PBS) using a single-screw extruder to modify the poor characteristics of these polymers. Furthermore, when both polymers were blended, the graft copolymer that was synthesized by partially saponified poly(vinyl alcohol) (PSPVA) and ε-caprolactone (ε-CL) was used as a novel compatibilizer. The structure of the synthesized compatibilizer was determined by ^{1}H or ^{13}C NMR. From this result, the ring-opening polymerization of the ε-CL occurred at the hydroxyl group of PSPVA. The structures of the PLLA/PBS solvent-cast blended films could be observed via *an optical microscope. From the optical microscopic observation, the structures of the solvent-cast blended films with the synthesized compatibilizer were more homogeneous than those of the solvent-cast blended films without the compatibilizer. The mechanical properties of the PLLA/PBS extruded blended films were determined by a tensile test. The result showed the tensile strength of the blended films with the synthesized compatibilizer was greater than that of the blended films without the compatibilizer.*

Keywords: Compatibilizer; Graft copolymer; Partially saponificated poly(vinyl alcohol) (PSPVA); Poly(butylenesuccinate); Poly(L-lactic acid)

Received 25 May 2005; in final form 10 February 2006.

Address correspondence to Tomoyuki Kasemura, Department of Applied Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido Gifu, Gifu 501-1193, Japan. E-mail: kasemura@cc.gifu-u.ac.jp

1. INTRODUCTION

Recently, a lot of plastics have been produced all over the world, and the amount produced is 100 million tons per year. To respond to the required performance standards, about 30% of produced plastics are multicomponent systems containing two or more kinds of polymer. It is said that this percentage will increase in the future. Against this background, there has been considerable interest in the study of polymer blends because of their importance from both academic and technical aspects. It is possible to modify the poor characteristics of polymers and acquire a variety of characteristics through polymer blends. Generally, when different polymers are blended, the blended usually phase separates because of the small entropy in mixing [1]. However, many compatibilizers have been prepared that make different polymers more miscible, and they have been used effective in practical applications [2].

In addition, many aliphatic polyesters, such as PLLA, poly(ε-caprolactone) (PCL), and PBS, have become more noticed because of their biodegradability. However, these polymers do not provide enough properties for practical application. For example, PLLA is too rigid and brittle, PCL has too low of a melting temperature, and PBS is too flexible. Therefore, many blend pairs such as PLLA and PDLLA [3,4], PLLA and poly(L-lactide-co-glycolide), and PCL and poly (L-lactide-co-glycolide) [5] have been investigated to improve these disadvantages.

In our previous reports, PLLA was blended with PCL or PBS using a single-screw extruder to modify the poor characteristics of these polymers. Furthermore, when the polymer was blended, the copolymer (LA-CL block copolymer) consisted of L-lactide (L-LA) and ε-CL, which was used as a compatibilizer. Then, we could spin the blend fibers and prepare blend films of PLLA/PCL and PLLA/PBS with uniform thickness. Moreover, it was significant that the LA-CL block copolymer acted as a compatibilizer in the PLLA/PBS blend. It was considered that this result demonstrated that a PCL segment in the LA-CL block copolymer could be compatible with PBS in the melt state [6]. Moreover, the surface tension of PCL was almost equal to that of PBS in the melt state (125–150°C) [17]. This result also showed that PCL could be compatible with PBS in the melt state.

In this article we focused on poly(vinyl acetate) (PVAc), which is miscible with PLLA [8]. Furthermore, we focused on research showing that the PCL segment could be grafted at the hydroxyl group of starch [9]. On the basis of this research, the PCL segment was grafted at the hydroxyl group of PSPVA. Our goal was to make the PCL segment compatible with PBS. Concretely, a novel compatibilizer was synthesized *via* bulk polymerization of PSPVA and ε-CL, and its characteristics were determined. In addition we tried to modify the PLLA/PBS blends by blending with the synthesized compatibilizer

2. EXPERIMENTAL

2.1. Materials

The PSPVA (Gohsefimer L-5407) was provided by Nippon Synthetic Chemical Industry Co., Ltd. (Osaka, Japan), and used as received. The degree of saponificaiton was 32.2 mol%. The chemical structure is shown in Table 1. ε-CL was purchased from Aldrich, distilled, and stored over molecular sieves 4 A 1/16 (Wako Pure Chemical Industries, Ltd., Osaka, Japan). Tin octoate [stannous 2-ehtylhexanoate; $Sn(Oct)_2$] was purchased from Wako Pure Chemical Industries, Ltd., and used as a catalyst as received, without further purification. All of the other chemicals were used as received.

PLLA (Lacea *H*-100) and PBS (Bionolle S1005) were provided by Mitsui Chemicals, Inc. (Tokyo, Japan), and Showa Highpolymer Co., Ltd. (Tokyo, Japan) respectively and were used as received. Their molecular weights were determined by gel permeation chromatography (GPC) as shown in Table 2.

2.2. Synthesis of Compatibilizer

A given amount of PSPVA and ε-CL were introduced under nitrogen into a separable round-bottom flask. The mixture was stirred at 130–140°C for about 30 min to dissolve the PSPVA. Next, a determined amount of $Sn(Oct)_2$ (0.5 mol% relative to ε-CL) was added to the

TABLE 1 Chemical Structure of PSPVA

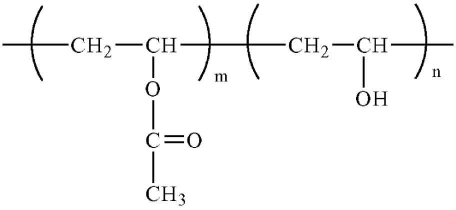
Polymer name	Structure
PSPVA	

TABLE 2 Molecular Weights of PLLA and PBS[a]

Polymer	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n
PLLA	9.83	17.5	1.78
PBS	6.98	14.2	2.04

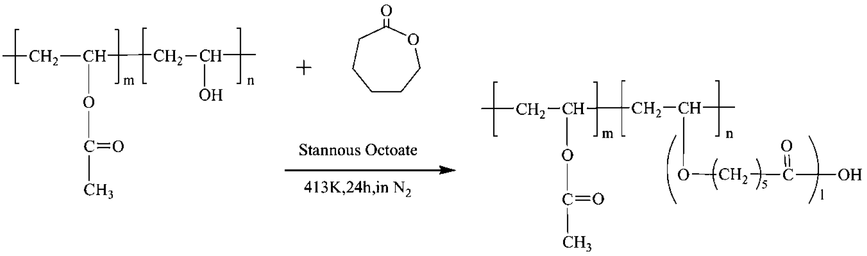
[a]Determined by GPC.

mixture [9,10]. The reaction mixture was heated at 140°C for 24 h under stirring and nitrogen. The obtained graft copolymer was used as a compatibilizer. The resultant product was used as polymerized without further purification. The compatibilizer was designated as P(VAc-g-CL)-X. X is the weight ratio of ε-CL to PSPVA. For example, P(VAc-g-CL)-2 shows that the feed ratio of PSPVA and ε-CL is 1:2. P(VAc-g-CL)-2-1 and P(VAc-g-CL)-2-2 were synthesized at different time though these were the same compositions. The synthetic mechanism of the compatibilizer was shown in Scheme 1.

2.3. Preparation of Blends

The PLLA/PBS film was prepared using a single-screw extruder at 180–200°C. When the both polymer were blended, the compatibilizer (1 wt% of total polymer) was added to the blend. PLLA/PBS blending ratios were 100/0, 80/20, 50/50, 20/80, and 0/100 by weight, respectively. This extruder film was used for the tensile test.

Solvent-cast film of PLLA/PBS was prepared by dissolving the chemicals in chloroform and casting on a glass Petri® dish at room temperature for 3 days and then drying at room temperature. When both polymers were blended, the synthesized compatibilizer (1 wt% of total polymer) was added to the blends. PLLA/PBS blending ratios



SCHEME 1

were 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90 by weight, respectively.

2.4. Measurement

^{1}H and ^{13}C NMR spectra were recorded on Varian 400- and 500-MHz spectrometers (Varian, Tokyo, Japan), respectively. Tetramethylsilane was used as an internal standard.

The number and weight average molecular weight (respectively, M_n and M_w) and molecular weight distribution (M_w/M_n) were determined by GPC using a TOSOH-8020 instrument (Tokyo, Japan) and chloroform as an eluent. The GPC system was calibrated according to the polystyrene standard.

The morphologies of solvent-cast film were observed with a polarization microscope (Shimadzu Kalnew Model EP, Kyoto, Japan) equipped with crossed polarizers and a CCD camera [Elmo Model TSN 401 A, Nagoya, Japan).

The tensile tests were performed on a TMI UTM-3 tensile testing machine (Toyo Baldwin Co., Ltd. Tokyo, Japan) according to JIS K7161. The mechanical properties of the blended films were measured using the tester at about 20°C with a crosshead speed of 20 mm min^{-1}.

3. RESULTS AND DISCUSSION

3.1. ^{13}C NMR of Synthesized Compatibilizer

Figure 1 shows the ^{13}C NMR spectra of PSPVA (Figure 1a) and the synthesized compatibilizer (Figure 1b).

In Figure 1a, the spectra consist of four general carbon resonance lines. Here, we focused on the methylene carbon resonance [38–46 ppm, (B)–(B2)]. The three methylene lines were assigned to $-CH(OH)-\underline{C}H_2-CH(OH)-$ (B_2), $-CH(OH)-\underline{C}H_2-CH(OAc)-$ (B_1), and $-CH(OAc)-\underline{C}H_2-CH(OAc)-$ (B) with increasing field strength [11–13].

In Figure 1b, in addition to the peak of PSPVA, new signals that were derived from PCL could be observed. Especially, a new signal (E) that corresponded to $-CH_2-CH(O\underline{C}O-CH_2-)-$ was observed in Figure 1b. This signal suggested that the PCL segment grafted onto the hydroxyl group of PSPVA. In addition, the signal (B_2) that corresponded to $-CH(OH)-\underline{C}H_2-CH(OH)-$ in Figure 1a disappeared in Figure 1b. This result demonstrated that ring-opening polymerization occurred at the hydroxyl group of PSPVA.

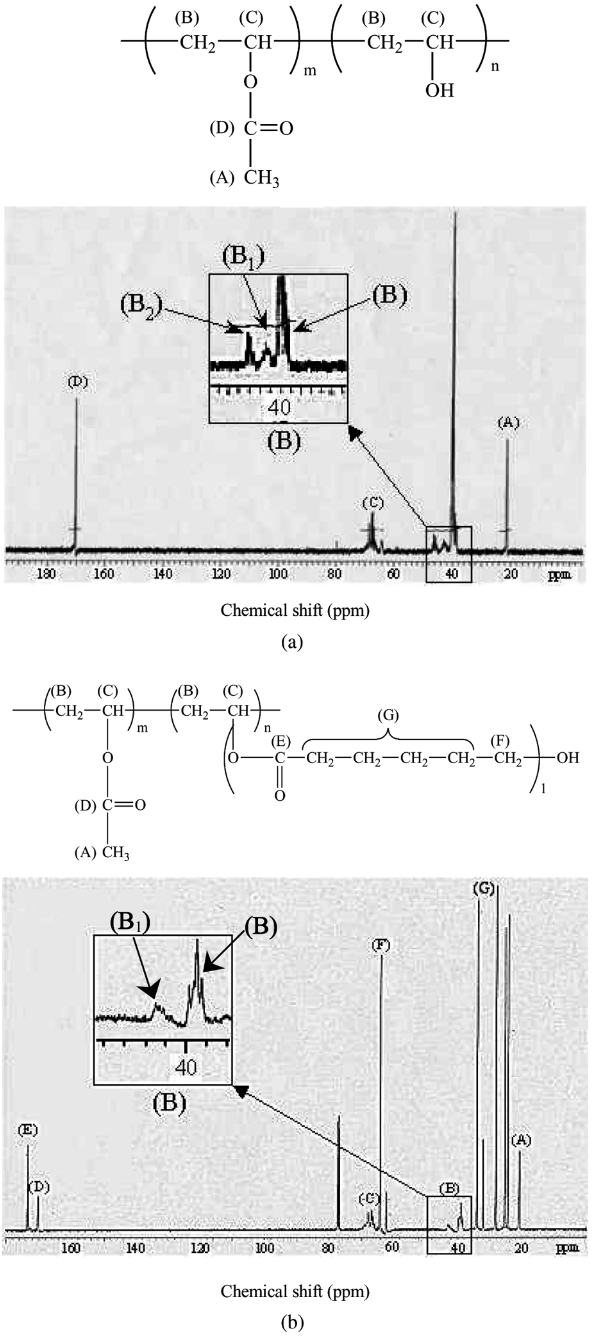


FIGURE 1 ^{13}C NMR spectra of PSPVA (a) and synthesized compatibilizer (b).

TABLE 3 Compositions of Synthesized Compatibilizers Determined by ^{1}H NMR

Sample	Feed (wt%) PSPVA (VAc segment): CL	Composition (mol%)[a] VAc segment: grafted PCL segment	Degree of polymerization for grafted PCL segment[b]
P(VAc-g-CL)-2-1	1:2	5:1	7
P(VAc-g-CL)-2-2	1:2	8:1	9
P(VAc-g-CL)-3	1:3	4:1	8
P(VAc-g-CL)-4	1:4	6:1	14
P(VAc-g-CL)-5	1:5	5:1	14

[a] Calculated according to the integrated area ratio of the resonance peaks due to the PCL block at 4.05 ppm and due to the PVAc block at 2.05 ppm.

[b] Calculated according to the integrated area ratio of the resonance peaks due to the methylene carbon of grafted PCL block at 4.05 ppm and due to the terminal methylene carbon of grafted PCL block at 3.65 ppm.

3.2. ^{1}H NMR of Synthesized Compatibilizer

The degree of polymerization of the grafted PCL segment was calculated according to the integrated area ratio of the resonance peaks due to the methylene carbon of grafted PCL block at 4.05 ppm and due to the terminal methylene carbon of the grafted PCL block at 3.65 ppm. In addition, the molar ratio of the vinyl acetate (VAc) group in PSPVA to the grafted PCL segment was calculated according to the integrated area ratio of the resonance peaks due to the PCL block at 4.05 ppm and due to the PVAc block at 2.05 ppm. These results are shown in Table 3.

These results demonstrate that there was more synthesized compatibilizer in the VAc group than in the grafted PCL segment. Furthermore, when the feed of ε-CL increased [in the case of P(VAc-g-CL)-4 and P(VAc-g-CL)-5], the degree of polymerization of the grafted PCL segment slightly increased.

3.3. Molecular Weight of Synthesized Compatibilizer

The molecular weights of PSPVA and the synthesized compatibilizers determined by GPC are shown in Table 4.

The molecular weights of synthesized compatibilizer were greater than those of PSPVA because the PCL segment being grafted by ring-opening polymerization of ε-CL. In addition, the molecular weight of P(VAc-g-CL)-2-2 was the smallest, and that of P(VAc-g-CL)-3 was mainly used for preparation of the blends.

TABLE 4 Molecular Weight and Polydispersity of Synthesized Compatibilizers[a]

Sample	M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n
PSPVA[b]	1.36	3.44	2.53
P(VAc-g-CL)-2-1	4.23	6.99	1.65
P(VAc-g-CL)-2-2	3.06	5.94	1.94
P(VAc-g-CL)-3	6.21	9.58	1.57

[a] Determined by GPC.

[b] After reacetification.

3.4. Mechanical Properties of PLLA/PBS-Blended Films with Synthesized Compatibilizer

The mechanical properties, such as strength and elongation, were evaluated from stress–stain curves. The experimental results of tensile strength and elongation percentage at the break are shown in Figures 2 and 3, respectively.

According to the data for PLLA and PBS homopolymer films, the tensile strength of PLLA was greater than that of PBS, whereas the elongation at the break of PBS was greater than that of PLLA. As the study of DSC has shown, it is because the T_g of PLLA is higher than room temperature and it is in a glass if state at room temperature [14]. Moreover, this is because the molecular chain of PLLA is relatively rigid and the entanglement density is small. Contrarily, because the T_g of PBS is below room temperature and is flexible at room temperature, the tensile strength showed a low value.

The tensile strengths of the blended films with compatibilizer improved when compared with those of the blended films without it in the whole blend composition. Moreover, the tensile strength improved with an increase in PLLA.

The percentage elongation at break of the blended films with compatibilizer slightly improved when compared with that of the blended films without it, except for PLLA/PBS = 20/80.

From these results, it is apparent that the tensile strengths of the PLLA/PBS blended films could be improved significantly by the addition of the compatibilizer. As is described in the next section, this was due to the formation of a microphase separation structure and stabilization of the phase structure of the film. The generation of the crack was repressed by the stabilization of the phase structure when the blended film was broken. Thus, the strength of the blended films improved. The elongation of the blended films could not be improved by the addition of compatibilizer. It was considered that the brittleness

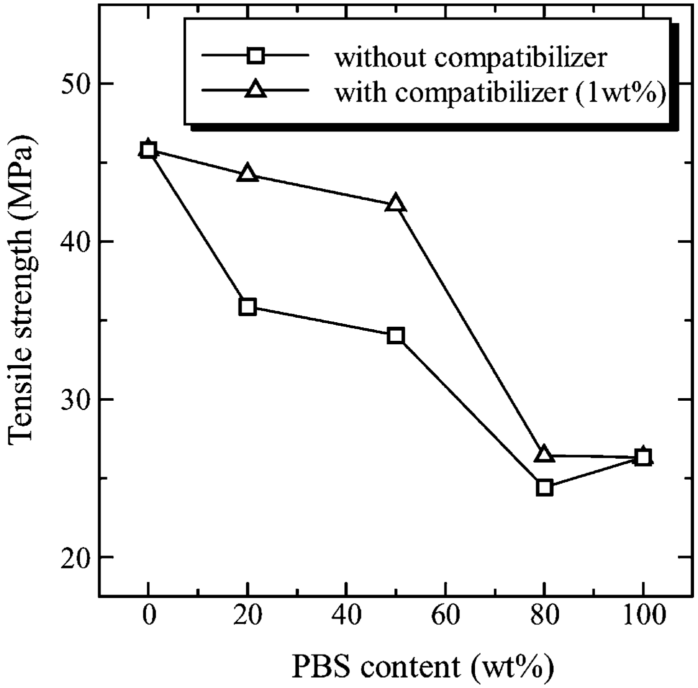


FIGURE 2 Tensile strength of PLLA/PBS blended films.

of PLLA influenced the elongation of the blend film and that the rigidity of PLLA improved the strength of the blend film because of the addition of the compatibilizer in the blend.

3.5. Optical Micrographs of a Solvent-Cast Blend Film

The structures of solvent-cast blend films with and without compatibilizer were observed by optical microscope.

Figures 4 and 5(a) show the optical micrographs of PBS and PLLA homopolymer solvent-cast films, respectively. Spherulites were not observed in these films because the temperature that evaporated the solvent was lower than crystallization temperature. However, small particles (semicrystallites) that could not grow up to spherulites were observed in the PLLA film. Moreover, when the sample of PLLA was annealed at 120°C for 24 h (Figure 5b), it exhibited spherulites with a Maltese cross and a diameter of 50–100 μm.

Optical micrographs of PLLA/PBS = 90/10 solvent-cast blended film without and with compatibilizer are shown in Figures 6a and 6b,

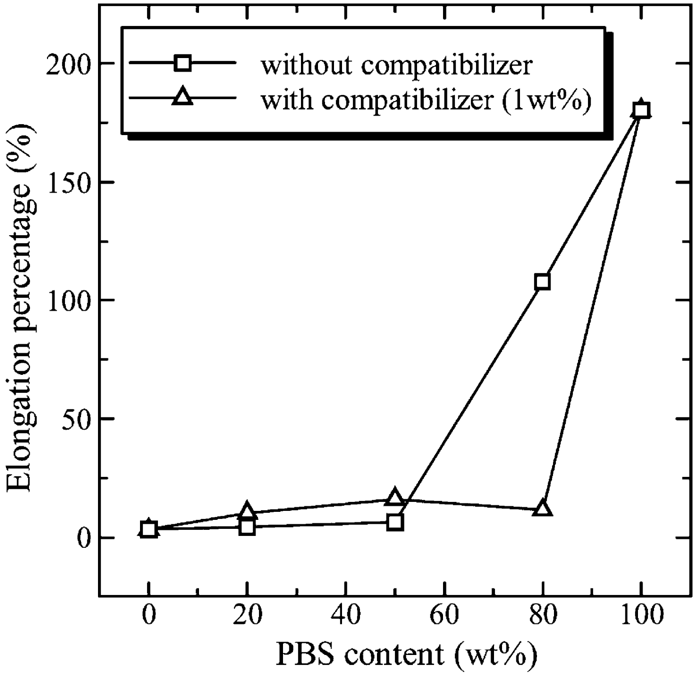


FIGURE 3 Elongation percentage at break of PLLA/PBS blended films.

respectively. Phase separation could not be observed in either figure. Also, the structures of these films were homogeneous. No remarkable difference could be observed in the structure of either film.

An optical micrograph of PLLA/PBS = 70/30 solvent-cast blended film without compatibilizer is shown in Figure 7a. In contrast of Figure 6a, the roughness could be observed clearly. Moreover, phase separation could also be observed. An optical micrograph of PLLA/PBS = 70/30 solvent-cast blend film with compatibilizer is shown in Figure 7b. The phase separation and the roughness were less than in Figure 7a. From these results, it is suggested that the synthesized compatibilizer stabilized the phase structure effectively.

Optical micrographs of PLLA/PBS = 50/50 solvent-cast films without and with compatibilizer are shown in Figures 8a and 8b, respectively. Unlike the composition of 90/10 or 70/30, phase separation could be observed clearly in Figure 8a. Moreover, many dark domains could be observed. However, although phase separation was observed in Figure 8b, the dark domains were smaller and more homogeneous than in Figure 8a. These results show that the synthesized compatibilizer also stabilized the phase structure effectively.

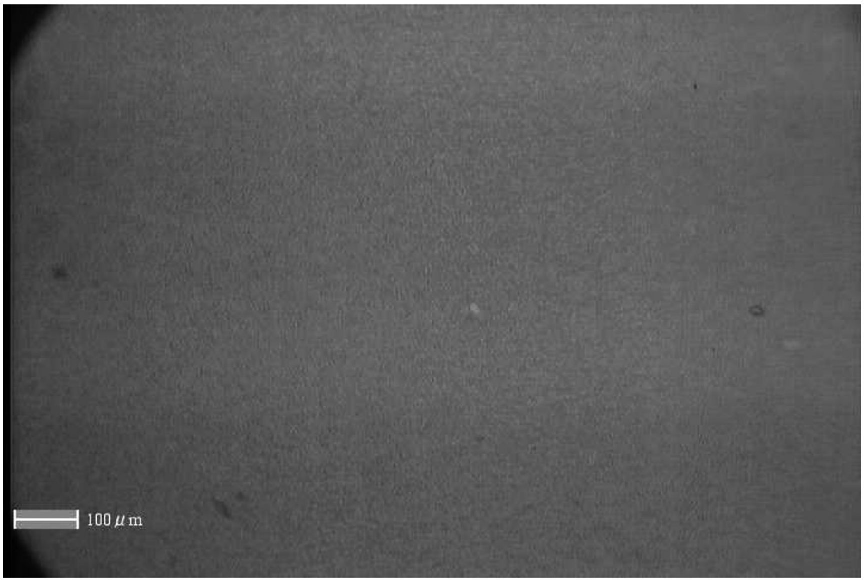
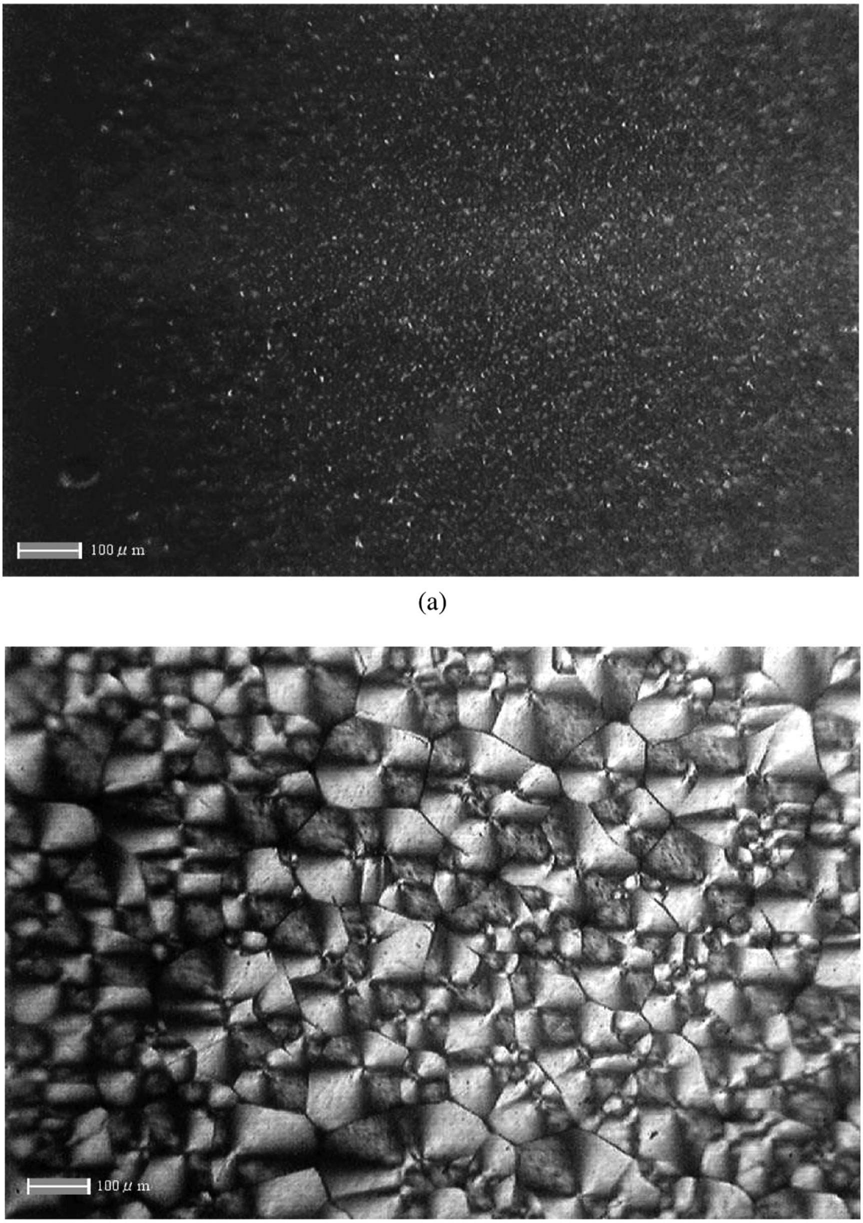


FIGURE 4 Photograph of the PBS solvent-cast film. Scale marker is 100 μm.

Optical micrographs of PLLA/PBS = 30/70 solvent-cast films without and with compatibilizer are shown in Figures 9a and 9b, respectively. The phase separation can be observed clearly in Figure 9a. Many dark domains from 10 to 100 μm were also observed. In Figure 9b, the phase separation structure could not be clearly observed compared with Figure 9a. These results show that the synthesized compatibilizer also stabilized the phase structure effectively in this blend system.

Optical micrographs of PLLA/PBS = 10/90 solvent-cast films without and with compatibilizer are shown in Figures 10a and 10b, respectively. In Figure 10a, although phase separation was observed, the dark domains were relatively small and homogeneous in contrast to Figures 8a or 9a. In Figure 10b, the phase separation structure could not be observed, and the phase structure of the film was homogeneous. These results, suggest that the synthesized compatibilizer also stabilized the phase structure effectively, similarly to PLLA/PBS = 70/30, 50/50, and 30/70.

These results show a clear difference in the phase structure of a film with and without the synthesized compatibilizer. For the blended films formed at 70/30 to 30/70, the difference in phase separation between with and without compatibilizer could be clearly distinguished. Moreover, the size of dark domains for the blended films without compatibilizer varied widely, whereas for the blended films



(a)

(b)

FIGURE 5 (a) Photograph of the PLLA solvent-cast film. Scale marker is 100 μm. (b) Photograph of spherulites on the PLLA solvent-cast film after annealing at 120°C for 24 h. Scale marker is 100 μm.

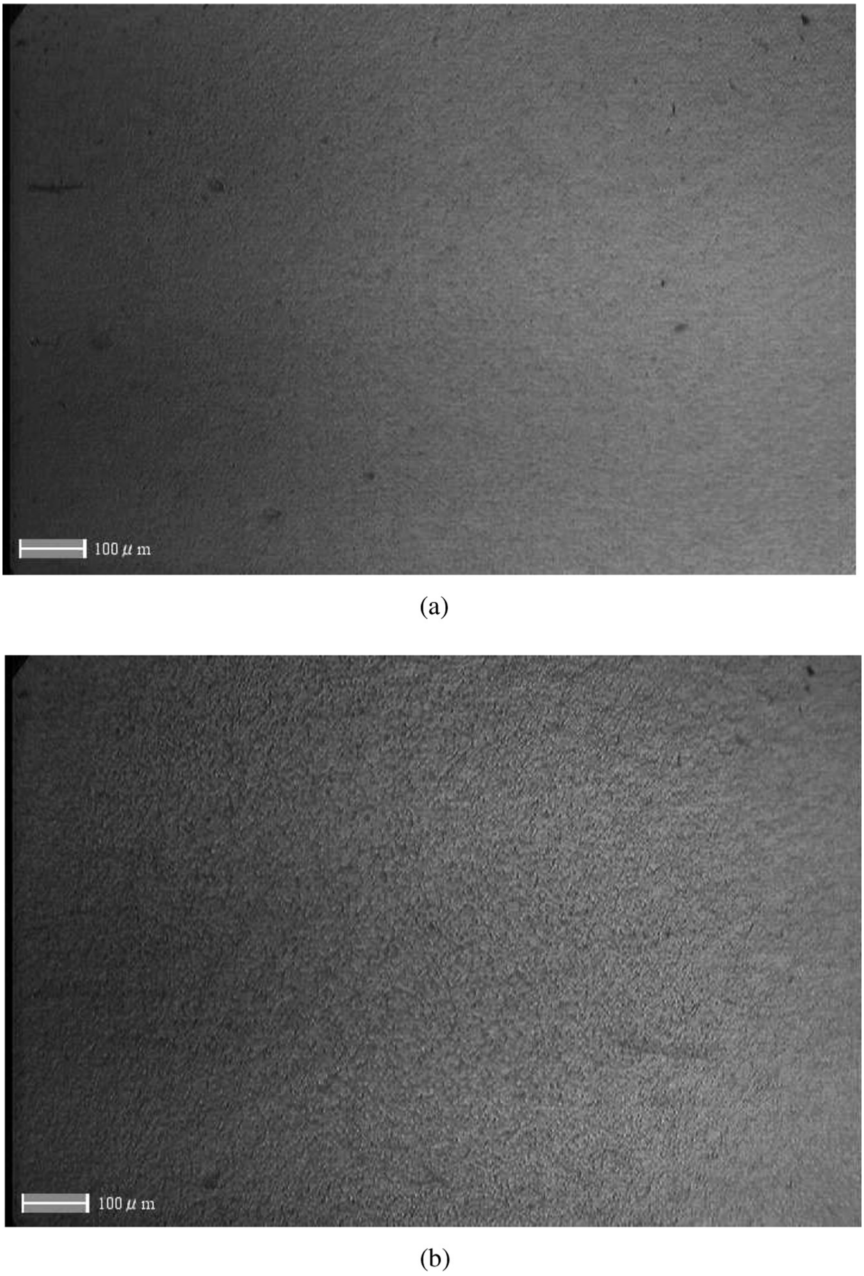
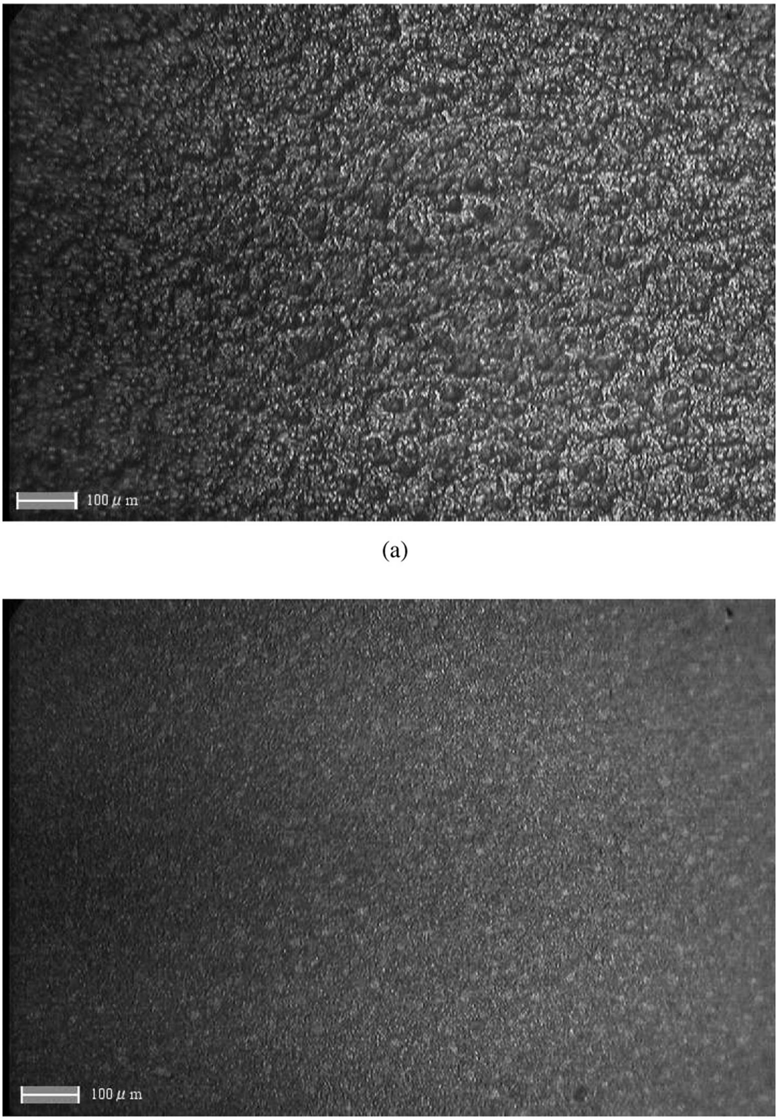


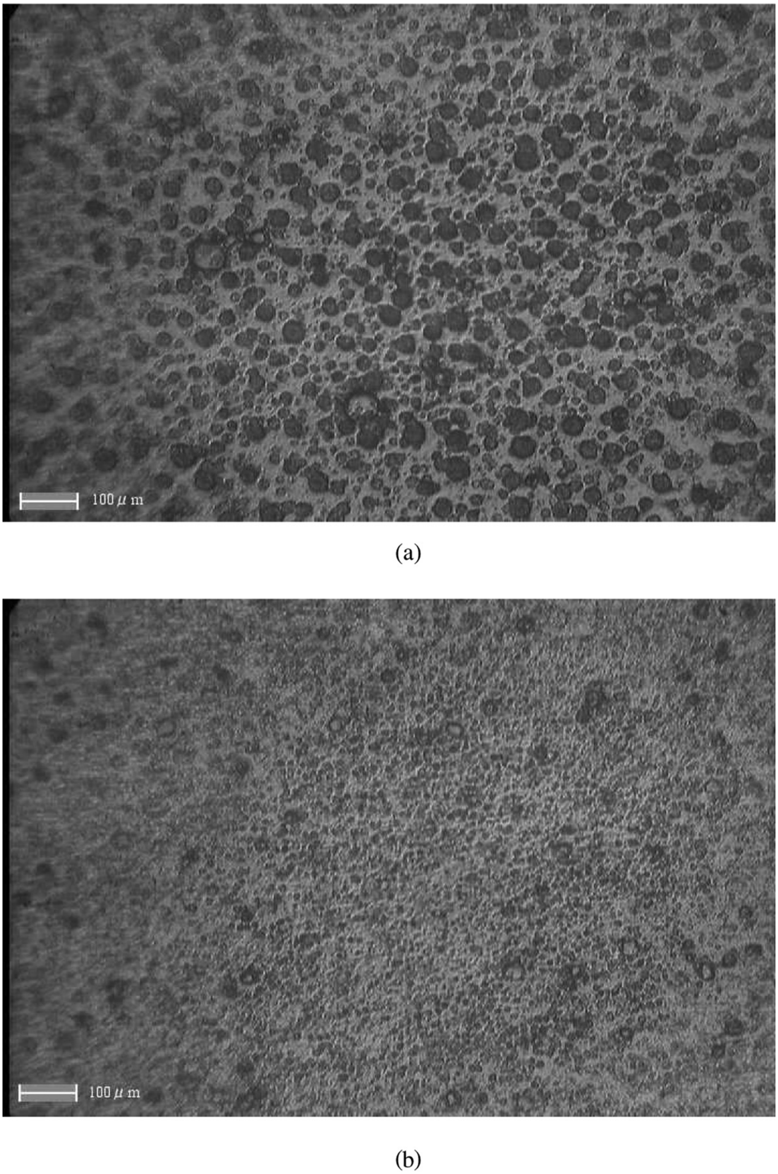
FIGURE 6 (a) Photograph of the PLLA/PBS = 90/10 solvent-cast film without compatibilizer. Scale marker is 100 μm. (b) Photograph of the PLLA/PBS = 90/10 solvent-cast film with compatibilizer (1 wt%). Scale marker is 100 μm.



(a)

(b)

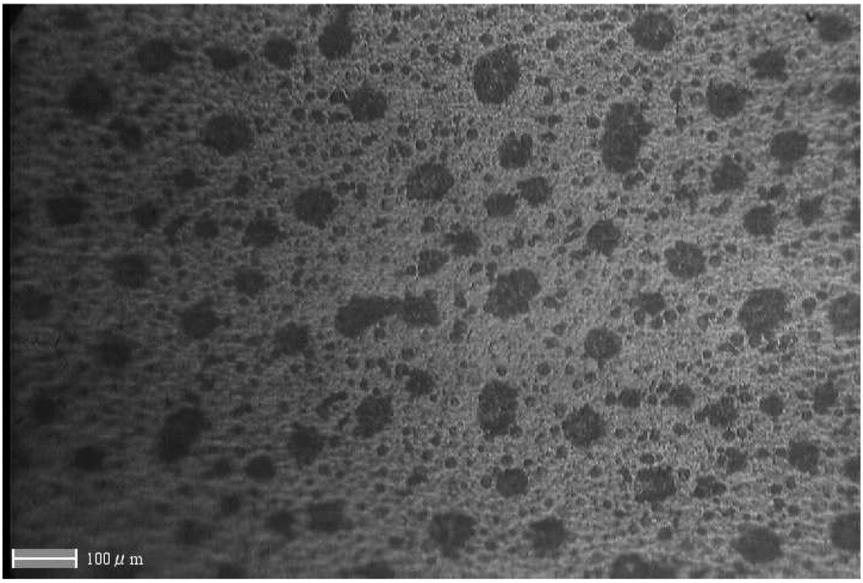
FIGURE 7 (a) Photograph of the PLLA/PBS = 70/30 solvent-cast film without compatibilizer. Scale marker is 100 µm. (b) Photograph of the PLLA/PBS = 70/30 solvent-cast film with compatibilizer (1 wt%). Scale marker is 100 µm.



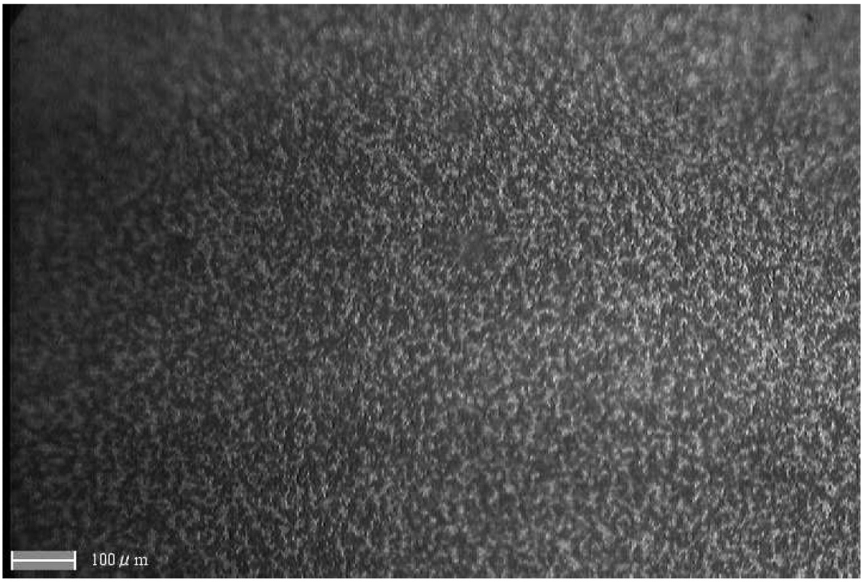
(a)

(b)

FIGURE 8 (a) Photograph of the PLLA/PBS = 50/50 solvent-cast film without compatibilizer. Scale marker is 100 μm. (b) Photograph of the PLLA/PBS = 50/50 solvent-cast film with compatibilizer (1 wt%). Scale marker is 100 μm.



(a)



(b)

FIGURE 9 (a) Photograph of the PLLA/PBS = 30/70 solvent-cast film without compatibilizer. Scale marker is 100 μm. (b) Photograph of the PLLA/PBS = 30/70 solvent-cast film with compatibilizer (1 wt%). Scale marker is 100 μm.

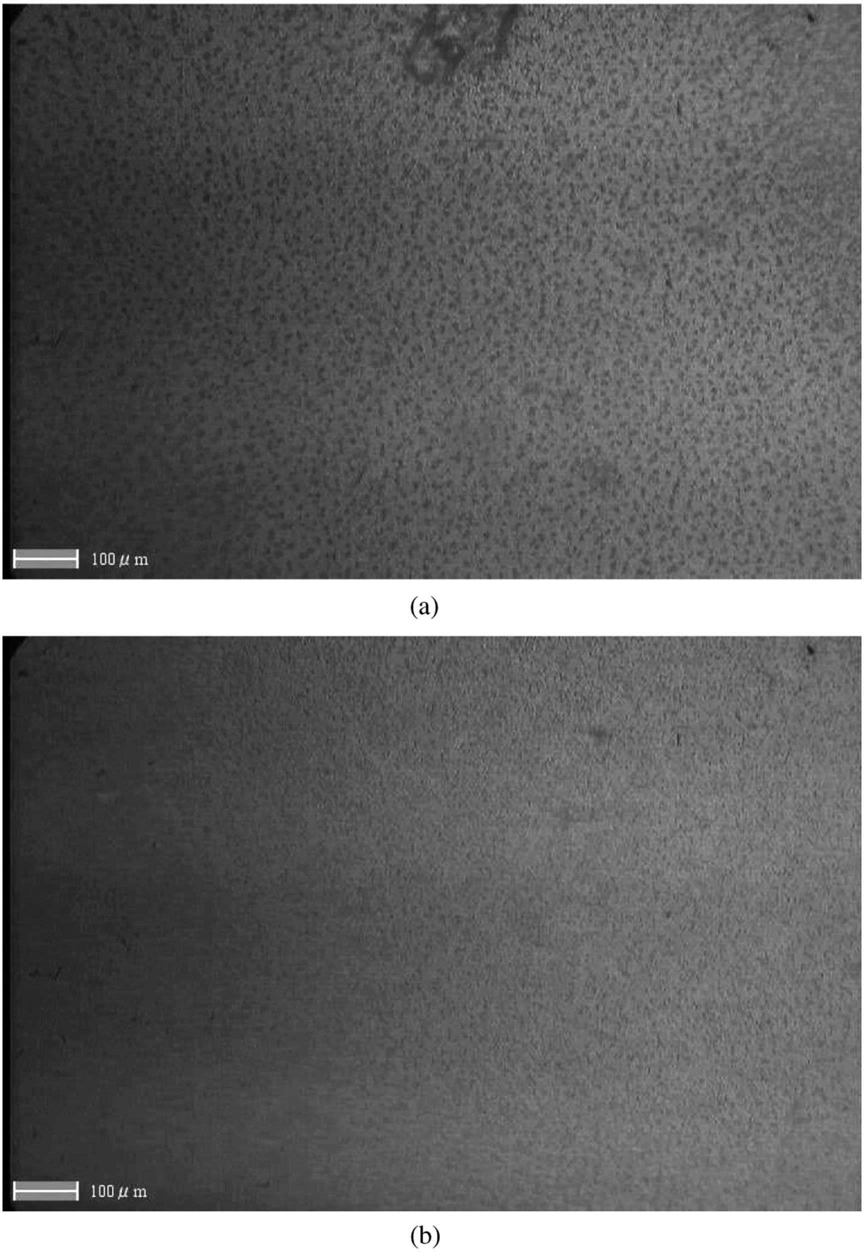


FIGURE 10 (a) Photograph of the PLLA/PBS = 10/90 solvent-cast film without compatibilizer. Scale marker is 100 μm. (b) Photograph of the PLLA/PBS = 10/90 solvent-cast film with compatibilizer (1 wt%). Scale marker is 100 μm.

with compatibilizer, microphase-separated domains were very small and the phase structure of the film was homogeneous. Therefore, becuase the synthesized compatibilizer in this study stabilized the phase structure of the film effectively, it is suggested that it acts as a compatibilizer.

4. CONCLUSIONS

A novel compatibilizer was synthesized by using PSPVA as an initiator for ring-opening polymerization of ε-CL. Moreover, the number and weight average molecular weight, the molecular weight distribution, and structure were characterized by GPC and NMR measurements. In particular, we suggest that the ring-opening polymerization of ε-CL occurred at the hydroxyl group of PSPVA.

Tensile test result showed that the tensile strength of the PLLA/PBS by blended films could be improved by the addition of a synthesized compatibilizer. This was due to the formation of a microseparation structure and stabilization of the phase structure of the film.

The phase structures of the PLLA/PBS blended films that were prepared by the solvent-cast method were observed with an optical microscope. It was found that the phase structure of the PLLA/PBS blended films with the added synthesized compatibilizer in this study could be stabilized efficiently.

ACKNOWLEDGMENT

This work was partly supported by Mitsui Chemicals, Inc., and Nippon Synthetic Chemical Industry Co., Ltd.

REFERENCES

[1] Ballauff, M. and Dorgan, J. R., *Polymer Blends*, Vol. 1: *Formulation* (John Wiley & Sons, New York, 2000), Chap. 7, pp. 187–217.

[2] Nishi, T., *High-Performance Polymer Alloys* (Maruzen, Tokyo, 1991), Chap. 1, pp. 1–7.

[3] Tsuji, H. and Ikada, Y., *J. Appl. Polym. Sci.* **60**, 2367–2375 (1996).

[4] Tsuji, H. and Ikada, Y., *Macromolecules* **25**, 5719–5723 (1992).

[5] Cha, Y. and Pitt, C. G., *Biomaterials* **11**, 108–112 (1990).

[6] Kuriyama, N., Takahashi, S., Kasemura, T., Nishimura, Y., and Kato, K., *Proceedings of the Fourth International Conference on Ecomaterials* (The Society on Non-traditional Technology ECOMATERIALS Forum, Gifu, Japan, 1999), pp. 611–614.

[7] Kasemura, T., Nojiri, M., and Takahashi, S., *Proceedings of the 16th International Symposium Swiss Bonding* (Swiss Bonding, Rapperswil, Switzerland, 2002), pp. 22–23.

[8] Gajria, A. M., Dave, V., Gross, R. A., and McCarthy, S. P., *Polymer* **37**, 437–444 (1996).

[9] Doubois, P., Krishnan, M., and Narayan, R., *Polymer* **40**, 3091–3100 (1999).

[10] In't Veld, P. J. A., Velner, E. M., Van de Witte, P., Hamhuis, J., Dijkstra, P. J., and Feijen, J., *J. Polym. Sci., Part A: Polym. Chem.* **35**, 219–226 (1997).

[11] Moritani, T. and Fujiwara, Y., *Macromolecules* **10**, 532–535 (1977).

[12] Bugada, D. C. and Rudin, A., *Polymer* **25**, 1759–1766 (1984).

[13] Toppet, S., Lemstra, P. J., and Van der Velden, G., *Polymer* **24**, 507–512 (1983).

[14] Takagi, J., *Biodegradable Plastic Handbook* (NTS Co., Japan, 1995), pp. 659–664.