

Crystallization of Amorphous Poly(lactic acid) Induced by Organic Solvents

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ABSTRACT: Crystallization of amorphous poly(lactic acid) (PLA) was investigated in various organic solvents, such as acetone, ethylacetate, diethylether, tetrahydrofuran, methanol, hexane, toluene, xylene, and *o*-dichlorobenzene. Most of the solvents, except hexane, induced crystallization of amorphous PLA. Acetone was the most effective solvent to accelerate the crystallization among the solvents used. The crystallization was induced by permeation of acetone into the amorphous phase of PLA, and the permeation obeyed Fick type diffusion. The crystallization

rate increased with increasing of conducting temperature. Crystallized PLA formed α crystalline structure. The permeated acetone in the crystallized PLA gradually evaporated as time passes, and the elimination of acetone affected thermal and mechanical properties of the crystallized PLA. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2058–2064, 2011

Key words: poly(lactic acid); organic solvent; acetone; crystallization

INTRODUCTION

Various types of biodegradable plastics have been developed. Poly(lactic acid) (PLA) is one of the most useable polymers among these plastics, and used in various products.^{1–3} Improvements of the properties of PLA will expand the application of PLA, especially in the following points. One is low crystallization rate and crystallinity of PLA. Crystallization of PLA is relatively slow due to its slow nucleation,^{4,5} and its slow crystallization causes long molding cycle for producing of products. Furthermore, amorphous phase of PLA shows the glass transition temperature at 60°C,^{6–8} which is not enough high for practical uses. The other point is low flexibility of PLA. Addition of plasticizer should be useful to improve the flexibility in PLA. Addition of a nucleating agent to PLA is effective to improve the crystallization rate, and some nucleating agents, such as benzoic acid hydrazide, for PLA have been developed.^{9–17} Naturally, PLA is a hard and brittle resin. Some plasticizers, such as acetyl tributyl citrate and diglycerin tetra-acetate, have been also developed to improve the flexibility.^{18–25} Both the nucleating agent and plasticizer are used to

improve the physical properties of PLA. However, use of the nucleating agent together with the plasticizer decreased the efficiency of the plasticizer.²⁶ Further addition of the plasticizer induces bleed out of itself from the PLA resin. From such point of view, a plasticizer that also has nucleating effect for PLA was developed.²⁷ Nanocomposite of PLA is an effective method to improve the properties of PLA. Okamoto and coworkers reported that the PLA nanocomposites with layered silicate or titanate enhanced the mechanical properties and increased the crystallization rate of PLA effectively.^{28–32}

PLA is one of a kind of polyesters. We focused on methods for improvement of properties of polyesters, especially most popular polyester of poly(ethylene terephthalate) (PET). Ouyang et al. reported that crystallization of PET is induced by acetone. Permeation of acetone into the amorphous phase of PET promoted the crystallization of PET.^{33–35} We applied the crystallization method to PLA and found that the crystallization was induced by some organic solvents, especially acetone. In this article, we investigated the solvent induced crystallization of amorphous PLA and its properties precisely, and found out that the acetone not only induced crystallization but also played a role of a plasticizer

EXPERIMENTAL

Materials

Sheet of amorphous PLA was kindly donated from Unitika and was used as received. Number average

Additional Supporting Information may be found in the online version of this article.

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molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the PLA were 83,600 and 2.5, respectively, calibrated with standard polystyrene samples. Sample sheet for the crystallization was cut as a size of 1 cm \times 2 cm \times 0.55 mm. Sample for polarized optical micrograph was prepared on the glass slide covered with cover glass. The sample was melted at 220°C for 5 min and rapidly cooled to room temperature. The specimens for elongation test were prepared by stamping out the amorphous PLA sheet by 0.2-mm thick with dumbbell cutter of No. 7 (1.5 cm \times 0.2 cm) defined by Japan Industrial Standards (JIS) at 60°C. Organic solvents, acetone, ethylacetate, diethylether, tetrahydrofurane, methanol, hexane, toluene, xylene, and *o*-dichlorobenene, were commercially obtained and used without further purification.

Crystallization of amorphous PLA in organic solvents

The crystallization was conducted in a 100-mL beaker in the presence of a solvent at desired temperatures. The amorphous PLA sample was immersed into the solvent for desired time, then immediately transferred into water at room temperature, and dried *in vacuo* at room temperature for 6 h.

Analytical procedures

Thermal properties of the PLA samples were investigated by a Rigaku DSC 8230 at a heating rate of 3°C/min to 200°C after previous cooling to 0°C and holding for 5 min. The polarized optical micrographs of the PLA were observed using an optical microscope (Olympus BX50). Wide angle X-ray diffraction (WAXD) patterns of the PLA samples were recorded on a Rigaku RAD-C using Cu-K α radiation. Elongation test was conducted with a TENSILON RTE-1210 (Orientech) at an elongation rate of 1 mm/min at room temperature.

RESULTS AND DISCUSSION

Crystallization of amorphous PLA in organic solvents

Amorphous PLA was immersed into the solvents, acetone (ketone), ethylacetate (ester), diethylether, tetrahydrofurane (ether), methanol (alcohol), hexane (nonaromatic hydrocarbon), toluene, xylene, and *o*-dichlorobenene (aromatic hydrocarbon), at room temperature for 10 min. Differential scanning calorimetry (DSC) profiles of the immersed PLA samples and the amorphous PLA sample (for a reference) are shown in Figure 1. In the DSC profile of the amorphous PLA [Fig. 1 (a)], endothermic and exothermic peaks derived from glass transition, crystallization

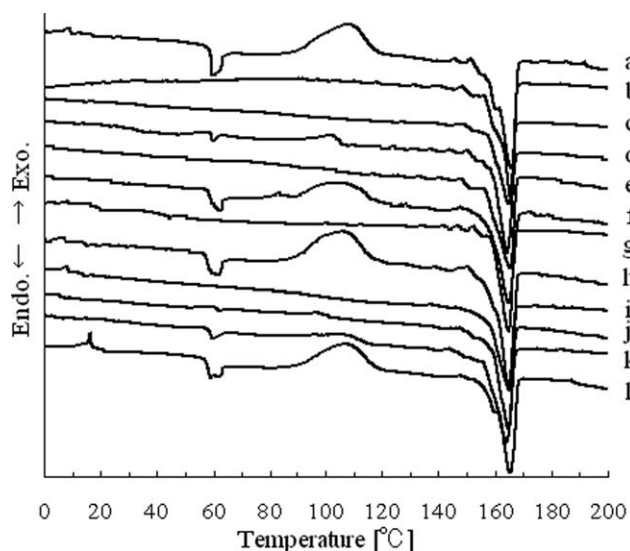


Figure 1 DSC thermograms of the amorphous PLA sample (a) and PLA samples immersed in various solvents; (b) acetone (10 min), (c) ethylacetate (10 min), (d) diethylether (10 min), (e) tetrahydrofurane (10 min), (f) methanol (10 min), (g) methanol (24 h), (h) hexane (24 h), (i) toluene (10 min), (j) xylene (10 min), (k) *o*-dichlorobenzene (10 min), and (l) H₂O (24 h) at room temperature.

of amorphous phase, and melting of crystalline phase were detected at 60°C, 110°C, and 165°C, respectively. Multiple melting peaks at \sim 161°C and 166°C in the DSC curve of amorphous PLA sample [Fig. 1 (a)] should be derived from transition from α' to α phase as previously reported.³⁶ The melting enthalpy of total crystalline phase (ΔH_m) corresponds to the sum of melting enthalpies of original crystalline phase (ΔH_{mc}) and crystallized amorphous phase (ΔH_{ma}). In the case of amorphous PLA sample, although a small amount of crystalline phase was contained, the values of ΔH_c and ΔH_m were almost same as shown in Table I. Crystallinity of the original PLA samples (X_c), therefore, was estimated from enthalpies of crystallization of amorphous phase (ΔH_c) and melting of total crystalline phase (ΔH_m) using a following equation.

$$X_c = (\Delta H_{mt} - \Delta H_{ca}) / \Delta H_m^0 \times 100$$

where ΔH_m^0 the theoretical melting enthalpy of PLA is 93 J/g.³⁷

The results are summarized in Table I. The crystallinities of most of the samples immersed in the solvents, except hexane, were higher than that of the amorphous sample, indicating that crystallization of amorphous PLA was induced by the solvents. Acetone, ethylacetate, tetrahydrofurane, and toluene, especially acetone, effectively accelerated the crystallization of amorphous PLA among the solvents used. Methanol slowly induced crystallization, and long time immersion, for 24 h, attained high

TABLE I
Results of Solvent-Induced Crystallization of Amorphous PLA

Solvent	Time ^a	ΔH_c	ΔH_m	X_c	SP ^b
		41.5	43.4	2.1	
Acetone	10 min	0.0	40.4	43.4	9.8
Ethylacetate	10 min	0.0	37.7	40.5	9.1
Diethylether	10 min	12.7	39.3	28.6	7.4
Tetrahydrofurane	10 min	0.0	38.8	41.7	9.1
Methanol	10 min	32.9	40.9	8.7	14.5
Methanol	24 h	0.0	37.5	40.3	14.5
Hexane	24 h	40.3	44.0	4.0	7.3
Toluene	10 min	0.0	37.0	39.8	8.9
Xylene	10 min	7.6	41.4	36.3	8.8
<i>o</i> -Dichlorobenene	10 min	8.1	39.8	34.0	10.0
H ₂ O	24 h	37.8	39.5	1.8	23.4

^a Immersion time in the solvent at room temperature.

^b Solubility parameter of the solvent.

crystallinity ($X_c = 40.3\%$). Hexane and H₂O did not induce the crystallization.

These results show good agreement with a relationship in solubility parameters between PLA and the solvents. The solubility parameters of the solvents that induce crystallization of PLA are similar to that of PLA (9.3–10.0) as summarized in Table I. The results indicate that the permeation of solvents into the amorphous phase of PLA should be necessary to induce the crystallization.

Crystallization behavior of amorphous PLA

Crystallization of amorphous PLA induced by permeation of acetone was traced by polarized optical micrograph. The crystallization was conducted in a Petri dish on the stage of a polarized optical microscope, as shown in Scheme 1. Figure 2 shows the polarized optical micrographs of PLA specimen at around the edge immersed in acetone at room temperature. The sample before immersion in acetone did not show birefringence, as shown in Figure 2(a). After the immersion of the sample in acetone, birefringence appeared at where acetone was permeated, and the area that showed the birefringence increased as time passed, as shown in Figure 2(b–d). A relationship between immersion time (square root of the time) and crystallization front (length from edge of the specimen to crystallization front) is shown in Figure 3. The plot clears that permeation distance of acetone is in proportion to square root of the immersion time, indicating that the permeation obeys Fick type diffusion.^{33–35} The same experiment was conducted at 40°C and 50°C, and the results are plotted in Figure 3. The rate of the permeation of acetone increased with increasing of the conducted temperature.

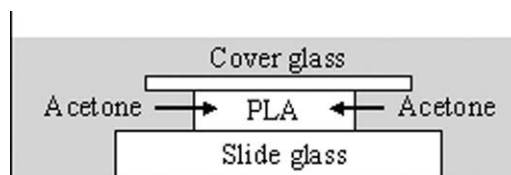
The crystallization process of amorphous PLA in acetone was also traced with DSC. Figure 4 shows

time evolution of DSC thermograms of the PLA immersed in acetone at room temperature. The samples immersed into acetone for 20–80 s showed another T_g (T_{gl}) ranging from 50°C to 35°C, which was lower than that of the amorphous PLA (T_{gh} at ~60°C). Two exothermic peaks of the crystallization were detected in the PLA samples immersed in acetone for 20–100 s. Those were low T_c (T_{cl}) ranging from 85°C to 70°C and high T_c (T_{ch}) ranging from 110°C to 90°C, and these temperatures decreased with increasing of the immersion time. Only an exothermic peak derived from crystallization was detected at ~60°C in the sample immersed for 120 s, and the peak disappeared in the sample immersed for 132 s.

These results can be explained by the supposing three phases in the PLA samples, amorphous phase without acetone (Area 1), amorphous phase containing small amount of acetone (Area 2), and crystalline phase (Area 3), as shown in Scheme 2. The T_{gl} and T_{cl} should be derived from the Area 2. The immersed acetone would play a role of a plasticizer, and decrease T_g and T_c . The T_{ch} also decreased with increasing the immersion time, indicating that the crystallization of Area 2 would induce the crystallization of Area 1. The DSC profile of the sample immersed for 100 s did not show T_{ch} indicating that immersion of acetone had reached to the center of the specimen. The DSC profile of the sample immersed for 132 s did not show any T_c indicating that the crystallization had completed. The same experiment was also conducted at 40°C and 50°C (DSC profiles of amorphous PLA samples crystallized in acetone at 40 °C or 50 °C are available in the Supplementary material). It took 40 or 30 s to reach acetone to the center of specimen at 40°C or 50°C, respectively. The acetone induce crystallization was completed within 80 or 70 s at 40°C or 50°C, respectively. Increase of the temperature was effective for the acceleration of the crystallization induced by acetone.

Structure and properties of PLA crystallized by acetone

WAXD patterns of PLA samples crystallized in acetone at different temperatures are shown in Figure 5. Diffraction peaks were observed at $2\theta = 14.7^\circ, 16.5^\circ,$



Scheme 1 Schematic of crystallization of amorphous PLA in Petri dish.

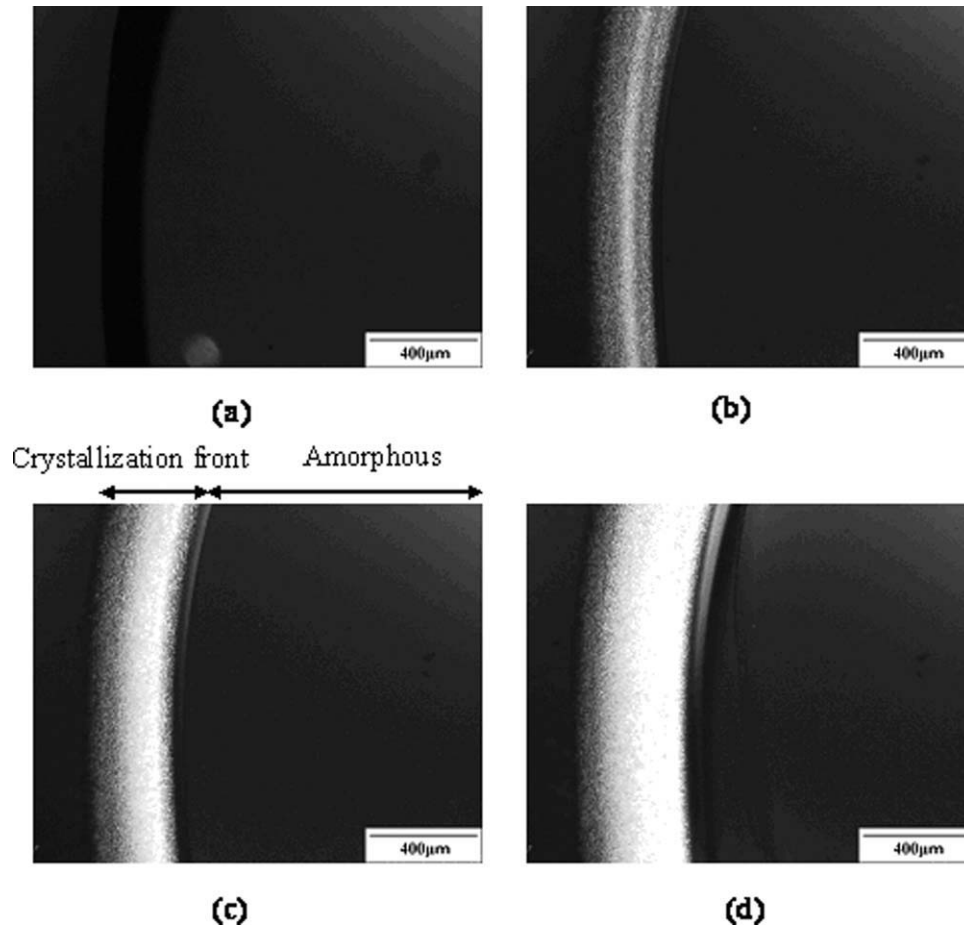


Figure 2 Polarized optical micrographs of PLA specimen at around the edge; (a) before immersion in acetone, (b) after immersion (crystallization) in acetone for 1 min, (c) 4 min, and (d) 16 min at room temperature.

18.9°, and 22.3° derived from 010, 110/200, 203, and 015 phases of α form, respectively.^{38–40} All the PLA samples showed the same profile independent of the

conducted temperature. The results indicate that the PLA crystallized by acetone preferentially forms the α form.

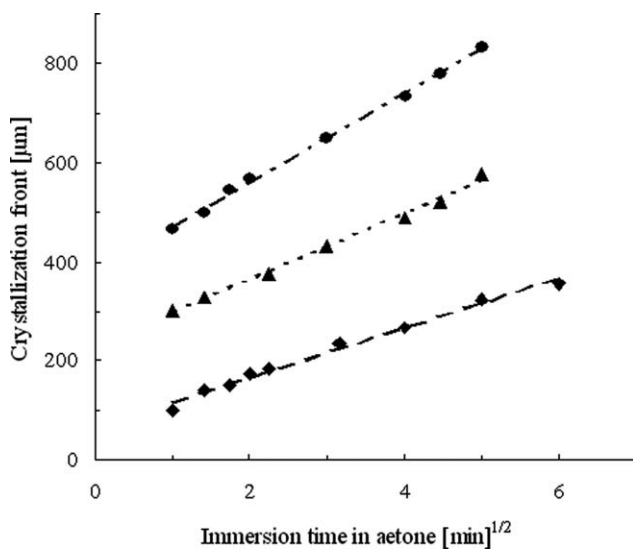


Figure 3 A relationship between immersion (crystallization) time (square root of the time) and crystallization front (length from edge of the specimen to crystallization front) of amorphous PLA sample at room temperature (diamond), 40°C (triangle), and 50°C (circle).

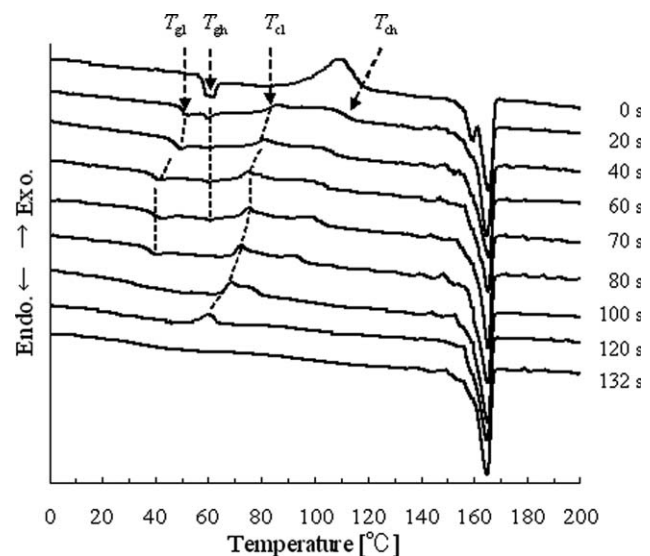
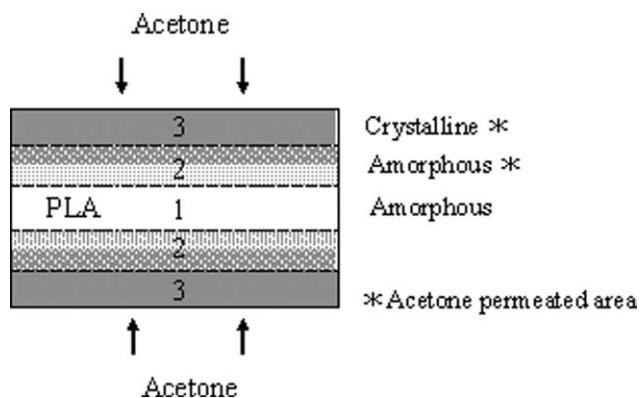


Figure 4 Effect of the crystallization (immersion) time in acetone at room temperature on the DSC profiles of amorphous PLA sample.



Scheme 2 Model of crystallization process of amorphous PLA by acetone.

Acetone plays a role of a plasticizer in PLA crystallized by acetone, as described earlier in the DSC analysis. The PLA sample crystallized by acetone for 1 min at room temperature contained 2 wt % of acetone, even after the sample was transferred into water and dried *in vacuo* at room temperature for 6 h. Time evolution of weight of PLA sample crystallized by acetone is shown in Figure 6. The weight of PLA sample lost ~ 1 wt % of acetone within 10 days at room temperature. The sample after 57 days from the crystallization contains 0.5 wt % of acetone. On the other hand, the sample stored at -22°C did not show decrease of the weight. Figure 7 shows time evolution of DSC profiles of PLA sample crystallized by acetone for 1 min at room temperature. The T_g ranging from 50°C to 35°C (T_{gl}), and the T_c ranging from 85°C to 65°C (T_{cl}) derived from the Area 2 (see Scheme 2) shifted to the higher temperature as time passed. These results indicate that evaporation of acetone would decrease free volume of the amorphous

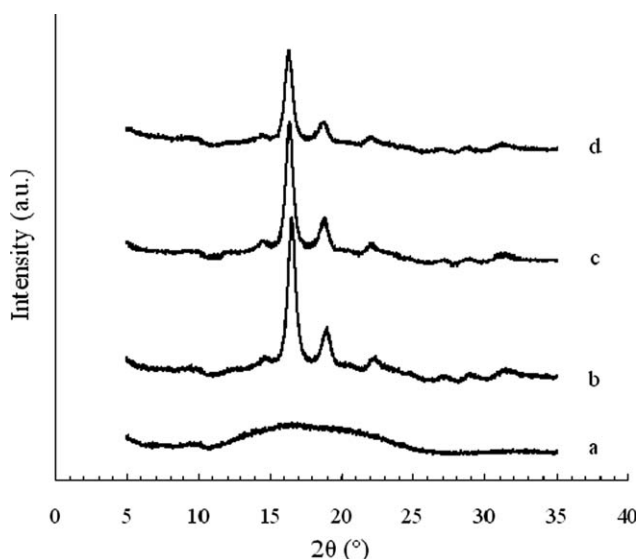


Figure 5 WAXD profiles of PLA samples; (a) amorphous PLA, (b) crystallized in acetone for 5 min at room temperature, (c) 40°C , and (d) 50°C .

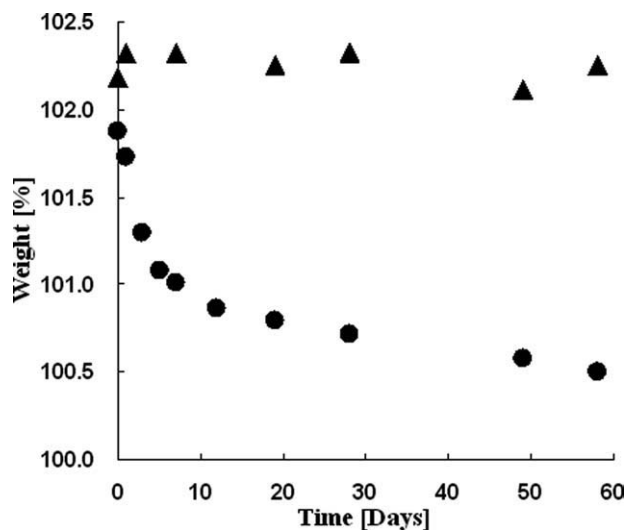


Figure 6 Time evolution of weight of PLA crystallized in acetone (for 1 min at room temperature) and stored at room temperature (circle) or at -22°C (triangle).

phase of PLA sample and should increase the temperatures of T_{gl} and T_{cl} .

Elongation test of PLA sample, which was crystallized by acetone for 1 min at room temperature, was conducted to study the time dependence on the mechanical properties. Stress–strain curves of the PLA samples are shown in Figure 8, and the results are summarized in Table II. The PLA sample after 1 day from the crystallization showed the stress–strain curves indicating soft and ductile features. The Young's modulus increased and the rupture strain decreased as time passes, decreasing of acetone content in the PLA sample. The time dependence of the stress–strain curves shows that the transition of the feature of PLA sample from soft and ductile to hard and brittle with decreasing of the acetone content.

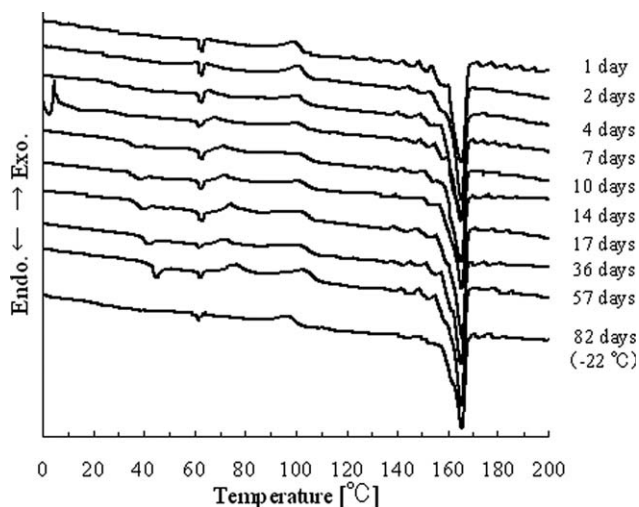


Figure 7 Time evolution of DSC profiles of PLA crystallized in acetone (for 1 min) at room temperature.

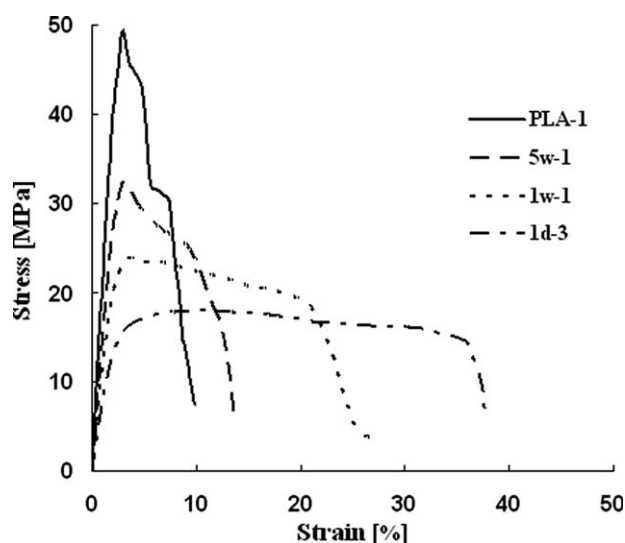


Figure 8 Stress–strain curves of PLA samples before crystallization (PLA-1), crystallized in acetone for 1 min at room temperature and stored at room temperature for 1 day (1d-3), 1 week (1w-1), and 5 weeks (5w-1).

The results are also clear that acetone plays a role of a plasticizer for PLA. The Young's modulus and yield stress of the crystallized sample were lower than those of the original amorphous PLA sample. The result should be derived from forming small bubbles in the crystallized samples.

CONCLUSIONS

Crystallization of amorphous PLA was carried out in various organic solvents. Acetone, ethylacetate,

TABLE II
Results of Elongation Test of PLA Crystallized by Acetone^a

Run	Time ^b	Acetone content (wt %)	Young's modulus (MPa)	Yield stress (MPa)	Yield strain (%)	Rupture strain (%)
1d-1	1 day	3.27	371.8	18.6	10.4	32.4
1d-2	1 day	3.03	368.5	19.3	10.4	37.0
1d-3	1 day	3.69	369.2	18.0	10.7	36.1
1d-average	1 day	3.33	368.8	18.6	10.5	35.2
1w-1	1 week	2.47	987.2	23.9	3.4	27.4
1w-2	1 week	2.51	807.7	21.0	3.7	29.6
1w-average	1 week	2.49	897.5	22.4	3.5	28.5
5w-1	5 weeks	1.37	1272	32.4	3.0	13.4
5w-2	5 weeks	0.95	1272	33.3	3.0	12.9
5w-3	5 weeks	1.12	1310	35.2	3.4	11.0
5w-average	5 weeks	1.15	1285	33.6	3.1	12.4
PLA ^c -1		0	1939	49.3	2.8	9.8
PLA-2		0	1938	46.7	2.6	9.8
PLA-average		0	1939	48.0	2.7	9.8

^a Immersed in the acetone at room temperature for 1 min.

^b Time after the crystallization.

^c PLA sample before the crystallization.

diethylether, tetrahydrofurane, methanol, toluene, xylene, and *o*-dichlorobenzene induce the crystallization of PLA. Acetone was most effective solvent for the crystallization of the amorphous PLA. Permeation of acetone into PLA induced the crystallization, and the permeation obeyed Fick type diffusion. Short time immersion of PLA in acetone caused lower T_g (T_{gl}) and T_c (T_{cl}) than the original amorphous PLA, and that indicate existence of the amorphous phase containing small amount of acetone, illustrated as Area 2 in Scheme 2. Acetone also plays a role of a plasticizer in PLA. The content of acetone in the crystallized sample decreased as the time passes. The properties of PLA sample changed from soft and ductile to hard and brittle with decreasing acetone content.

Solvent-induced crystallization should be one of the easy and useful methods to improve the properties of PLA. However, some points, transparency, mechanical properties, chemical safety, gradual evaporation and so on, should be solved for the practical use. Further investigations are now proceeding, and the results will be reported elsewhere.

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