Physical and Mechanical Properties of Poly(L-lactic acid) Nucleated by Dibenzoylhydrazide Compound

Naoshi Kawamoto, Atsushi Sakai, Takahiro Horikoshi, Tsuyoshi Urushihara, Etsuo Tobita*

Additives Department, Polymer Additives Research and Development Laboratory, ADEKA Corporation, Minami-Ku, Saitama-City, Saitama 336-0022, Japan

ABSTRACT: Benzoylhydrazide compounds were evaluated as a nucleating agent for poly(L-lactic acid) (PLA). From the results of the differential scanning calorimetry, octamethylenedicarboxylic dibenzoylhydrazide (OMBH) was found to be most effective for acceleration of PLA crystallization under higher cooling rate of $-50°C$ min^{-1}. PLA with OMBH of 1 wt % exhibited very short crystallization half-time with wide range of isothermal temperature from 90 to 130°C. The molding cycle time of PLA with OMBH in injection molding was less than 3 min, and the cooling time was one-third of ethylenebis(12-hydroxystearylamide)/talc system as a nucleating agent. Physical and mechanical properties improved extremely, and the heat distortion temperature of 124°C, flexural modulus of 4.1 GPa, and Izod impact strength of 7.9 kJ m^{-2} were achieved. This indicates that the utilization of OMBH makes it possible to extend the application range of PLA as automotive parts and electric appliances, which require higher heat resistance and stiffness. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 244–250, 2007

Key words: nucleating agent; nucleation; benzoylhydrazide; poly(L-lactic acid); heat resistance; injection molding; molding cycle time

INTRODUCTION

The raise in environment issue and energy and resources problems is building up the expectation of utilizing polymers produced by renewable resources, in particular, poly(L-lactic acid) (PLA).[1] PLA has many interesting properties such as biodegradability, biocompatibility, and good mechanical properties.[2] There are wide application spectra including medical devices as suture and implant devices, and food packages.[3,4] From the viewpoint of accelerating the creation of recycling-oriented society, Japan Association for the 2005 World Exposition promoted the biomass plastics utilization as a project at the World exposition EXPO 2005 AICHI JAPAN, where the utensils used for eating such as dishes, cups, and plates made from PLA were served at eating facilities in the site.[5] As background of growing social recognition of importance on renewable resources, the annual demand of PLA in Japan increased rapidly, from 60 metric ton in 1992 to 10,000 metric ton in 2002,[6] and the annual demand of over 20,000 metric ton in 2005 is expected by reflecting the contribution of EXPO 2005. The Japanese market of PLA has been growing at an annual rate of 60–70% since '90s. In the USA, the annual growth of biodegradable plastics by 2008 is predicted to be 13.7%.[7] Thus, the market is definitely growing in global. In addition, the recent rising in price of resins due to higher oil price has made many bioproducts price including PLA competitive.[8] The trend of the development of PLA application is body or housing for electric appliances and automotive parts instead of bulk polymers.[9–11] In the course of these development, the thermal properties, in particular, heat resistance, and the productivity and processability in mold processing have become an issue.[12] PLA is a crystalline polymer with a glass transition temperature (T_g) of around 60°C and melting temperature of $\sim 170°C$.[13] Heat distortion temperature (HDT) as heat resistance of molded articles is known to be around T_g, because the crystallinity is very low under practical molding conditions due to lower crystallization rate at higher cooling rate.[14] Poor processability is also ascribed to its lower crystallization rate.

In general, it is known that nucleating agents enhance the nuclei generation of semicrystalline polymers in crystallization process and leads to the higher crystallization rate at higher temperature, resulting in increasing crystallinity.[15,16] Thus, the utilization of nucleating agents improves physical and mechanical properties, processability, and productivity in mold processing. In fact, several nucleating agents are used for polypropylene (PP), and excellent benefits are received with economically or cost effectively. Thus,

*Correspondence to:* N. Kawamoto (naoshi@adeka.co.jp).
Present address: Information Media Materials Development Laboratory, ADEKA Corporation, 7-2-35 Higashi-ogu, Arakawa, Tokyo 116-8554, Japan.

the suitable utilization of nucleating agents is believed to be one of the solutions to the issues in practical application of PLA. The developments of nucleating agent for PLA were conducted by several groups and the developed nucleating agents were patented.[17–19] Although the nucleating agents in patent applications exhibited to enhance crystallization of PLA, the achieved heat resistance and processability were not enough for practical application as molded articles. In the course of our studies, benzoylhydrazide (BH) type compounds were found to exhibit excellent enhancement of crystallization of PLA, in particular, decamethylenedicarboxylic dibenzoylhydrazide was found to demonstrate highest crystallization temperature (T_c) of PLA.[20] The nucleation ability of the compound was superior to that of compounds in previous patent applications. This suggests that the PLA nucleated by BH compounds provides the PLA-molded articles having improved heat resistance with excellent processability. In this study, BH compounds were evaluated by differential scanning calorimetry (DSC) with higher cooling rate, and the crystallization rate at variety of isothermal conditions was also measured on the DSC for estimating the nucleation ability in response to more practical condition and determining suitable molding temperature. To evaluate the practicability of the nucleating agent, physical and mechanical properties of PLA nucleated by BH derivatives were evaluated via injection molding, and were compared with that of PP as one of the major bulk polymers.

EXPERIMENTAL

Materials

PLA used was NatureWorks 6202D from NatureWorks LLC. As reference nucleating agents for the hydrazide compounds, talc (fine particle size grade, Micro Ace P-6, Japan Talc, Japan) and ethylenebis-(12-hydroxystearylamide), EBHSA (MA-WAX-O, KF Trading, Japan, without any purification), were used. Octamethylenedicarboxylic dibenzoylhydrazide (OMBH, see Scheme 1) and decamethylenedicarboxylic dibenzoylhydrazide (DMBH, see Scheme 1) were synthesized according to previous literature.[20] Polypropylene
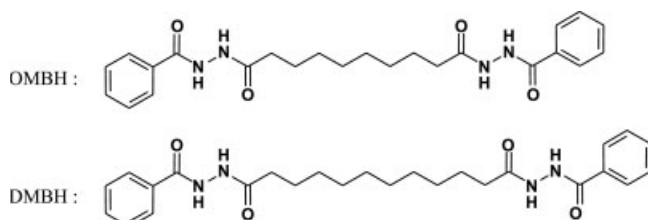
Scheme 1 Octamethlenedicarboxylic dibenzoylhyhydrazide (OMBH) and decamethylenedicarboxylic dibenzoylhydrazide (DMBH).

(PP) used was a standard homopolymer having melt flow rate of 10 dg min^{-1}, meting temperature of 163°C, which was polymerized by using highly active supported Ziegler–Natta catalyst system. Nucleating agent for PP used was NA-11 [methylenebis(2,4-di-*tert*-butylphenyl)phosphate sodium, ADEKA, Japan]. Phenolic antioxidant [ADK AO-60, tetrakis [methylene(3,5-di-*tert*-butyl-4-hydroxylphenyl propionate)]methane, ADEKA, Japan], phosphite (ADK 2112, tris(2,4-di-*tert*-butylphenyl)phosphite, ADEKA, Japan) and calcium stearate (CaSt, NOF, Japan) were used for suitable melt processing of PP.

Differential scanning calorimetry

Nucleating agents were dry-blended with PLA pellets, and the mixture (1 wt % of BH type compounds, and 1 wt % of both talc and EBHSA) was dried at a temperature of 90°C for 5 h *in vacuo*. The dried mixture was extruded by using twin-screwed extruder (Labo Plastomill Micro, Toyo Seiki Seisaku-sho, Japan) at a temperature of 200°C. T_c as a peak top temperature and crystallization enthalpy (ΔH_c) as an index of nucleation ability of nucleating agents were determined by using differential scanning calorimetry (Diamond DSC, PerkinElmer, USA) with following procedure and temperature program: PLA of 2 mg was cut from dried pellet, and then rolled up by aluminum pan. The sample was heated from room temperature to 200°C with a heating rate of 50°C min^{-1}, held for 5 min at 200°C, then cooled with a cooling rate of -20°C min^{-1} from 210 to 0°C. Crystallization half-time ($t_{1/2}$) was determined by DSC measurement with an isothermal crystallization according to following procedure. PLA of 2 mg was cut from dried pellet, and then rolled up by aluminum pan. The sample was heated from room temperature to 200°C with a heating rate of 50°C min^{-1}, held for 5 min at 200°C, and then cooled to a certain temperature with a cooling rate of -200°C. The exothermic heat due to crystallization at certain temperatures as 90, 100, 110, 130, and 145°C was monitored on the DSC. Here, the $t_{1/2}$ was the time at which the crystallization enthalpy was achieved to the half value of total enthalpy.

In addition, the degree of crystallinity χ_c and the lamellar crystal thickness l_c for injection-molded articles were also estimated by using DSC. The DSC crystallinity χ_c^D was calculated by using the following equation:

$$\chi_c^D = \frac{\Delta H_m}{\Delta H_m^0}$$

where ΔH_m is the observed heat of fusion and ΔH_m^0 is the equilibrium heat of fusion. Here, ΔH_m was measured on 1st run of heating process of DSC measurement with a heating rate of 20°C min^{-1}, and 93 J g^{-1}

was used as ΔH_m^0.[21] The l_c was calculated by using following equation:[22]

$$l_c = \frac{2\sigma_e}{\Delta H_f^0 \left(1 - \frac{T_m}{T_m^0}\right)} = \frac{2\sigma_e}{\Delta H_m^0 \rho \left(1 - \frac{T_m}{T_m^0}\right)}$$

where σ_e is the folded surface free energy of PLA lamellae (7.5×10^{-2} J m^{-1}), T_m is the observed melting point (DSC-1st run, same condition as ΔH_m), ρ is the density (1.27 g cm^{-3}), and T_m^0 is the equilibrium melting point (215°C).[21] The sample for DSC was microtomed from the injection-molded articles for flexural test, and then was set in the aluminum pan.

Physical and mechanical Properties

Nucleating agents were dry-blended with PLA pellets, and the mixture (1 wt % of BH type compound, and 1 wt % of both talc and EBHSA) was dried at a temperature of 90°C for 5 h *in vacuo*. The dried mixture was extruded by using twin-screw extruder (PCM-30-2V, Ikegai, Japan) at a temperature of 210°C. The extruded strand was cooled under water, and then cut into pellets. Before injection molding, the nucleated PLA pellets were dried at 90°C for 5 h *in vacuo*. Injection molding was conducted by an injection molding machine having 100 ton-mold clamping force (EC-100, Toshiba-Machine, Japan) with the mold based on the ISO. Injection and mold temperatures were 210 and 110°C, respectively. Molding cycle time was the sum of the injection and cooling time. The cooling time was estimated via ''trial and error,'' that is, necessary period (time) for cooling where no distortion of molded specimens was observed during the automatic demolding.

Molded specimens were aging at 23°C for 48 h under the atmosphere prior to the evaluation. Flexural test for the estimation of flexural modulus and strength was conducted by automatic flexural tester (Autograph AG-IS, Shimadzu, Japan) with a head cross speed of 100 mm min^{-1} at a temperature of 23°C. HDT was measured on the automatic HDT tester (Auto HDT.VSPT Tester 3A-2, Toyo Seiki Seisaku-sho, Japan) with a loading of 0.45 MPa. Izod impact strength was measured by using Izod impact tester (Impact Tester, Yasuda Seiki Seisakusho, Japan) with a 1.0 J hammer at a temperature of 23°C. Yellowness index (YI) of molded specimens was evaluated by using Multi Spectro Color Meter (Suga Test Instruments, Japan). Haze of molded plate having 1 mm-thickness was measured by Haze meter (Haze Gard II, Toyo Seiki Seisaku-sho, Japan) as an index of transparency.

Physical and mechanical properties of nucleated PP were also evaluated as a reference. NA-11 of 0.2 wt %, ADK AO-60 of 0.1 wt %, ADK 2112 of 0.1 wt %, and CaSt of 0.05 wt % were dry-blended with PP powder by Henschel mixer (Mitsui Miike, Japan), and the mixture was compounded by using single-screw extruder with pelletizer (PCM-30-2V, Ikegai, Japan) at a temperature of 230°C. Injection molding was conducted by an injection molding machine having 100 ton-mold clamping force (EC-100, Toshiba-Machine, Japan) with the mold based on the ISO. Physical and mechanical properties of PP were evaluated with the same conditions for PLA as mentioned above.

X-ray diffraction

The diffraction patterns for PLA injection-molded articles were obtained using a diffractometer (Rigaku, Japan) with Cu Kα ($\lambda = 0.1542$ nm) at a voltage of 50 kV and a current of 200 mA. The molded-PLA specimen was directly mounted on the standard sample holder. The measurement conditions were at step wise of 0.020° (2θ), with the starting angle of 5° (2θ) and the final angle of 40° (2θ). The χ_c is known to be closely related to the intensity of reflection associated by crystalline part and hollow associated by amorphous part. In general, correction coefficients for each diffraction peak are used for calculating χ_c. One of the examples is Natta's method for PP.[23] The correction coefficients have not been determined for PLA yet. Thus, the χ_c^* as an index of crystallinity was used in place of χ_c to make relative comparison of crystallinity among the samples in this article. The χ_c^* was calculated by using following equation:

$$\chi_c \propto \chi_c^* = \frac{I_c}{I_c + I_a}$$

where I_c is the intensity of the diffraction peaks associated by crystalline part and I_a is the intensity of the hollow associated by amorphous part.

RESULTS AND DISCUSSION

In our previous study, BH compounds were reported to enhance the crystallization of PLA, resulting in providing higher T_c and ΔH_c of PLA compared with market available nucleating agents.[20] In addition, OMBH and DMBH of 1 wt %-loading were also demonstrated to provide T_c of over 120°C together with ΔH_c of over 40 J g^{-1}, where the T_c and ΔH_c were measured on the DSC with a cooling rate of -20°C min^{-1}. The cooling rate of -20°C min^{-1} is ''fast'' for DSC measurement condition in general. However, the cooling rate in practical mold processing, where the injected molten polymer cools by the mold with lower temperature, is considered to be quite faster than -20°C min^{-1}, in particular, in contact with the surfaces of the mold. Taking this into consideration, the DSC measurement with -50°C min^{-1} was conducted for PLA nucleated

TABLE I
Crystallization Temperature and Enthalpy of Nucleated PLA
in Relation to the Cooling Rate

	Crystallization temperature T_c (°C) at		Crystallization enthalpy ΔH_c (J g^{-1}) at	
	−20°C min^{-1}	−50°C min^{-1}	−20°C min^{-1}	−50°C min^{-1}
OMBH[a]	120	111	37	27
DMBH[b]	120	111	35	26
EBHSA/talc[c]	120	n.d.[d]	17	n.d.[d]

[a] OMBH denotes octamethylenedicarboxylic dibenzoylhydrazide, 1 wt %-loading.
[b] DMBH denotes decamethylenedicarboxylic dibenzoylhydrazide, 1 wt %-loading.
[c] EBHSA denotes ethylenebis(12-hydroxystearylamide); EBHSA and talc of 1 wt % each were loaded.
[d] n.d.: Not detected.

by both OMBH and DMBH. Here, the higher cooling rate is considered to be slightly uncontrollable in DSC measurement. However, it is valuable to predict the crystallization behavior with nucleating agent or nucleation ability in actual processing with higher cooling rate. In addition, the PLA from NatureWorks LLC, which was easily available worldwide, was used in this study. Nucleating agent of EBHSA in combination with talc is current nucleating agent for PLA, and thus the talc/EBHSA was used as a reference in this study. Table I summarizes the T_c and ΔH_c obtained at cooling rates of both −20 and −50°C min^{-1} for 1 wt %-loading of OMBH and DMBH, and EBHSA in combination with talc (1 wt %-loading for each) was also listed as a reference. Table II summarizes the T_c and ΔH_c obtained at cooling rates of −20°C min^{-1} for 0.5 wt %-loading of OMBH and DMBH. At lower cooling rate of −20°C min^{-1}, the T_c and ΔH_c of PLA nucleated by DMBH of 1 wt %-loading were comparable to that by OMBH of 1 wt %-loading. On the other hand, the T_c and ΔH_c with OMBH were found to be higher than that with DMBH. This suggests that the nucleation ability of OMBH is superior to that of DMBH under higher cooling rate as practical processing condition. In addition, the PLA with OMBH of 0.5 wt %-loading exhibited better enhancement in T_c and ΔH_c than that with DMBH, and the resulted T_c and ΔH_c were superior to that of EBHSA/talc loading of 1 wt % each. From the practical standpoint, this result suggests that OMBH has an advantage in nucleation performance compared to DMBH and of course to EBHSA/talc. Furthermore, OMBH is considered to be more cost effective nucleating agent than DMBH due to the possibility in the reduction of loading level.

Figure 1 shows the DSC $t_{1/2}$ of nucleated PLA at various temperatures. Both systems, i.e., PLA nucleated by OMBH and EBHSA/talc, were found to exhibit minimum $t_{1/2}$ in relation to the isothermal temperature of around 110°C. The $t_{1/2}$ of PLA with OMBH provides shorter than that with EBHSA/talc in all temperature range. Thus, the acceleration of

crystallization process by OMBH was found to be superior to EBHSA/talc at all temperature range. Additionally, it is noted that no significant differences in $t_{1/2}$ with OMBH were observed at the temperature range from 90 to 130°C. This suggests that PLA nucleated by OMBH has an excellent processability, that is a wide processing or molding window. On the other hand, EBHSA/talc apparently provided shortest $t_{1/2}$ at a temperature of 110°C. Considering the above-mentioned results on $t_{1/2}$, the mold temperature for injection molding was decided to be 110°C.

PP is well-known bulk polymer and large amounts of PP have been produced globally for application to a wide range of products such as automotive parts, electric appliances, food packages, disposable medical devices, and so on.[15,16,24–26] In most cases, nucleated PP is used for the applications, which need higher stiffness and heat resistance. The stiffness, heat resistance, and processability of nucleated PP is considered to be a targeted value for nucleated PLA from the viewpoint of evaluating the possibility and applicability as molded articles of the nucleated PLA. In fact, there are some examples to promote the utilization of PLA as electric appliances and automotive parts instead of PP.[9–11] Thus, PP was used as a comparative or reference polymer in this study. Table III summa-
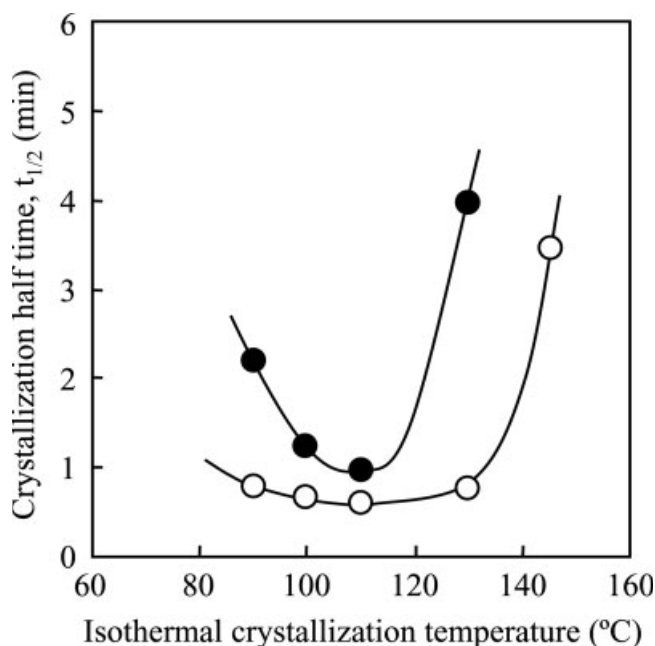
TABLE II
Crystallization Temperature and Enthalpy of Nucleated PLA with 0.5 wt %-Loading[a]

	Crystallization temperature T_c (°C)	Crystallization enthalpy ΔH_c (J g^{-1})
OMBH[b]	117	24
DMBH[c]	113	19

[a] Cooling rate: −20°C min^{-1}.
[b] OMBH denotes octamethylenedicarboxylic dibenzoylhydrazide.
[c] DMBH denotes decamethylenedicarboxylic dibenzoylhydrazide.

Figure 1 Changes in crystallization half-time, $t_{1/2}$, as a function of the isothermal crystallization temperature. (○): PLA with octamethylenedicarboxylic dibezoylhydrazide of 1 wt %, (●): PLA with ethylenebis(12-hydroxystearyla-mide) and talc of 1 wt % each.

rizes the molding cycle time as injection time and cooling time, physical and mechanical properties of nucleated and unnucleated PLA, and nucleated PP. At the mold temperature of 110°C, neat PLA resin could not be fabricated and be demolded because the resin could not be solidified at the temperature due to very low crystallization rate. Thus, the injection molding of neat resin was conducted at a mold temperature of 25°C, and was demolded as solidified amorphous specimens. Molding cycle time (MCT) of the PLA with EBHSA/talc was found to require over 6 min. This was almost six times longer than the typical PP-MCT. Drastic decrease in MCT was observed for the PLA with OMBH. It is noted that the cooling time of the PLA with OMBH was one-third of that with EBHSA/talc. Thus, the utilization of OMBH is indicated to improve the processability and molding productivity of PLA extremely. Neat PLA resin in an amorphous state gave very low HDT, which was considered to concern to the T_g. Flexural modulus of the neat resin was 3.5 GPa, and was 1.6 times higher than that of nucleated PP. This indicates that PLA has excellent stiffness in essential. Despite the measurement was conducted at lower temperature of the T_g of PLA, the Izod impact strength of neat resin was almost comparable to that of nucleated PP. The neat resin exhibited excellent transparency due to amorphous state. This is one of the excellent characteristics as same as poly(ethylene telephthalate) (PET); PET is essentially semicrystalline polymer, but the crystalli-

TABLE III
Molding Cycle Time, and Physical and Mechanical Properties of Nucleated PLA[a]

	Mold temperature (°C)	Injection time (min)	Cooling time (min)	Total cycle time (min)	Heat distortion temperature at 0.45 MPa (°C)	Flexural modulus (GPa)	Flexural strength (MPa)	Izod impact strength (kJ m^{-2})	Haze (%)	Yellowness index (%)
non[b]	25	–[e]	–[e]	–[e]	54	3.5	103	3.7	6.0	9.8
OMBH[c]	110	0.7	2.0	2.7	124	4.1	73	7.9	94	9.9
EBHS/talc[d]	110	0.7	6.0	6.7	110	4.1	90	7.7	81	18.5

[a] Injection molding.
[b] Neat resin (without any nucleating agents).
[c] OMBH denotes octamethylenedicarboxylic dibenzoylhydrazide, 1 wt %-loading.
[d] EBHSA denotes ethylenebis(12-hydroxystearylamide); EBHSA and talc of 1 wt % each were loaded.
[e] Not measured.

zation rate is known to be very slow as similar to PLA.[27] The major application is PET bottle, which is basically amorphous, transparent product. Thus, in the same manner, the application as eating utensils is the major for PLA at present.

Drastic improvements in HDT, flexural modulus, and Izod impact strength were observed for both nucleated PLA. Especially, it was note worthy that the HDT with OMBH was comparable to that of nucleated PP. It is considered that the HDT of over 120°C makes it possible to utilize as an industrial component such as in automotive use. Progress in crystallization gave rise to these improvements: nucleating agent brought out potential ability of PLA as a semicrystalline polymer. Clarity of crystallized PLA using nucleating agent was poor due to crystalline structure including spherulites.[14] Crystalline–amorphous microstructure as a hierarchical structure, folded chain crystal to lamellae crystal, lamellae crystal to lamellae stacks, lamellae stacks to spherulites, is known to decrease the clarity because of scattering of visible light due to over size of visible light wave length.[15,16] The YI of molded article with EBHSA/talc changed for the worse. On the other hand, the YI with OMBH was comparable to that of
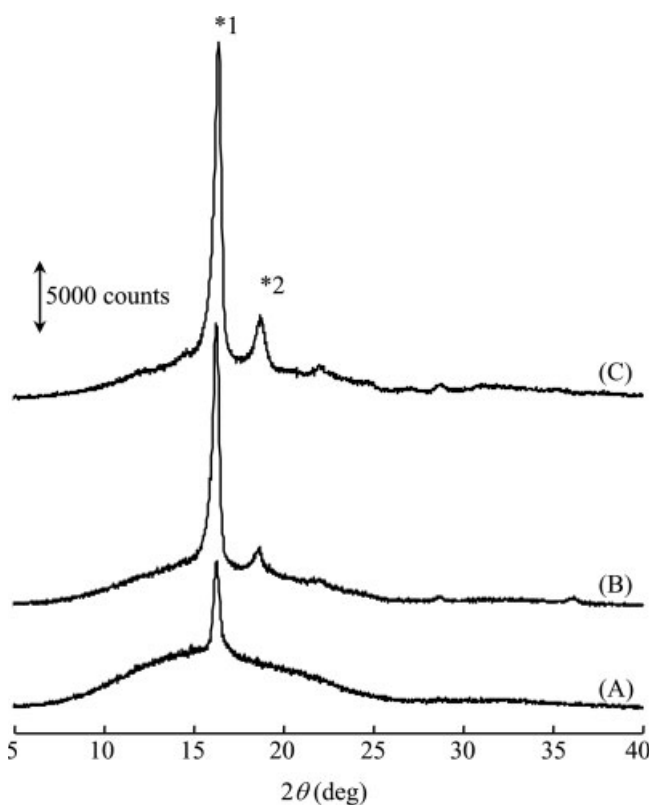
Figure 2 X-ray diffraction patterns of injection-molded articles of PLA with and without nucleating agent. (A) PLA without nucleating agent; (B) PLA with ethylene-bis(12-hydroxystearylamide) and talc of 1 wt % each; and (C) PLA with octamethylenedicarboxylic dibezoylhydrazide of 1 wt %. *1: (020); *2: (023).

TABLE IV
Degree of Crystallinity χ_c^* and χ_c^D, and Lamellar Crystal Thickness l_c of Nucleated PLA

Nucleating agent[a]	$\chi_c^{*\mathrm{b}}$	$\chi_c^{D\mathrm{c}}$	l_c^{c} (nm)
OMBH	0.56	0.48	12.0
EBHSA/talc	0.31	0.30	11.8

[a] 1 wt %-loading.
[b] Estimated by XRD measurement (see Experimental).
[c] Estimated by DSC measurement (see Experimental).

neat resin. This is one of the advantages of OMBH in practical applications instead of EBHSA/talc.

Figure 2 shows the X-ray diffraction patterns for injection-molded PLA with and without nucleating agent. Figure 2(A) shows the patterns for the molded articles of PLA neat resin. Broad hollow ascribed to the amorphous and a weak reflection peak (16.36°) associated by the (020) reflection was observed for (A).[28] On the other hand, the decrease in hollow and the increase in the peak intensity were observed for the nucleated PLA specimens of both (B) and (C) in Figure 2. Here, the (020) reflection was $2\theta = 16.36°$ for (B) and $2\theta = 16.42°$ for (C), respectively. This suggests that the spacing of (020) of (C) was slightly smaller than that of (A) and (B). In addition, another reflection was observed for both (B) and (C) at $2\theta = 18.76$ for (B) and $2\theta = 18.78$ for (C), which was ascribed to the (023) reflection. Thus, the intensity of the reflections associated by the crystalline part was increased by the addition of nucleating agent. In general, the intensity ratio of diffraction peak and hollow is known to be closely related to the degree of crystallinity. Here, χ_c^* (see Experimental) was estimated by the XRD patterns for the molded articles with OMBH and talc/EBHSA. In addition, χ_c^D (the degree of crystallinity) and l_c (lamellar thickness) were also estimated by using DSC, and these data were summarized in Table IV. The crystallinity of PLA with OMBH was found to be much higher than that with talc/EBHSA. The difference in crystallinity χ_c^* between article with OMBH and with talc/EBHSA was slightly larger than that in χ_c^D. Although this difference may be ascribed to the no correction in the calculation of χ_c^*, that is without using ''correction coefficient'' (see Experimental), the tendency was almost the same. The lamellar crystal thickness l_c was almost the same among them. Thus, the higher crystallinity was considered to provide excellent in mechanical properties, in particular superior HDT of PLA with OMBH.

CONCLUSIONS

It was demonstrated that octamethylenedicarboxylic dibenzoylhydrazide (OMBH) enhanced the PLA crystallization and 1 wt % of OMBH provided excel-

lent crystallization temperature and enthalpy even at a higher cooling rate of $-50°C$ min^{-1} and lower loading level. PLA with OMBH of 1 wt % exhibited very short crystallization half-time with wide range of isothermal temperature from 90 to 130°C. The molding cycle time of PLA with OMBH was less than 3 min, and the cooling time was one-third of current system of EBHSA/talc. Excellent heat distortion temperature of over 120°C, which was comparable to nucleated PP, was obtained by using OMBH, and thus the higher heat resistance and stiffness with excellent balance between stiffness and impact strength can be achieved by the nucleating agent, OMBH. These findings will have the great importance on the viewpoint of manufacturing several molded articles of PLA such as automotive parts and electric appliances.

References

1. Mochizuki, M. Petrotech 2000, 23, 735.
2. Ljungberg, N.; Colombini, D.; Wesslén, B. J Appl Polym Sci 2005, 96, 992.
3. Kimura, Y.; Shiratani, K.; Yamane, H.; Kitao, T. Macromolecules 1988, 21, 3338.
4. Lipinsky, E. S.; Sinclair, R. G. Chem Eng Prog 1986, 82, 26.
5. Available at http://www.expo2005.or.jp/en/eco/biomass.html and http://www.expo2005.or.jp/en/eco/eco_tech_list.html.
6. Kimura, K. Plastics 2004, 56, 72.
7. Editorial Staff, Modern Plastics, Chemical Week Associates, January 1, 2005.
8. Hassell, A.; von Bella, M. Modern Plastics, August 1, 2005.
9. Mohanty, A. K.; Drzal, L. T.; Rook, B. P.; Misra, M. (Michigan State University). U.S. Pat. 6,869,985.
10. Takehara, A. In Proceedings of Polymer Materials Forum; Society of Polymer Science: Nagoya, Japan, 2004; 2PA14.
11. Shioya, T. Presented at the JSAE Meeting, Society of Automotive Engineers of Japan, Nagoya, Japan, November 2004.
12. Defosse, M. Modern Plastics, January 1, 2005.
13. Baiarrdo, M.; Frisoni, G.; Scandola, M.; Rimelen, M.; Lips, D.; Ruffieux, K.; Wintermantle, E. J Appl Polym Sci 2003, 90, 1731.
14. Tsuji, H.; Ikada, Y. Polymer 1995, 36, 2709.
15. Kawamoto, N.; Tobita, E.; Goman, P.; Funamizu, T. Polyolefins 2003; Society of Plastics Engineers: Houston, TX, 2003.
16. Funamizu, T.; Goman, P.; Kawamoto, N.; Fukushima, M.; Yukino, T.; Tobita, E. Polyolefins 2005; Society of Plastics Engineers: Houston, TX, 2005.
17. Suzuki, K.; Watanabe, T.; Kitahara, Y.; Ajioka, M. (Mitsui Toatsu Chemicals, Inc.). Jpn. Pat. 06,299,054.
18. Ikeda, N.; Yoshimura, M.; Kimura, Y. (New Japan Chem, Co., Ltd.). Jpn. Pat. 10,087,975.
19. Sato, N.; Noguchi, T.; Mori, H.; Miyashita, M. (SONY Co.). Jpn. Pat. 238,779 (2003).
20. Kawamoto, N.; Sakai, A.; Horikoshi, T.; Urushihara, T.; Tobita, E. J Appl Polym Sci, to appear.
21. Kalb, B.; Pennings, A. J. Polymer 1980, 21, 607.
22. Varga, J. In Polypropylene-Structure, Blends and Composites: Crystallization, Melting and Supermolecular Structure of Isotactic Polypropylene; Karger-Kocsis, J., Ed.; Chapman & Hall: London, 1995; p 63.
23. Natta, G.; Corradini, P.; Cesari, M. Rend Accad Naz Lincei 1957, 22, 11.
24. Kawamoto, N.; Mori, H.; Terano, M.; Yui, N. J Biomater Sci Polym Ed 1997, 8, 859.
25. Kawamoto, N.; Mori, H.; Nitta, K.-h.; Sasaki, S.; Yui, N.; Terano, M. Macromol Chem Phys 1998, 199, 261.
26. Kawamoto, N.; Horikoshi, T.; Nomura, K.; Yokota, H.; Negishi, Y.; Tobita, E.; Terano, M. J Appl Polym Sci 2006, 99, 1350.
27. McIntyre, J. E. In Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters; Scheirs, J., Long, T. E., Eds.; Wiley: Chichester, West Sussex, 2003, p 195.
28. Pluta, M.; Galeski, A. J Appl Polym Sci 2002, 86, 1386.