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Description	



Transparent Poly(Lactic Acid) Film Crystallized by Annealing beyond Glass Transition Temperature

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1 **ABSTRACT**

2 The effect of post-processing annealing beyond the glass transition temperature on
3 optical transparency was studied using poly(lactic acid) (PLA) films containing a
4 nucleating agent such as *N,N'*-ethylenebis(stearamide) (EBS) or
5 *N,N'*-ethylenebis(12-hydroxystearamide) (EBHS). Although the PLA films without
6 the nucleating agent became opaque after exposure to annealing, the film with an
7 appropriate amount of the nucleating agent was found to be transparent (the haze
8 value was lower than 10%). Since the crystallinity was enhanced by annealing, the
9 film showed excellent heat resistance. As compared with EBS, moreover, EBHS had a
10 better capability to produce a transparent film because the aggregates, which appeared
11 during cooling from the molten state, were small. In the case of EBHS, a network
12 structure of fibrous EBHS in molten PLA was confirmed, which was responsible for
13 the reduced size of the PLA crystals and prevented spherulite formation.

14

15 Keywords; Poly(lactic acid); Polymer processing; Transparency

16

17 Introduction

18 In recent years, concern has been increasing rapidly about environmental issues
19 related to plastic packaging materials because most materials used in packaging
20 containers are petroleum-based plastics and are not biodegradable. Besides the
21 depletion of fossil resources and global warming due to CO₂ emissions into the
22 atmosphere, illegal dumping will have a negative impact on the ecosystem. This
23 situation is accelerating research and development on plant-derived and biodegradable
24 plastics. Poly(lactic acid) (PLA) is one of the most well-known plant-derived
25 biodegradable resins. Because of its low level of environmental load, much attention
26 has been paid to PLA [1-6]. For example, the rheological properties in the molten
27 state, and thus the processability, were modified by the addition of flexible fine fibers,
28 which provided strain-hardening in transient elongational viscosity [7,8].
29 Stereo-complex crystals [9] and reactive polymeric modifiers having glycidyl
30 functions [10-12] also have the capability to give strain-hardening in elongational
31 viscosity. The improvement of mechanical toughness has been another major target
32 for research and development because PLA is a brittle material. Besides the
33 conventional method, i.e., rubber addition [13-19], a recent study of the annealing
34 history should be mentioned. According to Huang et al., exposure to annealing near
35 the glass transition temperature T_g improved the mechanical toughness greatly, even
36 without rubber addition, which is attributed to conformational changes of PLA chains
37 [20,21].

When PLA products are obtained by a quenching process, they show very low or no crystallinity, leading to reduced light scattering. Consequently, PLA shows good transparency, which is quite useful for packaging containers that require visibility. However, poor heat resistance owing to its low T_g without crystallization is inevitable [22,23]. It is widely known that the heat resistance of PLA is greatly improved by enhancement of the crystallinity, which is attained by the addition of nucleating agents, including nanofillers and/or plasticizers [1-6,22-29]. Once the crystallinity is enhanced, however, a product usually loses its good transparency because of light scattering.

According to Norris and Stein, the following factors have to be considered when discussing the transparency of a crystalline polymer [30]: (i) light scattering and reflection from surface roughness, impurities, and voids, (ii) light scattering originating from the spherulite texture, and (iii) light scattering due to the polarizability difference of crystalline aggregates. For the last mechanism, the Rayleigh ratio $R(\theta)$ is used to express the scattered intensities as a function of the angle θ between the direction of the incident light and that of the scattered light by the following equation [30]:

$$R(\theta) = \frac{\langle \eta^2 \rangle \pi^2}{\lambda_0^4} \left[4\pi \int_0^\infty \frac{\sin(vsr)}{vsr} r^2 \gamma(r) dr \right] \quad (1)$$

$$v = \frac{2\pi}{\lambda} \quad (2)$$

$$s = 2 \sin \frac{\theta}{2} \quad (3)$$

where $\langle \eta^2 \rangle$ is the mean-square dielectric constant fluctuation, and λ_0 and λ are the wavelengths of light in a vacuum and medium, respectively. Finally, $\gamma(r)$ is the

60 correlation function describing the correlation between the fluctuations in a vacuum of
61 elements separated by a distance r , which is expressed by the following relationship
62 [31]:

63
$$\gamma(r) = \exp\left(-\frac{r}{a}\right) \quad (4)$$

64 where a is the correlation distance.

65 As described by these equations, light scattering is pronounced when the
66 correlation distance is in the range of the wavelength of visible light. In other words,
67 light scattering is reduced even for a product having high crystallinity when a is much
68 shorter/longer than the wavelength of visible light. In fact, a transparent product of
69 polypropylene (PP) has been developed by addition of a nucleating agent [32-36]. In
70 particular, sorbitol derivatives are well-known nucleating agents, and are called
71 “clarifiers”. They are known to form fibrous structures in the PP resin. Then, the
72 crystallization of PP occurs from the surface of fibrous sorbitol derivatives. Under a
73 flow field, the fibrous nucleating agent orients in the flow direction, leading to a high
74 level of orientation of PP chains [37-39]. As a result, the correlation length increases
75 beyond the wavelength of visible light, which is detected in the skin layer of an
76 injection-molded product [33]. Under quiescent conditions, including the core layer in
77 an injection-molded product, the fibrous nucleating agent forms a network structure in
78 a molten resin. Because the mesh size of the network is much smaller than the
79 wavelength of visible light, the size of PP crystals grown from the network surface is
80 small enough to avoid light scattering [33]. Of course, the network structure prevents

81 spherulite formation. Therefore, PP products containing a “clarifier” show good
82 transparency.

83 Here, we developed a transparent PLA film with high crystallinity, which can be
84 prepared by T-die extrusion, i.e., a common method of film and sheet forming. During
85 T-die extrusion, a molten resin is extruded from a T-shaped die and subsequently
86 quenched by chill rolls. Furthermore, the sheet can be reheated successively after
87 passing through the chill rolls to promote cold crystallization, i.e., crystallization
88 during the reheating process. Considering the productivity in an actual processing
89 operation, however, it is necessary to increase the crystallization rate in the
90 cold-crystallization process. Although numerous studies on the crystallization rate of
91 PLA have been reported, there have been few reports on cold crystallization, and in
92 the existing reports the transparency of the films was not discussed [24,26,40-42].

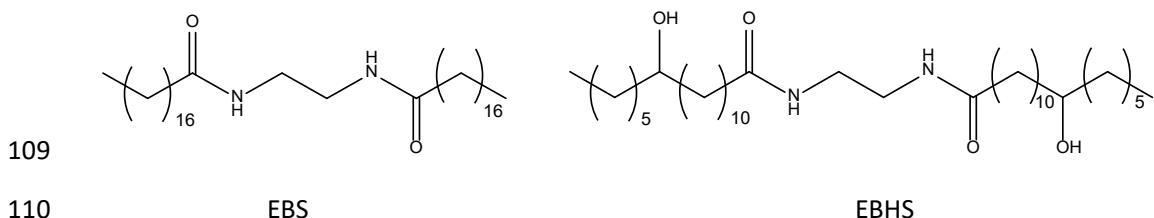
93

94 **Materials**

95 The polymer used to evaluate the crystallinity and transparency was
96 commercially available poly(lactic acid) (PLA) (Ingeo 4032D, NatureWorks, MN,
97 USA) containing 1.40% of the D-isomer. The number- and weight-average molecular
98 weights, evaluated by size exclusion chromatography, were 160,000 and 210,000,
99 respectively, with reference to a polystyrene standard. Furthermore, another
100 poly(lactic acid) containing a large amount of the D-isomer (Sigma-Aldrich, UK)
101 (PDLLA) was employed for rheology measurements. The weight-average molecular
102 weight of PDLLA was 10,000–18,000. As nucleating agents,

103 *N,N'*-ethylenebis(stearamide) (EBS) (Itohwax J-550S, Itoh Oil Chemicals, Japan) and
 104 *N,N'*-ethylenebis(12-hydroxystearamide) (EBHS) (Itohwax J-530, Itoh Oil
 105 Chemicals) were used. The chemical structures are given in Figure 1. The sample
 106 code indicates the species of the nucleating agent and the weight content. For example,
 107 PLA-EBHS-0.5 denotes the PLA sample containing 0.5 wt% of EBHS.

108



111 **Figure 1.** Chemical structures of EBS and EBHS

112

113 **Sample preparation**

114 Prior to melt mixing, PLA pellets were dried at 110 °C for 3 h. PLA and EBS or
 115 EBHS were mixed in a molten state using an internal mixer (Labo Plastmill, Toyo
 116 Seiki Seisaku-sho, Japan) for 5 min at 200 °C with a blade rotational speed of 100
 117 rpm. The concentrations of EBHS or EBS were 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.5, and 2.0
 118 wt%. The obtained mixtures were compressed into flat films of thickness 250 µm by
 119 a compression-molding machine (Labo Press, Toyo Seiki Seisaku-sho) at 200 °C
 120 under 20 MPa for 120 s, and then quenched at 25 °C for 2 min; the samples are
 121 referred to as “quenched films”. Films of relatively high crystallinity were obtained by
 122 annealing the quenched films at 100 °C for 2 h.

123 Besides the blends obtained by internal mixing, other blend samples of PDLLA

124 and the nucleating agent were prepared by manually stirring the mixtures with a
125 spatula in a polytetrafluoroethylene beaker at 200 °C for 5 min. Then the sample was
126 sandwiched between polyimide films (Yuprex, Ube Industry, Japan) on a hot plate at
127 200 °C. Thereafter, the film was quenched between metal plates at 25 °C.

128

129 **Measurements**

130 The thermal properties of the PLA films were evaluated using differential
131 scanning calorimetry (DSC) (DSC 8500, PerkinElmer, MA, USA). Approximately 10
132 mg of the sample, cut out from the sheet, were encapsulated in an aluminum pan.
133 After holding the sample at 200 °C for 10 min, it was quenched to 20 °C at the
134 maximum cooling rate and kept at this temperature for 3 min. Thereafter, the heating
135 run was performed at a rate of 10 °C/min to evaluate the cold-crystallization behavior.
136 The crystallization half time was also measured by DSC. The sample was quenched to
137 20 °C after melting at 200 °C, and then heated to various crystallization temperatures
138 at the maximum heating rate. The actual heating/cooling rates are shown in the
139 following table.

140

141 **Table 1 Heating and cooling rates at the DSC measurements**

Start temp. (°C)	200	20	20	20	20	20	20
End temp. (°C)	20	80	90	100	110	120	130
Rate (°C/min)	-233	169	189	211	225	240	254

142

143 The crystallization behavior was examined also by a polarized optical microscope
144 (DMLP, Leica, Germany) equipped with a hot-stage (FP90, Mettler, OH). The
145 quenched films were heated to 100 °C at 20 °C/min and kept at the temperatrue to
146 evaluate the isothermal crystallization behavior.

147 The transparency of the PLA film of thickness 250 μm was measured using a
148 haze meter (LDH 5000, Nippon Denshoku Industries, Japan). The measurements were
149 performed three times and the average value was calculated. Furthermore, light
150 scattering measurements were performed using a helium neon laser with a wavelength
151 of 632.8 nm to evaluate the spherulite texture.

152 Wide-angle X-ray diffraction (WAXD) patterns of the PLA films were collected
153 with an XRD machine (miniFlex600, Rigaku, Japan) using Cu-K α radiation at 40 kV
154 and 15 mA. The scanning speed was 10°/min over the 2 θ range from 5° to 40°. The
155 measurements were performed three times.

156 The temperature dependence of the dynamic tensile modulus of the PLA films
157 was evaluated using a dynamic mechanical analyzer (Rheogel E-4000, UBM, Japan).
158 Rectangular samples of width 5 mm and length 20 mm, which were cut out from the
159 compression-molded film of thickness 250 μm , were employed. The samples were
160 heated from room temperature to 180 °C at a heating rate of 2 °C/min. The applied
161 frequency was 1 Hz.

162 The frequency dependence of the oscillatory shear modulus of the PDLLA
163 samples was measured using a cone-and-plate rheometer (Rheosol G-3000, UBM,
164 Japan) at 100 °C under a nitrogen atmosphere.

165 The morphology of the nucleating agent was observed by scanning electron
166 microscopy (SEM) (FE-SEM S-4000, Hitachi High-Technologies, Japan). The sample
167 was prepared as follows. First, the PDLLA films annealed at 100 °C were immersed
168 in chloroform at 25 °C. After dissolution of the PDLLA, the solution was filtered
169 using a membrane filter with 1.0 µm pores. The residual materials on the filter were
170 used for the SEM observations after vacuum drying.

171 The tensile test was performed by a universal tensile machine (AG-IS, Shimazu,
172 Japan) at 25 °C using the dumbbell-shaped specimens cut out from the compressed
173 films (JIS K6251, Number 6). The initial distance between the clamps was 50 mm and
174 one of the clumps moved at a constant speed of 50 mm/min. The measurements were
175 carried out five times for each sample and the average value was calculated.

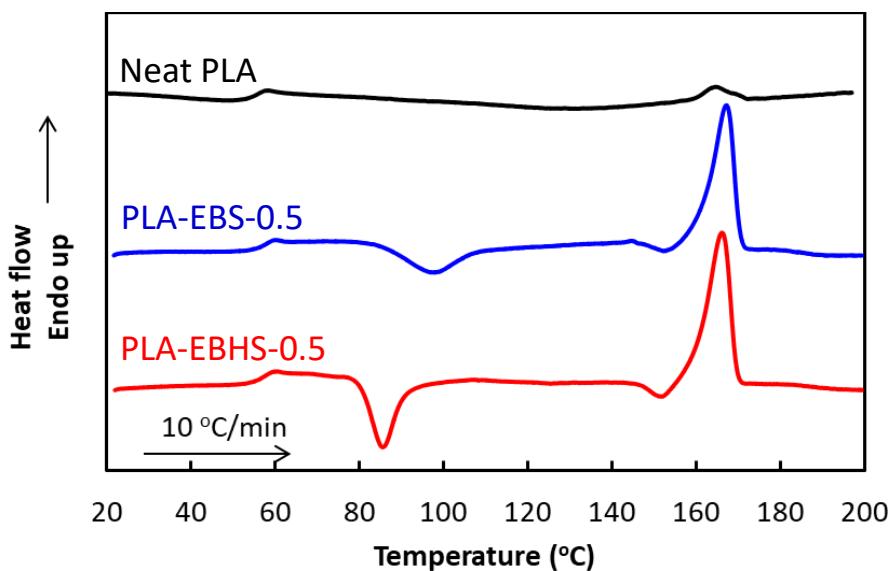
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177 Results and Discussion

178 Figure 2 shows the DSC heating curves at 10 °C/min for quenched films of PLA
179 and PLA containing 0.5 wt% of the nucleating agent. All the samples clearly show T_g
180 at around 60 °C, suggesting that the quenched samples have low/no crystallinity. It
181 should be noted that a cold-crystallization peak was not observed for neat PLA,
182 although the samples with the nucleating agent had a distinct peak. This result
183 suggested that PLA with the nucleating agent has a number of embryonic crystalline
184 nuclei even after rapid cooling. Therefore, crystallization occurred rapidly once
185 molecular motion was allowed beyond T_g . In contrast, pure PLA hardly showed cold
186 crystallization, leading to a small peak at the melting point. The peak

187 cold-crystallization temperatures were 84 °C for PLA-EBHS-0.5 and 87 °C for
 188 PLA-EBS-0.5. Furthermore, PLA-EBHS-0.5 gave a sharp peak at the
 189 cold-crystallization point, suggesting that EBHS has a better nucleating ability.

190



191

192 **Figure 2.** DSC heating curves at 10 °C/min after quenching from 200 °C.

193

194 The degree of crystallinity (χ_c) of the samples was calculated with equation (1)
 195 using the heat of fusion ΔH_m and exothermic heat of cold crystallization ΔH_{cc} [21];

$$196 \quad \chi_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{100\%}} \times 100 \quad (1)$$

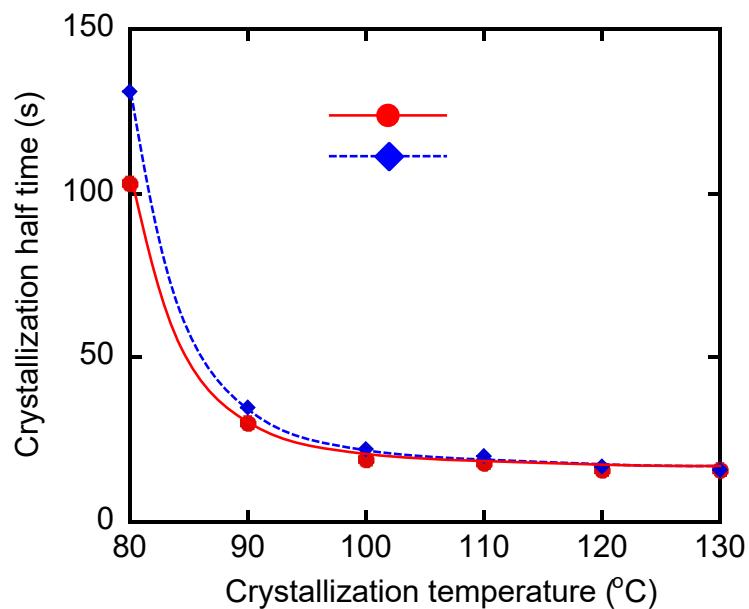
197 where $\Delta H_{100\%}$ is the heat of fusion for a perfect PLA crystal; *i.e.*, 93.1 J/g.

198 The degrees of crystallinity of PLA, PLA-EBS-0.5, and PLA-EBHS-0.5 were
 199 calculated to be 1.4, 3.7, and 6.1 %, respectively.

200 The crystallization half times at isothermal crystallization are summarized in
 201 Figure 3. As seen in the figure, the crystallization half times of PLA-EBHS-0.5 were
 202 shorter than those of PLA-EBS-0.5 in the temperature range lower than 110 °C. Since

203 the difference was pronounced at low crystallization temperatures, EBHS is a useful
204 nucleating agent in conventional processing operations in which water is used as the
205 cooling medium. Xing et al. also compared the nucleating abilities of EBS and EBHS,
206 and obtained a similar result [25]. According to them, the hydroxyl groups in EBHS
207 are responsible for the interactions with the carbonyl groups in PLA, which results in
208 a better nucleating ability. At 120 and 130 °C, both samples showed short
209 crystallization half times owing to the enhanced linear growth rate at crystallization.
210 In fact, the linear crystallization rate is known to be maximum at 120 °C for PLA, i.e.,
211 the middle of T_g and the equilibrium melting point [22].

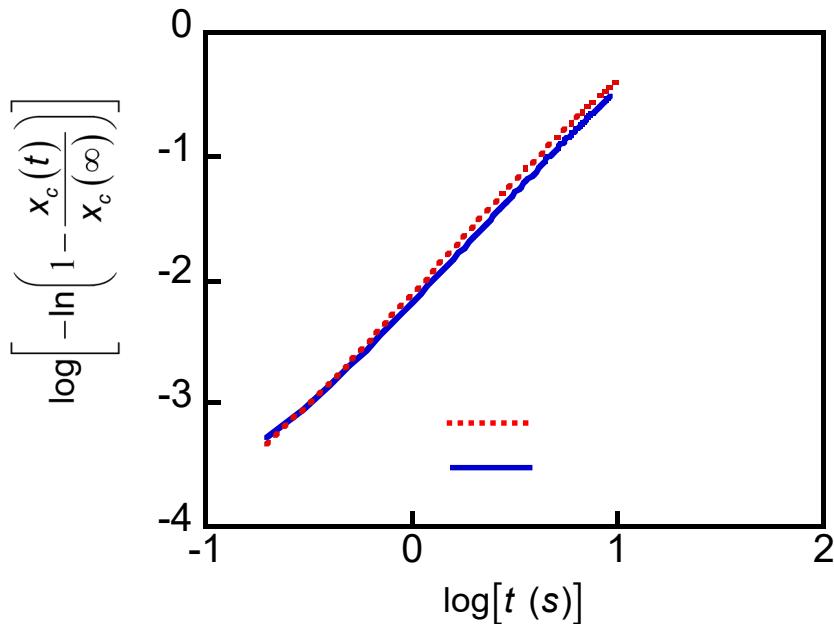
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213

214 **Figure 3.** Crystallization half times at various crystallization temperatures for (circles)
215 PLA-EBHS-0.5 and (diamonds) PLA-EBS-0.5.

216



217

218 **Figure 4.** Avrami plots for isothermal crystallization at 100 °C for (dotted line)

219 PLA-EBHS-0.5 and (solid line) PLA-EBS-0.5.

220

221 The classical Avrami plots are shown in Figure 4, in which $x_c(t)$ is the volume
 222 fraction of crystals at time t . The crystallization temperature was 100 °C. As seen in
 223 the figure, there was no difference in the crystallization kinetics between
 224 PLA-EBHS-0.5 and PLA-EBS-0.5.

225 The crystallization behavior was also studied using a polarizing optical
 226 microscope as shown in Figure 5. Before annealing, the samples were optically
 227 isotropic at room temperature, and therefore, nothing was detected under crossed
 228 polars. This is reasonable because all sample films had low degrees of crystallinity.
 229 After annealing at 100 °C for 5 min, which was slightly shorter than the
 230 crystallization half time of pure PLA (7.2 min), the difference in the crystalline
 231 structure was obvious between the pure PLA film and the films containing the

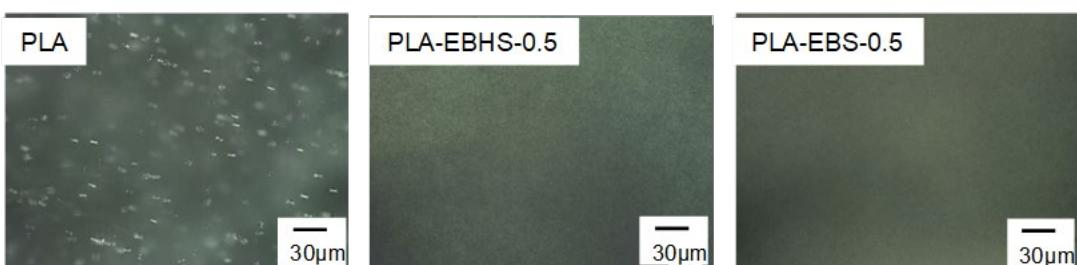
232 nucleating agents. In the case of the pure PLA film, spherulite texture was clearly
233 detected. In contrast, the crystalline structure was too fine to characterize, which was
234 attributed to a large number of crystalline nuclei.

235

Before annealing



After annealing at 100 °C for 5 min



236

237 **Figure 5.** Polarized optical photographs under crossed polars for pure PLA,
238 PLA-EBHS-0.5, and PLA-EBS-0.5. (top) Before annealing (quenched films) and
239 (bottom) after annealing at 100 °C for 5 min.

240

241 It should be noted that the annealing procedure strongly affected the transparency,
242 as shown in Figure 6. Although the quenched pure PLA film without annealing was
243 transparent (haze value was $1.2 \pm 0.1\%$), it became opaque after exposure to
244 annealing at 100 °C for 2 h (haze value was $76 \pm 4\%$).

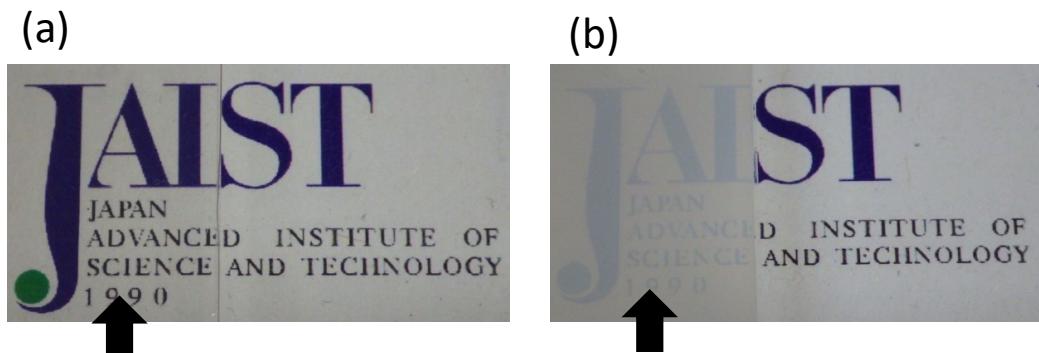


Figure 6. Optical photographs of PLA films with 250 μm thickness.

(a) Before annealing (quenched film) and (b) after annealing at 100 $^{\circ}\text{C}$ for 2 h.

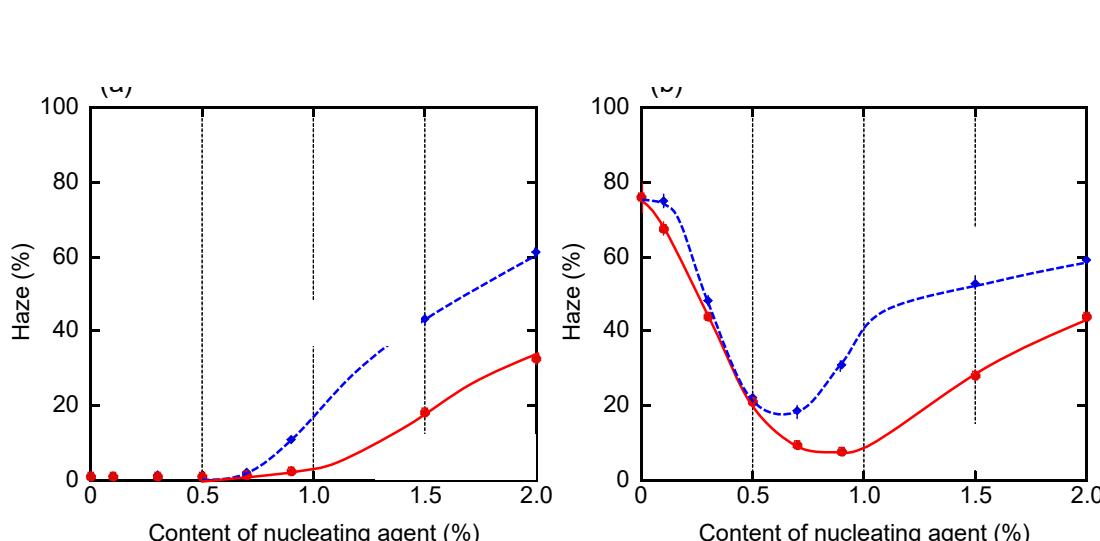


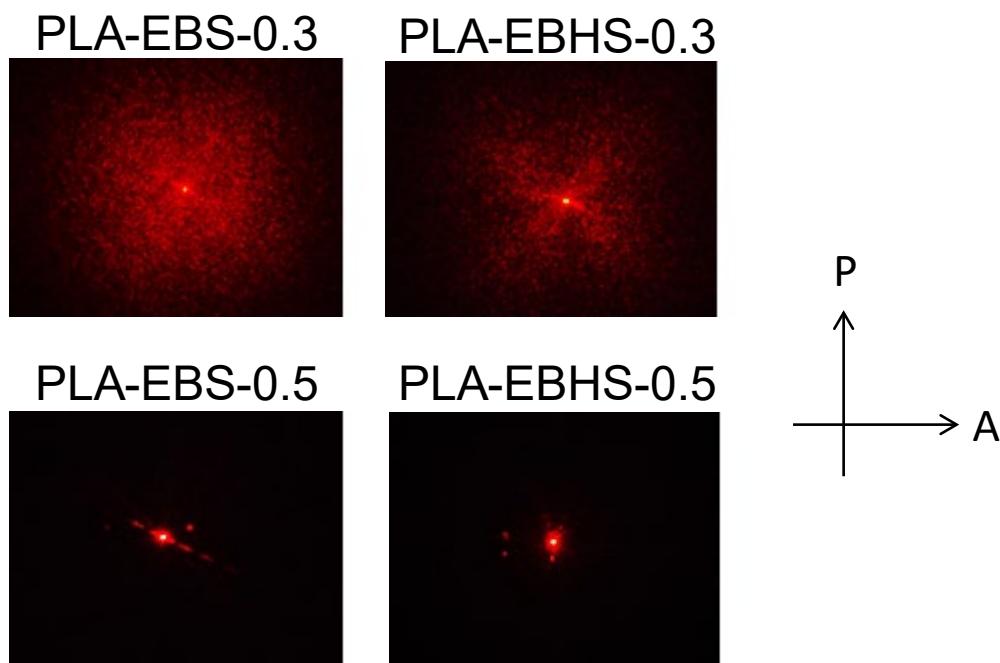
Figure 7. Transparencies of PLA films containing (circles) EBHS and (diamonds)

EBS. (a) Before annealing (quenched films) and (b) after annealing at 100 $^{\circ}\text{C}$ for 2 h.

The transparencies of the films containing various amounts of the nucleating agent are shown in Figure 7 with error bars. As seen in the figure, the experimental error was significantly small. Therefore, the error bar was not visible in the figure for some points. For the quenched films, the addition of large amounts of the nucleating agents caused the transparency to deteriorate, even without annealing treatment. It was confirmed that no diffraction peaks ascribed to crystals were detected by WAXD

259 measurements for all the films. Compared with the films with EBS, however, those
260 with EBHS exhibited good transparency, indicating that the species of a nucleating
261 agent affected the light scattering originating from its aggregated state in the film, as
262 shown later. It is suggested that EBHS is more uniformly dispersed than EBS in PLA.
263 After exposure to annealing at 100 °C for 2 h, the films became opaque, as shown in
264 Figure 6(b). However, it should be noted that the haze value decreased when the
265 amount of nucleating agent was less than 0.7 wt%. Furthermore, the difference
266 between the effects of EBHS and EBS was obvious when the amount of nucleating
267 agent was greater than 0.7 wt% for both quenched and annealed films.

268



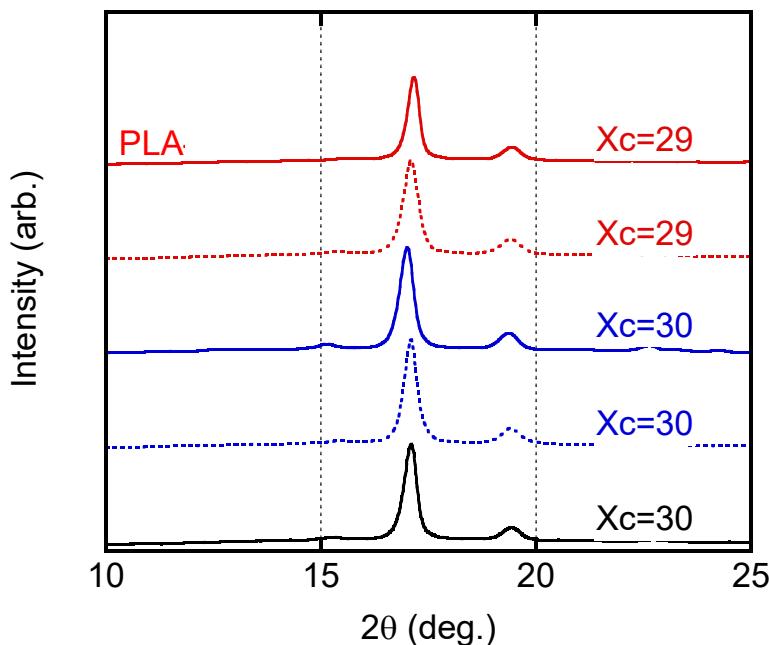
270 **Figure 8.** HV light scattering patterns of PLA films after annealing at 100 °C for 2 h.
271

272 Since light scattering was also caused by the spherulite texture, the HV light
273 scattering images of the annealed films containing the nucleating agent were observed,

274 and are shown in Figure 8. The films with 0.3 wt% of the nucleating agent showed
275 four-leaves patterns, with intense light scattering of the film with EBS. In contrast, the
276 films with 0.5 wt% of the nucleating agent showed almost no light scattering, without
277 four-leaved patterns. The results indicated that addition of the nucleating agent
278 prevented the formation of a spherulite texture.

279 The WAXD profiles for some annealed films with their degrees of crystallinity X_c
280 are exemplified in Figure 9. The measurements were performed three times for each
281 sample film, and we confirmed that the experimental error of the crystallinity was
282 smaller than 1 %. There was no significant difference in the crystallinity of all the
283 films after annealing, demonstrating that a transparent PLA film with a high degree of
284 crystallinity was successfully obtained by annealing a quenched film containing the
285 specific nucleating agent. The difference in transparency between the films with
286 EBHS and those with EBS can be attributed to the aggregation state of the nucleating
287 agent.

288



289

290 **Figure 9.** WAXD patterns of PLA films annealed at 100 °C for 2 h. The degree of
291 crystallinity X_c (%) is also denoted in the figure.

292

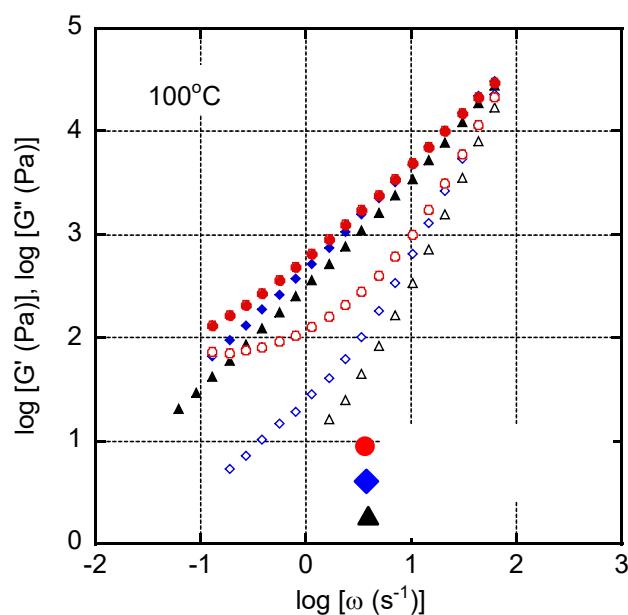
293 It is known that a nucleating agent derived from sorbitol, called a “clarifier”,
294 forms a fibrous structure in polypropylene (PP) resin and improves the transparency
295 [32-36]. When the nucleating agent shows aggregation in the resin, however, the
296 aggregates cause light scattering [33].

297 The performance of the “clarifier” is determined mainly by its nucleating ability
298 and the development of a network structure comprising nanofibrils in the resin. The
299 latter can be evaluated by viscoelastic measurements [32-35]. Therefore, we evaluated
300 the frequency dependence of the oscillatory shear modulus of the resin in the molten
301 state. In this experiment, PDLLA, i.e., an amorphous resin, was employed, to remove
302 the effect of crystals on the viscoelastic properties. The PDLLA used has a low
303 molecular weight, which enabled us to evaluate the long time, i.e., low frequency,

region without the effect of reptation of polymer chains. Since the reptation relaxation mode shifted to high frequency because of the low molecular weight, the existence of a network structure, which must appear in the low-frequency region, was easily detected.

As shown in Figure 10, PDLLA showed typical rheological properties in the terminal region, i.e., G' and G'' were proportional to ω^2 and ω , respectively. In contrast, a secondary plateau, which was much lower than the rubbery plateau modulus of PLA [5], appeared in the low-frequency region for samples containing a nucleating agent. The secondary plateau modulus for the sample with EBHS was significantly higher than that with EBS. Considering that both G' and G'' in the high frequency region, i.e., near rubbery region, were not changed greatly by the addition of the nucleating agent, at least EBHS forms a well-developed network structure in the molten resin, similarly to sorbitol derivatives in molten PP [32-35].

317



318

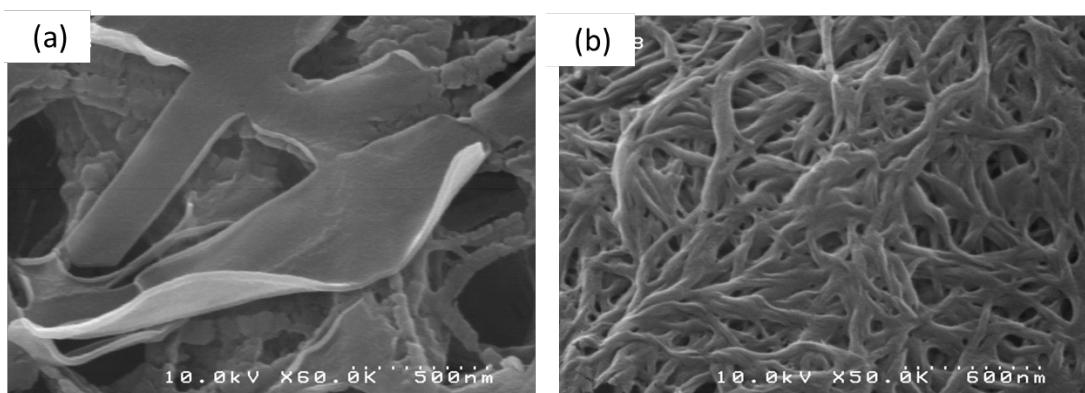
319 **Figure 10.** Angular frequency dependence of oscillatory shear moduli, namely (open

320 symbols) storage modulus G' and (closed symbols) loss modulus G'' , at 100 °C for
321 (circles) PDLLA-EBHS-0.5, (diamonds) PDLLA-EBS-0.5, and (triangles) PDLLA.

322

323 Moreover, we directly observed the nucleating agent. The PDLLA films with the
324 nucleating agent (0.5 wt%) were washed with chloroform to remove PDLLA. Then,
325 the residual material, i.e., the nucleating agent, was observed by SEM after drying.
326 The SEM images are shown in Figure 11. As seen in the figure, EBHS formed a
327 uniform network structure composed of fibers of diameter ca. 50–100 nm, i.e., smaller
328 than the wavelength of visible light. In contrast, a plate-like structure of width about
329 100–600 nm was detected for EBS. The result indicated that the size of the nucleating
330 agent aggregate is a critical factor in deciding the transparency, irrespective of the
331 annealing procedure, at least for the films containing more than 0.7 wt% of the
332 nucleating agent. The hydroxyl groups in EBHS presumably play an important role in
333 the self-organization behavior.

334



335
336 **Figure 11.** SEM images of (a) EBS and (b) EBHS.
337

338 Since the fibrous structure was well developed for EBSH, leading to a network
 339 structure, high transparency was detected even after cold crystallization. Figure 12
 340 shows the PLA film containing 0.9 wt% of EBHS, i.e., the most transparent film after
 341 annealing (haze value was $7.9\% \pm 0.8\%$). A comparison with Figure 6(b) shows that
 342 the transparency was significantly improved.

343

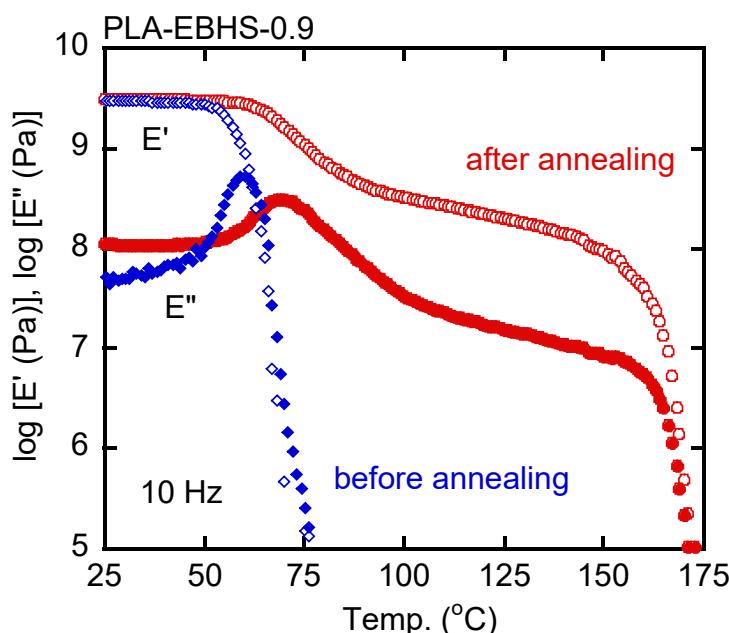


344



345 **Figure 12.** Optical photograph of PLA-EBHS-0.9 film after annealing at 100 °C for 2
 346 h. The film thickness is 250 μm .

347



348

349 **Figure 13.** Temperature dependence of (open symbols) tensile storage modulus E'
350 and (closed symbols) loss modulus E'' for PLA-EBHS-0.9 (diamonds) without and
351 (circles) with annealing treatment at 100 °C for 2 h.

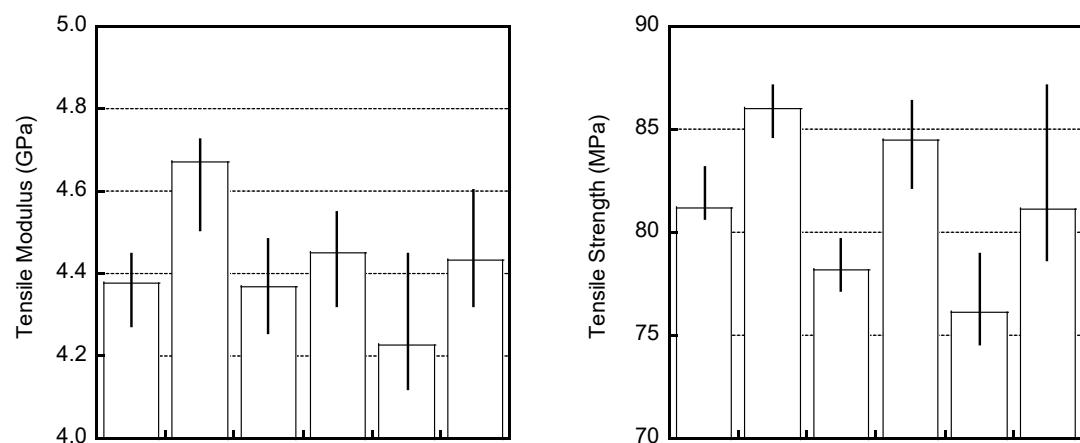
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353 Figure 13 shows the temperature dependence of the dynamic tensile moduli, i.e.,
354 storage modulus E' and loss modulus E'' , for films of PLA-EBHS-0.9. As seen in the
355 figure, the film without the annealing procedure showed an abrupt drop in its modulus
356 at T_g , i.e., at around 60 °C. Since the film can be deformed easily near T_g , the service
357 temperature was lower than 60 °C. This is a typical phenomenon for quenched PLA
358 films. After exposure to annealing, however, the modulus decreased gradually and fell
359 off at around the melting point. The temperatures to show $E' = 100$ MPa, which can be
360 used as a measure of the heat resistance, were as follows; 65 °C for the pure PLA film
361 and 144 °C for the film of PLA-EBHS-0.9. The result indicates that the heat
362 resistance was greatly improved by the addition of the nucleating agent.

363 The peak area of E'' ascribed to the glass-to-rubber transition was reduced with
364 the decrease in the amorphous region, i.e., an increase in the crystallinity. The peak
365 temperature was shifted to a high temperature. This is reasonable because the increase
366 in the crystallinity restricts the motion of amorphous chains, leading to a high T_g .
367 After annealing, the dynamic mechanical properties were similar to those of PP, which
368 is known to be a plastic with high heat resistance. Considering that PP is fairly
369 transparent, the annealed PLA film containing EBSH is a good candidate for use as a
370 substitute for PP.

371 The tensile test was performed to clarify the mechanical properties at room
 372 temperature. It was found that all samples exhibited brittle fracture prior to the
 373 yielding point, which is usually detected for pure PLA. The initial tensile modulus and
 374 tensile strength, i.e., stress at the break point, are summarized in Figure 14 with error
 375 bars. After the annealing treatment, both modulus and strength increase slightly,
 376 which must be ascribed to the enhanced crystallinity.

377



378

379 **Figure 14.** Tensile properties such as (a) tensile modulus and (b) tensile strength for
 380 PLA, PLA-EBS-05, and PLA-EBHS-0.5 with (A) or without (NA) annealing
 381 treatment at 100 °C for 2 h.

382

383 This technique, i.e., exposure to annealing for quenched PLA films containing the
 384 specific nucleating agent, is suitable for T-die extrusion with equipment consisting of
 385 annealing rollers and/or annealing baths after passing through the chill rolls. Since the
 386 heat resistance is improved greatly without losing transparency, the products will be
 387 preferentially employed in various applications, including packaging containers.

388

389 **Conclusion**

390 The structures and properties of PLA films containing a specific nucleating agent
391 were studied, considering the optical transparency and the degree of crystallinity as
392 measures of the heat resistance. In particular, the role of annealing beyond T_g was
393 evaluated using quenched films. The PLA film obtained by a quenching process
394 showed good transparency but no crystallinity. Therefore, the service temperature was
395 lower than 60 °C, i.e., T_g . After exposure to annealing at 100 °C for 2 h, the
396 crystallinity was enhanced (ca. 30%). Therefore, the films exhibited excellent heat
397 resistance, although the PLA films lost their transparency. The films containing
398 appropriate amounts of the specific nucleating agent, especially EBHS, however,
399 showed good transparency even after the annealing procedure. The haze values of the
400 films containing 0.7–0.9 wt% of EBHS were lower than 10%, even though the
401 crystallinity was the same as that of the annealed PLA, i.e., good heat resistance. SEM
402 observations of the nucleating agent in the resin and the viscoelastic measurements in
403 the molten state revealed that EBHS exists as fibers of diameter 50–100 nm and forms
404 a network structure. Crystallization on the fibrils of the network reduces the size of
405 the PLA crystals and prevents the growth of a spherulite texture. As a result, a
406 transparent film with high heat resistance is obtained.

407

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