

Title	Modifying the thermal and mechanical properties of poly(lactic acid) by adding lithium trifluoromethanesulfonate
Author(s)	Tomie, Shota; Tsugawa, Naoya; Yamaguchi, Masayuki
Citation	Journal of Polymer Research, 25(9): Article:206
Issue Date	2018-08-27
Type	Journal Article
Text version	author
URL	http://hdl.handle.net/10119/16125
Rights	This is the author-created version of Springer, Shota Tomie, Naoya Tsugawa, and Masayuki Yamaguchi, Journal of Polymer Research, 25(9), 2018, Article:206. The original publication is available at www.springerlink.com , http://dx.doi.org/10.1007/s10965-018-1605-4
Description	

**Modifying the thermal and mechanical properties of
poly(lactic acid) by adding lithium
trifluoromethanesulfonate**

Shota Tomie¹⁾, Naoya Tsugawa^{1,2)}, and Masayuki Yamaguchi^{1)*}

1) School of Materials Science, Japan Advanced Institute of Science and Technology
1-1 Asahidai, Nomi, Ishikawa 923-1292 JAPAN

2) TOSOH Analysis and Research Center Co.,
1-8 Kasumi, Yokkaichi, Mie 510-8540 JAPAN

*Corresponding author. E-mail address: m_yama@jaist.ac.jp (Masayuki Yamaguchi)
Phone: +81-761-51-1621
Fax: +81-761-51-1149

1 ABSTRACT

2 The effect of the addition of lithium trifluoromethanesulfonate (LiCF_3SO_3) on the
3 linear viscoelastic properties, crystallization behavior, and mechanical properties of
4 poly(lactic acid) (PLA) was studied. The glass transition temperature (T_g) was enhanced
5 by adding LiCF_3SO_3 , without any loss of transparency of the PLA. This was attributed
6 to the ion-dipole interaction between the lithium cation and oxygen atom in the PLA
7 carbonyl group. The interaction weakened at higher temperature. Consequently, the
8 rheological terminal region was clearly detected, which suggested that the system
9 possessed good melt-processability. The Young's modulus and yield stress at room
10 temperature were also enhanced by the addition of LiCF_3SO_3 , although the toughness
11 was reduced due to the brittle failure. Finally, the presence of LiCF_3SO_3 retarded the
12 crystallization of PLA, because the segmental motion of the PLA chains was reduced.

13

14 **Keywords;** Poly(lactic acid); Rheology; Crystallization; Glass transition temperature

15

16 Introduction

17 Poly(lactic acid) (PLA) is a well-known biomass-based plastic. It has various
18 attractive properties, such as carbon neutrality, biocompatibility, biodegradability,
19 optical transparency, and good processability [1-5]. Therefore, PLA and its
20 blends/composites have been studied greatly and used in many applications including
21 packaging and housing of electronic products [6-8]. However, its application is still
22 limited by its poor heat resistance [1-5,9], because the glass transition temperature (T_g)
23 of PLA is around 60 °C. A well-known method for enhancing the heat resistance is to
24 increase the crystallinity [1-5]. PLA containing a large amount of crystals exhibits
25 similar dynamic mechanical properties to isotactic polypropylene in the solid state [10].
26 Much effort has therefore focused on enhancing the crystallization rate of PLA. The
27 addition of nanofillers was proposed for this purpose [11,12], and is now utilized in
28 industry. Addition of nucleating agents [13-15] and/or plasticizers [16-18] can also
29 enhance the crystallization rate. However, high crystallinity usually results in opaque
30 materials owing to light scattering. There is a strong demand for a new technology to
31 prepare transparent PLA products with good heat resistance.

32 Increasing the molecular weight and introducing crosslinking points will generally
33 enhance the T_g of polymers [19,20] including PLA [21-23]. However, these techniques
34 also tend to result in PLA losing its good melt-processability, and thus are not
35 recommended. In the case of ionomers that have a carboxylic acid group in the polymer
36 chain, the ion-dipole interaction acts as a crosslink point which enhances the T_g [24-26].
37 Increasing the temperature leads to this interaction weakening, which in turn leads to
38 thermoplastic properties. This strategy for material design can be used to improve the

39 heat resistance of PLA. The enhancement of the T_g of poly(methyl methacrylate)
40 (PMMA) by adding a specific lithium salt was reported recently, despite PMMA
41 containing no acidic or hydroxyl groups in its main chain [27]. In this system, segmental
42 motion was reduced by the ion–dipole interaction between the lithium cation and
43 PMMA carboxyl group, at temperatures around the T_g . Furthermore, the interaction
44 decreased at high temperature [27]. Although such interaction is expected in various
45 polar polymers, there have been a couple of reports only on PMMA [28,29]. Moreover,
46 the effect of the ion-dipole interaction on crystallinity has not been clarified yet in our
47 previous reports.

48 In the current study, we added lithium trifluoromethanesulfonate (LiCF_3SO_3) into
49 PLA, i.e., one of the most important polyesters and biomass-based materials, to reduce
50 the segmental motion by exploiting the ion-dipole interaction. The rheological
51 properties in the molten state, crystallization behavior, and tensile properties in the solid
52 state were investigated for the resulting blends. The reduced segmental motion of PLA
53 due to the interaction with the salt affected the viscoelastic properties and thermal
54 properties including the crystallization behavior. Although the LiCF_3SO_3 addition loses
55 the cost-performance, these findings must provide basic information pertinent to
56 designing various polar polymers including biomass-based plastics.

57

58 **Experimental**

59 **Materials**

60 Two types of commercially available PLA were used. One was crystalline PLA

61 (cPLA) containing 1% D-lactide. The other was amorphous PLA (aPLA) containing 12%
62 D-lactide. The number-average molecular weight (M_n) and weight-average molecular
63 weight (M_w), as evaluated by gel permeation chromatography (HLC-8020, Tosoh, Japan)
64 using TSK-GEL GMHXL as a polystyrene standard, were $M_n = 9.8 \times 10^4$ and $M_w =$
65 1.7×10^5 for cPLA and $M_n = 1.0 \times 10^5$ and $M_w = 1.7 \times 10^5$ for aPLA. Details of the PLA
66 samples are described in our previous papers [30,31]. LiCF_3SO_3 was purchased from
67 Kanto Chemical and was used without further purification.

68

69

Sample preparation

70 Prior to melt-mixing, PLA pellets were dried at 80 °C for 4 h under vacuum. PLA
71 and LiCF_3SO_3 were mixed in a molten state using an internal mixer (Labo Plastmill,
72 Toyo Seiki, Japan) for 5 min, with a blade rotation speed of 30 rpm. Mixing was
73 performed at 180 °C for aPLA and at 200 °C for cPLA. The concentrations of LiCF_3SO_3
74 were 0, 5, 10, and 20 wt.%. The obtained mixtures were dried at 160 °C for 4 h under
75 vacuum, and then compressed into flat films 300 μm in thickness by a compression-
76 molding machine at 200 °C under 30 MPa for 90 sec. The resulting films were cooled
77 at 25 °C for 3 min. The films were then used immediately to avoid the effects of
78 moisture, since it is known that the moisture may affect the T_g greatly [32].

79

80

Measurements

81 The temperature dependence of dynamic tensile moduli was measured from 25 °C
82 to 200 °C using a dynamic mechanical analyzer (Rheogel E-4000, UBM, Japan). The

83 frequency and heating rate were 10 Hz and 2 °C/min, respectively.

84 The frequency dependence of the oscillatory shear modulus was measured using a
85 cone-and-plate rheometer (AR2000ex, TA Instruments, USA) at various temperatures
86 from 90 °C to 180 °C, under a nitrogen atmosphere.

87 The thermal properties were evaluated using a differential scanning calorimeter
88 (DSC) (DSC 8500, PerkinElmer). The samples were heated from 25 °C to 190 °C at a
89 heating rate of 10 °C/min, and then cooled from 190 °C to 25 °C at a cooling rate of
90 2 °C/min. Analyses were carried out on approximately 10-mg samples encapsulated in
91 aluminum pans.

92 Infrared spectra were collected using a Fourier-transform infrared (FT-IR)
93 analyzer (Spectrum 100, PerkinElmer, USA) at room temperature. The measurements
94 were performed in the attenuated total reflection (ATR) mode using KRS-5 as an ATR
95 crystal.

96 Tensile tests were performed using a uniaxial tensile machine (LSC-50/300, Tokyo
97 Testing Machine, Japan). Dumbbell-shaped specimens with an initial gage length of 10
98 mm were used for tensile tests. Specimens were cut from the sample films using a
99 dumbbell cutter (SDL-200; Dumbbell, Japan). One of the cross-heads of the uniaxial
100 tensile machine moved at a stretching speed of 10 mm/min; *i.e.*, an initial strain rate of
101 0.017 s^{-1} . The average value of 10 measurements was calculated for each sample.

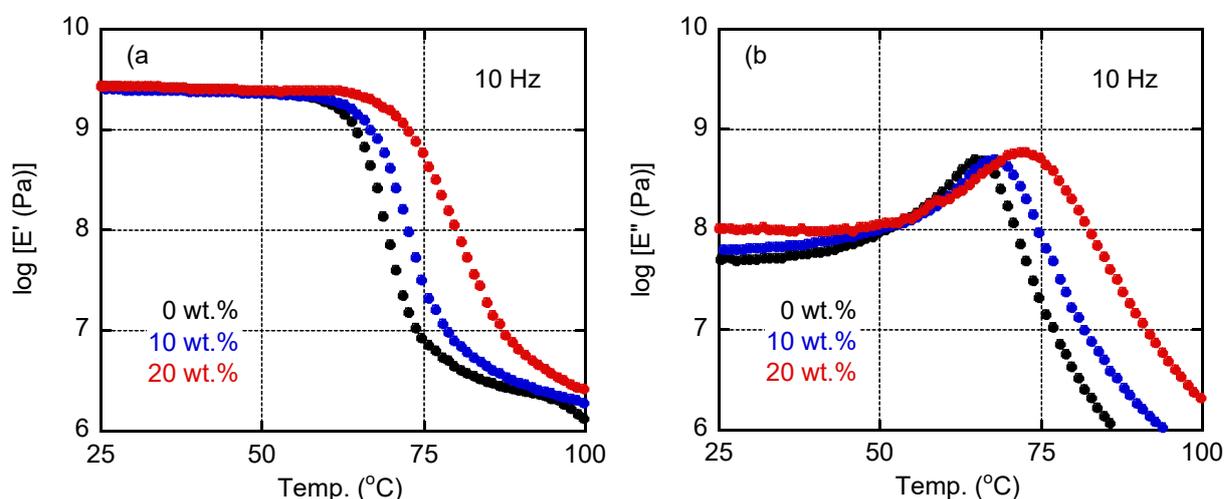
102

103 **Results and discussion**

104 The temperature dependence of dynamic tensile moduli such as the storage

105 modulus (E') and loss modulus (E'') for aPLA containing LiCF_3SO_3 is shown in Figure
106 1. The profiles in Figure 1 are typical of the dynamic mechanical properties for
107 amorphous polymers. The glassy and transition regions are clearly detected with the
108 end of the rubbery region. The storage modulus in the glassy region is around 2 GPa
109 for pure PLA, which is not affected by the LiCF_3SO_3 addition. Around at T_g , the E'
110 drops off sharply, whereas the E'' shows a sharp peak. It is apparent that adding
111 LiCF_3SO_3 greatly enhances the T_g . The peak temperature of the E'' , i.e., the T_g , is
112 located at 65 °C for pure aPLA, 68 °C for aPLA with 10 wt.% LiCF_3SO_3 , and 72 °C for
113 aPLA with 20 wt.% LiCF_3SO_3 . The width of the E'' peak becomes slightly broad, and
114 therefore the E' gradually decreases, especially in the high temperature region. This
115 suggests that the relaxation time distribution also becomes broad.

116

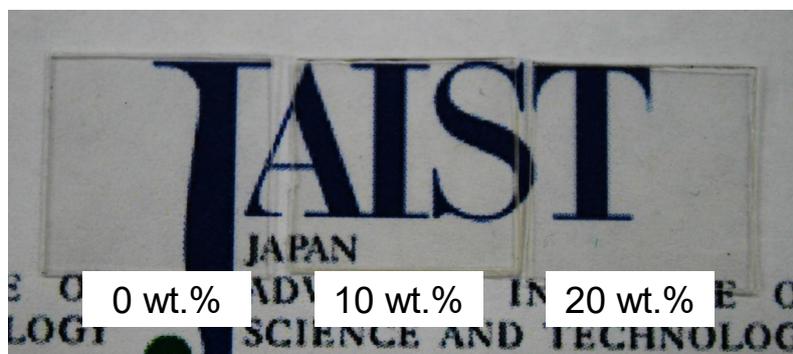


117 **Fig. 1** Temperature dependence of dynamic tensile moduli such as the (a) storage
118 modulus (E') and (b) loss modulus (E'') at 10 Hz for (black) aPLA, (blue)
119 aPLA/ LiCF_3SO_3 (90/10), and (red) aPLA/ LiCF_3SO_3 (80/20).

120

121 Photographs of the samples are shown in Figure 2. It is found that adding
122 LiCF_3SO_3 improves the heat resistance of aPLA, without loss of optical transparency.

123



124

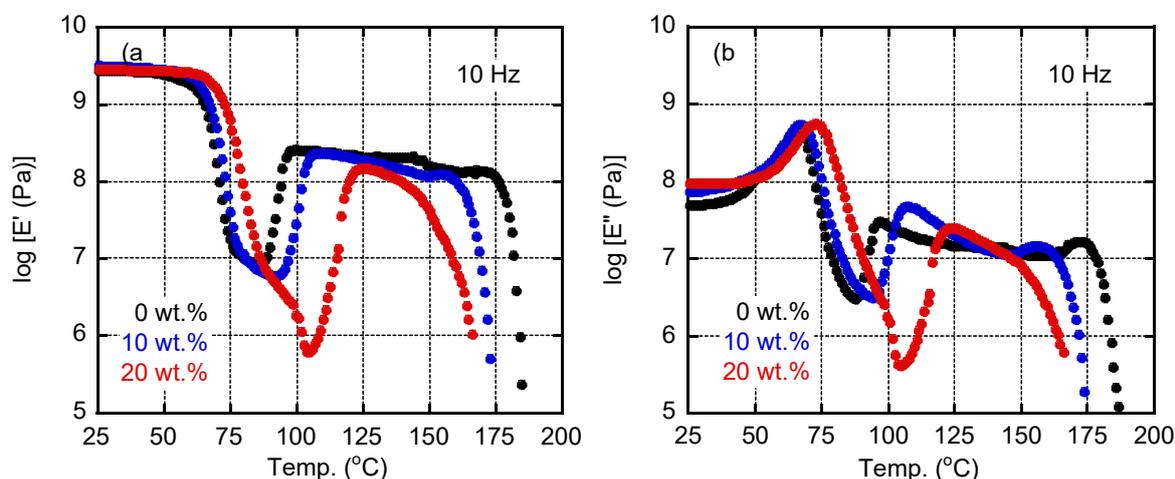
125 **Fig. 2** Photograph of 300- μm -thick films of (left) aPLA, (center) aPLA/ LiCF_3SO_3
126 (90/10), and (right) aPLA/ LiCF_3SO_3 (80/20).

127

128 Figure 3 shows the dynamic mechanical properties for cPLA containing LiCF_3SO_3 .
129 For pure cPLA, the storage modulus significantly decreases at around 60 °C because of
130 the glass-to-rubber transition, and then increases again at above 85 °C. This is attributed
131 to cold-crystallization, which is often observed for crystalline PLA products obtained
132 by rapid cooling [18]. Specifically, the sample preparation conditions employed in this
133 study, i.e., cooling at 25 °C in a compression-molding machine, are quenching
134 conditions which do not allow cPLA to become sufficiently crystallized. Cold-
135 crystallization occurs at high temperatures for the samples containing LiCF_3SO_3 ,
136 because the addition of LiCF_3SO_3 enhances the T_g . The modulus finally decreases at
137 170 °C, which corresponds to the melting point. The melting point decreases with
138 increasing LiCF_3SO_3 content. This result suggests that the size of the PLA crystallites
139 generated during the measurement decreases with increasing LiCF_3SO_3 content. Cold-

140 crystallization occurs at high temperature because of the reduced segmental motion, so
 141 the crystallites cannot grow as much in samples containing LiCF_3SO_3 .

142

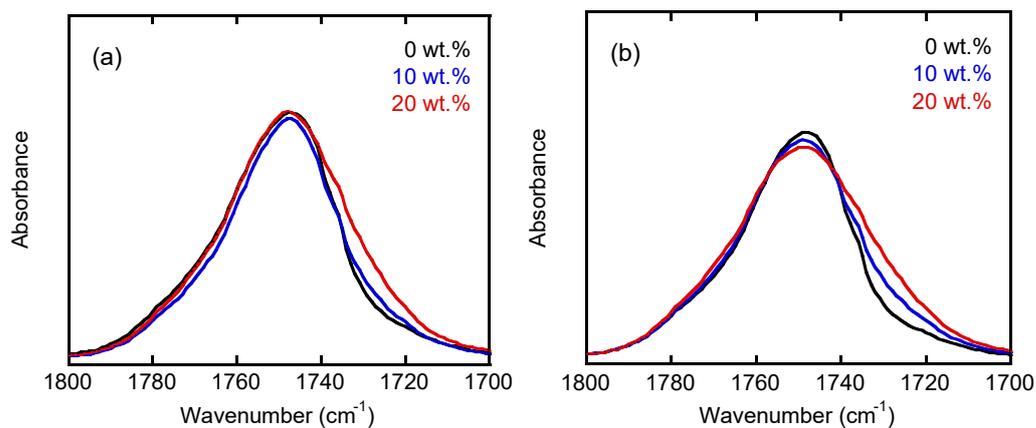


143 **Fig. 3** Temperature dependence of dynamic tensile moduli such as the (a) storage
 144 modulus (E') and (b) loss modulus (E'') at 10 Hz for (black) cPLA, (blue)
 145 cPLA/ LiCF_3SO_3 (90/10), and (red) cPLA/ LiCF_3SO_3 (80/20).

146

147 The effect of the addition of LiCF_3SO_3 on the FT-IR spectra of the blends,
 148 particularly on the carbonyl symmetric stretching region, is shown in Figure 4. It is well
 149 known that strong electrostatic interaction with oxygen atoms in carbonyl groups
 150 provides the shoulder in the low wavenumber region as demonstrated in the blends of
 151 PMMA and LiCF_3SO_3 [27]. The peak broadens in the low wavenumber region upon the
 152 addition of LiCF_3SO_3 , irrespective of the type of PLA (i.e., aPLA and cPLA). This
 153 suggests an ion-dipole interaction between the lithium cations dissociated in PLA and
 154 carbonyl groups. This interaction leads to reduced segmental motion, and is responsible
 155 for the T_g enhancement and retarded cold-crystallization behavior.

156



157

158 **Fig. 4** FT-IR spectra for (a) aPLA/LiCF₃SO₃ and (b) cPLA/LiCF₃SO₃.

159

160 Master curves for the frequency dependence of oscillatory shear moduli are shown

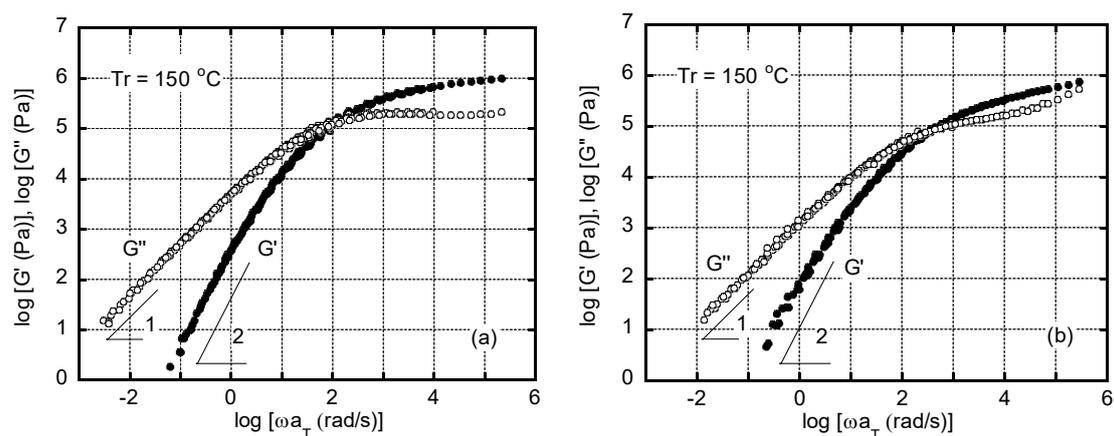
161 in Figure 5. The measurements were performed for the aPLA system, to avoid the

162 effects of crystallization. As seen in the figure, the time-temperature superposition

163 principle is applicable to pure aPLA and aPLA containing LiCF₃SO₃, in the temperature

164 range of 90–180 °C.

165



166 **Fig. 5** Master curves of frequency dependence of oscillatory shear moduli at the

167 reference temperature of 150 °C for (a) aPLA and (b) aPLA/LiCF₃SO₃ (80/20).

168

169 There is an obvious difference between the samples in the high frequency region.
 170 The gap between the storage modulus G' and the loss modulus G'' at high frequencies
 171 is large for pure aPLA, indicating that the sample is in a rubbery region even at 10^5 s^{-1} .
 172 In contrast, G'' is almost equal to G' at high frequencies (10^5 – 10^6 s^{-1}) for the
 173 aPLA/LiCF₃SO₃ (80/20) blend, suggesting the transition region. This is due to the glass-
 174 to-rubber transition occurring at high temperature, i.e., at low frequency. The lowest
 175 frequency of the rubbery region shifts to high frequency upon the addition of LiCF₃SO₃;
 176 therefore, the rubbery region of the blend is narrower. In the low frequency region, the
 177 flow (terminal) region is clearly detected as reported for conventional PLA samples
 178 [33]. Since the slopes of G' and G'' are 2 and 1, respectively, the rheological terminal
 179 parameters such as the zero-shear viscosity (η_0), steady-state compliance (J_e^0), and
 180 weight-average relaxation time (τ_w), can be calculated from the following equations:

$$181 \quad \eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (1)$$

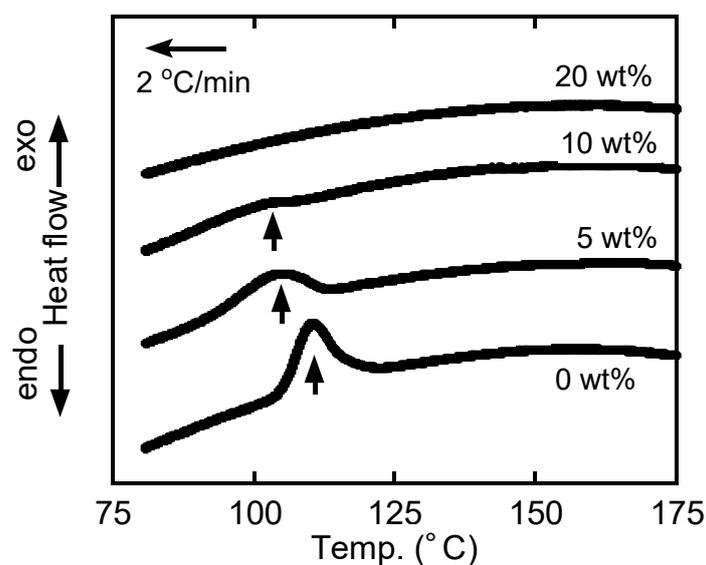
$$182 \quad J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{G''^2} \quad (2)$$

$$183 \quad \tau_w = \eta_0 J_e^0 \quad (3)$$

184 The values calculated at the reference temperature 150 °C are $\eta_0 = 5.3 \times 10^3 \text{ (Pa s)}$,
 185 $J_e^0 = 1.4 \times 10^{-5} \text{ (Pa}^{-1}\text{)}$, and $\tau_w = 7.5 \times 10^{-2} \text{ (s)}$ for aPLA, and $\eta_0 = 1.1 \times 10^3 \text{ (Pa s)}$, $J_e^0 =$
 186 $6.0 \times 10^{-5} \text{ (Pa}^{-1}\text{)}$, and $\tau_w = 7.6 \times 10^{-2} \text{ (s)}$ for aPLA/LiCF₃SO₃ (80/20). The τ_w is almost the
 187 same for both samples, although the blend shows a lower η_0 . Since the blend shows a
 188 higher J_e^0 , it has a broad distribution of the relaxation time. The ion-dipole interaction
 189 presumably affects the relaxation time distribution.

190 The ion-dipole interaction also affects the crystallization behavior of cPLA, as
191 indicated in Figure 3. DSC cooling curves for cPLA/LiCF₃SO₃ blends at a cooling rate
192 of 2 °C/min are shown in Figure 6. The exothermic peak ascribed to the crystallization
193 is detected at 112 °C for pure cPLA, which is consistent with results from a previous
194 study [10]. The peak shifts to lower temperature upon the addition of 5 wt.% LiCF₃SO₃,
195 and becomes very weak in the curve for cPLA/LiCF₃SO₃ (90/10). These results
196 demonstrate that adding LiCF₃SO₃ retards the crystallization growth for cPLA. This is
197 attributed to the reduced segmental motion of PLA chains by the ion-dipole interaction.
198 Finally, no peak is detected upon the addition of 20 wt.% LiCF₃SO₃, despite the slow
199 cooling rate. In other words, 20 wt.% of LiCF₃SO₃ is good enough to provide the “anti-
200 crystallization” property for cPLA, leading to a transparent product without scattering
201 entities originated from crystalline structure.

202



203

204 **Fig. 6** DSC cooling curves at a cooling rate of 2 °C/min, for cPLA/LiCF₃SO₃ with

205

different compositions.

206

207 Furthermore, these results suggest that the blends with LiCF_3SO_3 may be utilized
208 for transparent applications with improved heat resistance due to the T_g enhancement
209 even using PLA samples with a low concentration of L-lactide.

210 The mechanical properties in the solid state were evaluated by tensile testing using
211 aPLA/ LiCF_3SO_3 blends. Stress-strain curves for aPLA/ LiCF_3SO_3 are shown in Figure
212 7. Both stress and strain are engineering values. As summarized in Table 1, adding
213 LiCF_3SO_3 greatly enhances the Young's modulus and yield stress. The results indicate
214 that the rigidity is effectively enhanced by the ion-dipole interaction. In contrast, the
215 blends exhibit brittle behavior, which leads to the decrease in the mechanical toughness.
216 This problem will be severe as increasing the LiCF_3SO_3 content. Presumably, the
217 applied stress of the blends is beyond the critical one of crazing, or the critical stress
218 for shear yielding increases upon the addition of LiCF_3SO_3 . Moreover, the decrease in
219 the density of the entanglement couplings by the LiCF_3SO_3 addition, which is believed
220 to provide brittle fracture, plays an important role. In either mechanism, another
221 technique will be required to improve the mechanical toughness of the blends with
222 LiCF_3SO_3 . The addition of rubbery materials, one of the most well-known methods,
223 and the appropriate annealing treatment to reduce the critical stress for shear yielding,
224 which leads to ductile behavior as reported recently [30,31], are highly recommended.

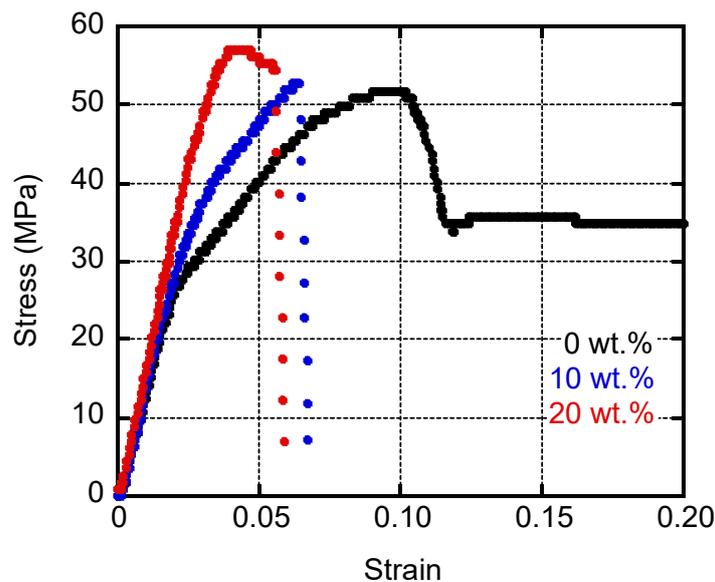


Fig. 7 Stress-strain curves for aPLA/LiCF₃SO₃ with different compositions.

Table 1 Tensile properties of aPLA/LiCF₃SO₃ blends

LiCF ₃ SO ₃ content (wt.%)	Young's Modulus (GPa)	Yield Stress (MPa)	Elongation at Break (%)
0	1.50	51.7	340
10	1.68	52.8	6
20	1.79	57.1	6

Conclusion

The structures and properties of PLA/LiCF₃SO₃ blends were studied. Adding LiCF₃SO₃ restricts the segmental motion of the PLA chains. This is attributed to the ion-dipole interaction, which is pronounced at around the T_g . As a result, the T_g is enhanced for both aPLA and cPLA, without loss of transparency. The Young's modulus and yield stress of aPLA are also enhanced by adding LiCF₃SO₃ with the reduced mechanical toughness due to brittle fracture. The restricted segmental motion greatly decreases the crystallization rate. Consequently, the crystallization peak is not detected

238 for cPLA/LiCF₃SO₃ (80/20), even at a slow cooling rate of 2 °C/min. Cold-
239 crystallization, which is detected by dynamic mechanical analysis, occurs at higher
240 temperature upon the addition of LiCF₃SO₃ because of the T_g enhancement with the
241 restricted segmental motion. The ion-dipole interaction becomes weak at high
242 temperature. Therefore, the rheological terminal region is clearly detected. This
243 suggests that adding LiCF₃SO₃ does not significantly affect the melt-processability,
244 although it broadens the distribution of the terminal relaxation mode. Considering that
245 the ion-dipole interaction between the carbonyl group and lithium cation is responsible
246 for the phenomenon, a similar result is expected for various polyester materials.

247

248 **ACKNOWLEDGEMENTS**

249 A part of this work was supported by JSPS Grant-in-Aid for Scientific Research (B)
250 Grant Number 16H04201.

251

252 **Reference**

- 253 [1] Auras R, Lim LT, Selke SEM, Tsuji H (2010) Poly(lactic acid): synthesis, structures,
254 properties, processing, and applications, Wiley, Hoboken.
- 255 [2] Saeidlou S, Huneault MA, Li H, Park CB (2012) Poly(lactic acid) crystallization.
256 Prog Polym Sci 37:1657-1677.
- 257 [3] Jimenez J, Peltzer M, Ruseckaite R (2014) Poly(lactic Acid) science and technology:
258 Processing, properties, additives, and applications. Royal Society of Chemistry,
259 Oxfordshire.
- 260 [4] Yamaguchi M (2016) Manufacturing of high performance biomass-based polyesters
261 by rheological approach. in: V.K. Thakur, M.K. Thakur (Eds.), Handbook of
262 composite from renewable materials. Wiley, New York, Chap. 2.
- 263 [5] Lorenzo MRD, Androsch R (2018) Synthesis, structure and properties of poly(lactic

-
- 264 acid). Springer.
- 265 [6] Dubey SP, Thakur VK, Krishnaswamy S, Abhyankar HA, Marchante V, Brighton
266 JL (2017) Progress in environmental-friendly polymer nanocomposite material
267 from PLA: Synthesis, processing and applications. *Vacuum* 146:655-663.
- 268 [7] Krepsztul JW, Rydzkowski T, Borowski G, Szczypinski M, Klepka T, Thakur VK
269 (2018) Recent progress in biodegradable polymers and nanocomposite-based
270 packaging materials for sustainable environment. *Int J Polym Anal Charact* 23:383-
271 395.
- 272 [8] Madhumitha G, Fowsiya J, Roopan SM, Thakur VK (2018) Recent advances in
273 starch–clay nanocomposites. *Int J Polym Anal Charact* 23:331-345.
- 274 [9] Dorgan J, Lehermeir H, Mang M (2000) Thermal and rheological properties of
275 commercial grade poly(lactic acid)s. *J Polym Environ* 8:1-9.
- 276 [10] Huang T, Miura M, Nobukawa S, Yamaguchi M (2014) Crystallization behavior
277 and dynamic mechanical properties of poly(L-lactic acid) with poly(ethylene
278 glycol) terminated by benzoate. *J Polym Environment* 22:183-189.
- 279 [11] Ray SS, Okamoto M (2003) Polymer/layered silicate nanocomposites: a review
280 from preparation to processing. *Prog Polym Sci* 28:1539-1641.
- 281 [12] Nam JY, Okamoto M, Okamoto H, Nakano M, Usuki A, Matsuda M (2006)
282 Morphology and crystallization kinetics in a mixture of low-molecular weight
283 aliphatic amide and polylactide. *Polymer* 47:1340-1347.
- 284 [13] Liao R, Yang B, Yu W, Zou C (2007) Isothermal cold crystallization kinetics of
285 polylactide/nucleating agents. *J Appl Polym Sci* 104:310-317.
- 286 [14] Wu J, Zou X, Jing B, Dai W (2015) Effect of sepiolite on the crystallization
287 behavior of biodegradable poly(lactic acid) as an efficient nucleating agent.
288 *Polym Eng Sci* 55:1104-1112.
- 289 [15] Zou GX, Jiao QW, Zhang X, Zhao CX, Li JC (2015) Crystallization behavior and
290 morphology of poly(lactic acid) with a novel nucleating agent. *J Appl Polym Sci*
291 132:41367.
- 292 [16] Sheth M, Kumar RA, Dave V, Gross RA, MaCarthy SP (1997) Biodegradable
293 polymer blends of poly(lactic acid) and poly(ethylene glycol). *J Appl Polym Sci*

-
- 294 66:1495-1505.2009
- 295 [17] Okamoto K, Ichikawa T, Yokohara T, Yamaguchi M (2009) Miscibility,
296 Mechanical and Thermal Properties of Poly(lactic acid)/polyester-diol blends. *Eur*
297 *Polym J* 45:2304-2312.
- 298 [18] Hassouna F, Raquez JM, Addiego F, Dubois P, Toniazzi V, Ruch D (2011) Grafting
299 of poly (ethylene glycol) (PEG) via reactive extrusion. *Eur Polym J* 47:2134-2144.
- 300 [19] Gedde UW (1995) *Polymer Physics*, Kluwer Academic Publishers, Dordrecht.
- 301 [20] Bicerano J (2011) Glass transition, in: J. Bailey (Ed.) *Properties and behavior of*
302 *polymers*, Wiley, Hoboken.
- 303 [21] Mitomo M, Kaneda A, Quynh TM, Nagasawa N, Yoshii F (2005) Improvement of
304 heat stability of poly(L-lactic acid) by radiation-induced crosslinking. *Polymer*
305 46:4695-4703.
- 306 [22] Yang LS, Wu HZ, Yang W, Yang BM (2008) Thermal and mechanical properties
307 of chemical crosslinked polylactide (PLA). *Polym Test* 27:957-963.
- 308 [23] Rahmat M, Ghasemi I, Karrabi M, Azizi H, Zandi M, Riahinezhad M (2015) Silane
309 crosslinking of poly(lactic acid): The effect of simultaneous hydrolytic degradation.
310 *eXPRESS Polym Lett* 9:1133-1141.
- 311 [24] Eisenberg A, Kim JS (1998) *Introduction to ionomers*, Wiley, New York.
- 312 [25] Vanhoorne P, Jerome R, Teyssie P, Laupretre F (1994) Direct NMR evidence for a
313 local restriction in the segmental chain mobility of a model ionomer.
314 *Macromolecules* 27:2548-2552.
- 315 [26] Ro JA, Huang JS, Weiss AR (2008) Synthesis and thermal properties of telechelic
316 poly(lactic acid) ionomers. *Polymer* 49:422-431.
- 317 [27] Miyagawa A, Ayerdurai V, Nobukawa S, Yamaguchi M (2016) Viscoelastic
318 properties of poly(methyl methacrylate) with high glass transition temperature by
319 lithium salt addition. *J Polym Sci Polym Phys Ed* 54:2388-2394.
- 320 [28] Ito A, Phulkard P, Ayerdurai V, Soga M, Courtoux A, Miyagawa A, Yamaguchi M
321 (2018) Effects of residual solvent on glass transition temperature of poly(methyl
322 methacrylate). *Polym J* in press. DOI: 10.1038/s41428-018-0080-4.
- 323 [29] Tsugawa N, Ito A, Yamaguchi M (2018) Effect of lithium salt addition on the

-
- 324 structure and optical properties of PMMA/PVB blends. *Polymer* 146:242-248.
- 325 [30] Huang T, Miura M, Nobukawa S, Yamaguchi M (2015) Chain packing and its
326 anomalous effect on mechanical toughness for poly(lactic acid). *Biomacromol.*
327 16:1660-1666.
- 328 [31] Huang T, Yamaguchi M (2017) Effect of cooling conditions on the mechanical
329 properties of crystalline poly(lactic acid). *J Appl Polym Sci* 134:44960.
- 330 [32] Ito A, Ayerdurai V, Miyagawa A, Matsumoto A, Okada H, Courtoux A, Yamaguchi
331 M (2018) Effects of residual solvent on glass transition temperature of poly(methyl
332 methacrylate). *Nihon Reoroji Gakkaishi* 46:117-121.
- 333 [33] Yokohara T, Yamaguchi M (2008) Structure and properties for biomass-based
334 polyester blends of PLA and PBS. *Eur Polym J* 44:677-685.
- 335