**ORIGINAL ARTICLE**

# Phase structure and electrical and mechanical properties of PLLA/ionic conductive polyether blends prepared by melt mixing

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## Abstract

Poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA) is known as an ionic conductive polymer and exhibits ionic conductivity when it forms a complex with a metal salt. In this study, poly(L-lactic acid) (PLLA)/POEGMA/poly(methyl methacrylate) (PMMA) blends were manufactured to develop high-performance polymer materials that exhibit high mechanical moduli (>1 GPa) and ionic conductivities in the semiconductive region ($1.0 \times 10^{-9}$–$1.0 \times 10^{-7}$ cm$^{-1}$) at room temperature. In addition, crystallized blends were prepared by annealing the amorphous blends and were subsequently evaluated. By mixing PLLA and the compound consisting of POEGMA and PMMA using a two-roll mill, a blend with a maximum ionic conductivity of $\sim 1.1 \times 10^{-7}$ S cm$^{-1}$ was obtained. The scanning electron microscopy results indicated that the ionic conductive phases were finely dispersed within the blends. By comparing the storage modulus values of the crystallized blends to those of amorphous blends, we found that the crystallized blends were harder at approximately the glass transition temperature of PLLA.

## Introduction

Polyethers such as polyethylene oxide (PEO) dissolve alkali metal salts in the solid phase and exhibit ionic conductivity because dissociated ions can be transported by the segmental motion of the molecular chains. Such a polymer is called an ionic conductive polymer (ICP), which exhibits ionic conductivity even in the solid state. Hence, ICPs are expected to be used as new electronic materials, such as antistatic materials or electrolytes of rechargeable batteries [1–5]. Fenton et al. [6] reported that PEO forms a complex with a metal salt and exhibits an ionic conductivity of approximately $10^{-8}$ S cm$^{-1}$ at room temperature. Armand et al. [7] suggested the application of the complexes of PEO and lithium salts to solid electrolytes. However, the ionic conductivities of the complexes of PEO and alkali metal salts are comparatively low, owing to the existence of crystalline domains that hinder ionic conduction [6, 8]. Therefore, poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA), which is amorphous and can be easily polymerized by radical reactions, was used in this study. The reason POEGMA is amorphous is that it exhibits a comb-type structure with ether groups in the side chains. This structural feature of POEGMA provides a relatively high ionic conductivity [9–11].

Lithium perchlorate is often used for ICP electrolytes in consideration of applications to lithium ion secondary battery systems; however, sodium perchlorate was used in this study. Sodium perchlorate presents advantages in that it is inexpensive and easily accessible, difficult to alloy with aluminum, and less likely to absorb moisture compared to lithium salt [12].

Recently, research on electronic materials for various applications has been actively carried out. As an example, research on electrically conductive polymer composites filled with carbon particles has been conducted, and the composites have been applied industrially to antistatic materials [13]. A polymer composite filled with carbon black is a material that exhibits a high storage modulus, good stability at room temperature, and electrical conductivity in the semiconductive or conductive region.

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However, this composite presents some disadvantages such as poor transparency and filler detachment.

Therefore, in this study, we aimed to develop a material that does not suffer from such disadvantages and exhibits a high mechanical modulus (>1 GPa) and ionic conductivity in the semiconductive region $(1.0 \times 10^{-9} - 1.0 \times 10^{-7} \, \text{S cm}^{-1})$ at room temperature. To develop such a material, we manufactured novel polymer blends containing an ICP. However, ICPs have some characteristic physical properties such as a low mechanical modulus and low moisture residence that degrade their applicability as antistatic materials. To manufacture a blend with a high mechanical modulus and moisture residence, we tried mixing the ICP with a matrix polymer. To manufacture this blend, a continuous ionic conductive phase must be formed with less ICP content.

In this study, the ICP blends were prepared by the melt mixing method, which is a solvent-free process that can be performed with various molding methods such as compression and injection. However, it is known that POEGMA and the matrix polymer, which we used in this study, are immiscible due to the occurrence of phase separation. Consequently, a sea-island structure is formed when they are mixed by this method with less POEGMA, as the ionic conductivity of the blend decreases when a sea-island structure is formed. To manufacture a blend that exhibits a high ionic conductivity with as little POEGMA as possible, it is essential to form a continuous phase of POEGMA. Therefore, we prepared an ionic conductive compound (ICC) as a master batch and blended it with a matrix polymer to control the phase structure and form a continuous ionic conductive phase. The ICC was prepared by solution casting and the in situ radical polymerization [14, 15] of poly(ethylene glycol) methyl ether methacrylate (OEGMA), a monomer of POEGMA, in the presence of poly(methyl methacrylate) (PMMA) and a cross-linking agent. ICCs are composed of two phases: a hard phase formed by dissolving cross-linked POEGMA and PMMA together and an ionic conductive phase of POEGMA. When the composition of POEGMA in the ICC is large, as in this study, the ionic conductivity of the ICC is enhanced when the ionic conductive phase becomes continuous. In addition, it is known from past research that the dispersibility of ICCs during melt mixing changes depending on the composition of the ICC. Therefore, it is considered that a continuous ICC phase can be formed in the blend when these factors are appropriate.

We used poly(L-lactic acid) (PLLA) as the matrix polymer in this study. It has previously attracted attention as a biodegradable polymer [16, 17]. PLLA exhibits a reasonable molding processability and reasonable physical properties among biodegradable polymers. The features of PLLA include a high biocompatibility, high mechanical
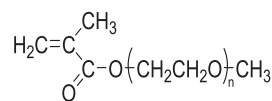


**Fig. 1** Chemical structure of OEGMA

modulus, transparency in an amorphous state, and high $T_g$ (~60 °C). In addition, it is expected to be used as a sustainable material that does not depend on petroleum resources because it can be synthesized from plant resources. Owing to these advantages, we used this polymer as the matrix polymer of the blend.

In this study, we prepared the ICP blends by mixing the ICC and PLLA using a two-roll mill and then studied the relationship between the resultant phase structures and physical properties such as electrical properties and mechanical properties.

# Materials and methods

## Materials

As a polyether, OEGMA ($M_n = 950$) was purchased from Aldrich Co., USA, and the chemical structure is illustrated in Fig. 1. As matrix polymers, PLLA ($M_w = 160,000$ Toyota Motor Co., Japan) and PMMA ($M_w = 92,600$, Mitsubishi Rayon Co., Japan) were used. As a cross-linking agent, diethylene glycol dimethacrylate (DEGDM) was purchased from Sigma-Aldrich Co., USA. As a polymerization initiator, benzophenone (BP, Kanto Chemical Co., Japan) was used as received. Sodium perchlorate ($NaClO_4$, Kanto Chemical Co., Japan) was used after drying under vacuum.

## ICC preparation

The ICCs containing OEGMA, DEGDM, and PMMA were prepared by solution casting and UV curing. OEGMA, PMMA, DEGDM, $NaClO_4$, and BP were dissolved in chloroform. The weight ratio of OEGMA + $NaClO_4$: DEGDM: PMMA was fixed at 60: y: z, wherein the weight ratios of DEGDM: PMMA were 40: 0, 30: 10, 20: 20, 10: 30, and 0 : 40, which represent ICC(60/40/0), ICC(60/30/10), ICC(60/20/20), ICC(60/10/30), and ICC(60/0/40), respectively. The $NaClO_4$ content was 5 mol% with respect to the EO unit of OEGMA. Benzophenone was added to represent 2 mol% with respect to OEGMA. This solvent mixture was cast on a Petri dish and dried at 60 °C for 24 h, and UV light (8.0 J/cm$^2$), and then, the cast film was irradiated to polymerize OEGMA at 50 °C for 1 h. After drying under vacuum at 20 °C for 24 h, the ICC was obtained. The UV curing reaction of ICCs was examined by FT-IR (Figure S1). The peaks assigned to the C=C bonds of OEGMA
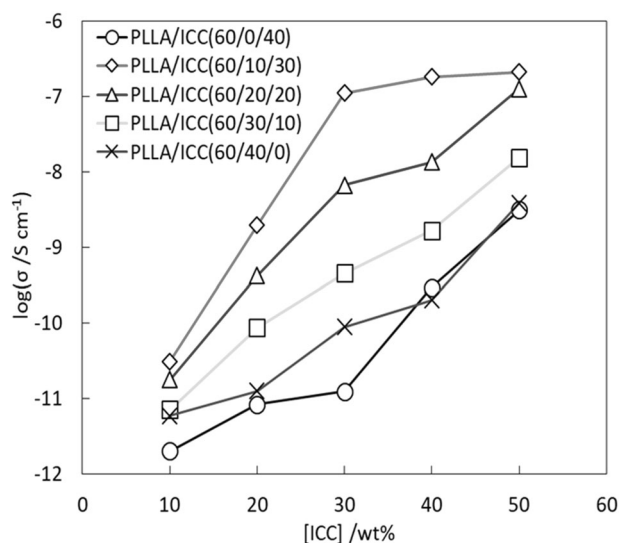
Fig. 2 Relationship between ionic conductivity at 30 °C and weight fraction of ionic conductive compound (ICC) for PLLA/ICC(60/y/z) blends
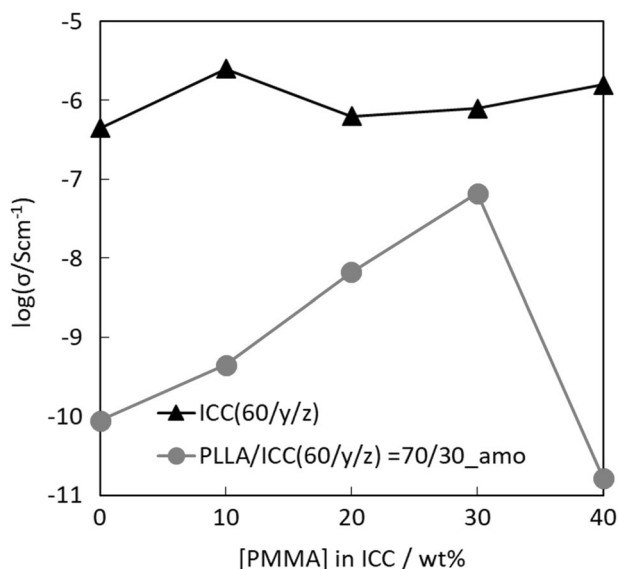


Fig. 3 Relationship between ionic conductivity at 30 °C and the weight fraction of PMMA in ICC (z) for ICC(60/y/z) and amorphous PLLA/ICC(60/y/z) = 70/30 blends

and DEGDM at 1620–1640 cm$^{-1}$ disappeared after 60 min of UV irradiation. This result verifies the successful photo-cross-linking polymerization of OEGMA/DEGDM [18, 19].

## Preparation of PLLA/ICC blend films

The ICC (4.5 g) and PLLA (10.5 g) were weighed and then mixed using a two-roll mill (Nishimura Machine Works Co., Ltd, Japan) at 190 °C. This process was performed as follows. PLLA was kneaded for 10 min, and the ICC was then added and kneaded for 5 min. To prepare the amorphous films of the blends, after preheating at 190 °C for 5 min, melt compression molding was carried out under a pressure of 20 MPa for 1 min using a hot press (Techno Supply Co., Ltd, Japan), followed by quenching with liquid nitrogen. After drying under vacuum at 20 °C for 24 h, amorphous films of the PLLA/ICC blends with a thickness of ~0.5 mm were obtained. To prepare the crystallized films of the blends, the amorphous films were heat-treated at 130 °C for 0.5, 1, 1.5, and 2 h under the atmosphere using a hot stage (FP900 Thermo System, Mettler-Toledo International Inc, USA). After water cooling and drying under vacuum at 20 °C for 3 days, crystallized PLLA/ICC films were obtained.

## Measurements

The ionic conductivity was measured by the direct current two-terminal method using an 8340A Ultra High Resistance Meter (ADC Co., Japan) in a shield box with Ar gas flow. The measurement temperature was 30 °C. A voltage of 100 V was applied to samples expected to have

relatively high ionic conductivity (ICC(60/y/z), PLLA/ICC(60/10/30) = 70/30, 60/40, and 50/50 blends); a voltage of 1000 V was applied to samples expected to have relatively low ionic conductivity (PLLA/ICC(60/y/z) = 90/10, 80/20, and PLLA/ICC(60/0/40) = 70/30 blend); and a voltage of 500 V was applied to the other samples. The phase structures of the blends were observed after gold coating using an S-4700 scanning electron microscope (SEM) (Hitachi, Ltd., Japan) operated at an accelerating voltage of 15 kV. Wide-angle X-ray diffraction (WAXD) measurements were performed using a RINT-2100 (Rigaku Co., Japan) with CuKα radiation ($\lambda = 0.15418$ nm), which was operated at 40 kV and 40 mA. The degrees of crystallinity of the blends were evaluated by WAXD measurements. Rheological measurements were performed using a DVA-200S (IT Keisoku Seigyo Co., Japan). The temperature dispersion of the complex modulus was measured over the temperature range from –60 to 200 °C at a heating rate of 5 °C/min with a strain of 0.05% and frequency of 10 Hz.

## Results and discussion

The relation between the ionic conductivity and weight fraction of the ICC in the blends is illustrated in Fig. 2. At the ICC(60/10/30) weight fraction of 30 wt.% or more, the ionic conductivity is above $1.0 \times 10^{-7}$ S cm$^{-1}$. For a high mechanical modulus and reasonable moisture residence, it is preferable that the weight fraction of the ICC is as small as possible. In addition, we fixed the weight fraction of the ICC at 30 wt.% because the ionic conductivity can be
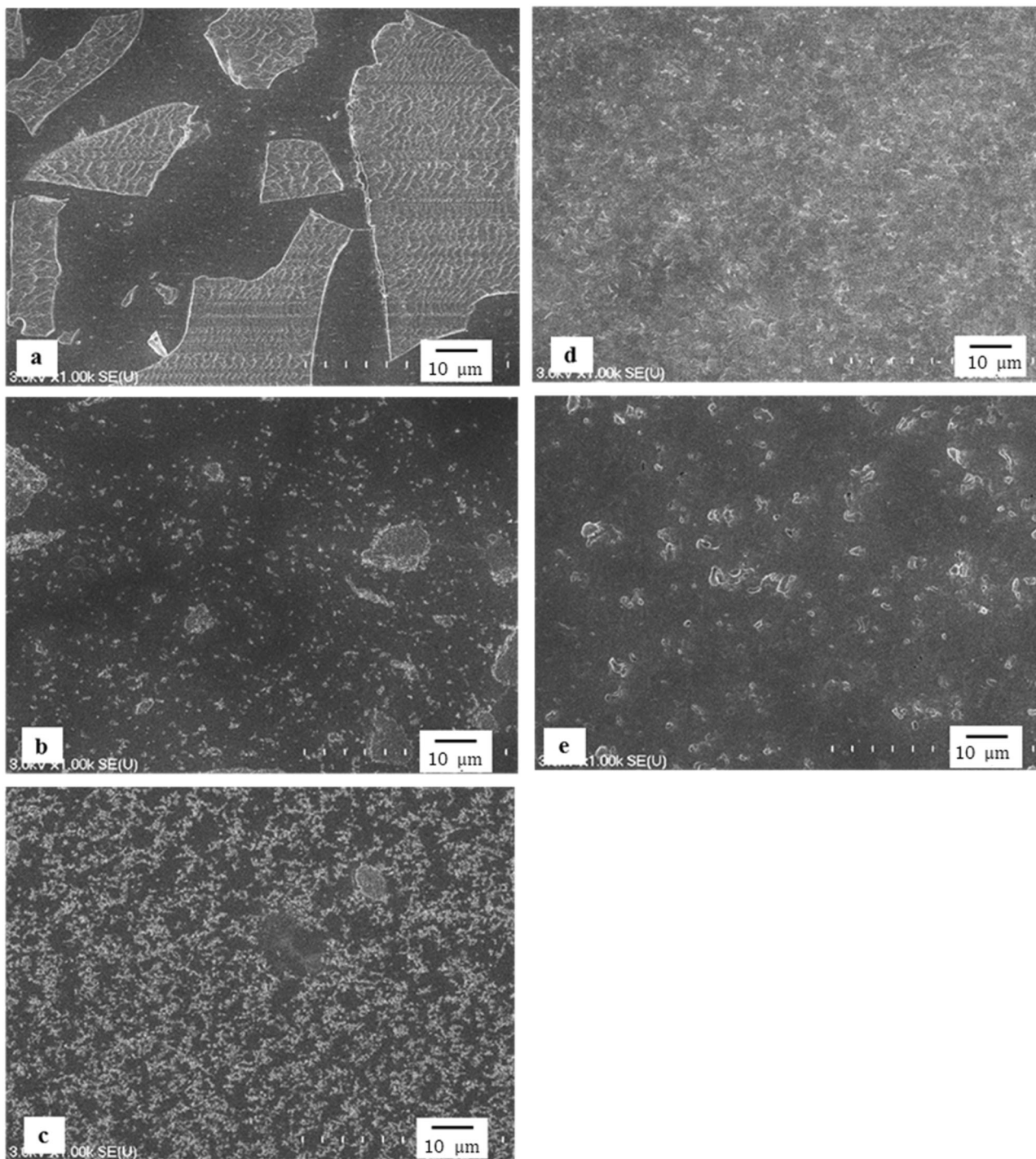
**Fig. 4** Scanning electron microscopy images of amorphous PLLA/ICC(60/$y$/$z$) = 70/30 blends. The compositions of ICC are: **a** (60/40/0), **b** (60/30/10), **c** (60/20/20), **d** (60/10/30), and **e** (60/0/40)

controlled in a wide range at this fraction by changing the composition of the ICC.

The relationship between the ionic conductivity and weight fraction of PMMA in the ICC (=$z$) for PLLA/ICC (60/$y$/$z$) = 70/30 blends is shown in Fig. 3. The maximum ionic conductivity of the blends ($1.1 \times 10^{-7}$ S cm$^{-1}$) is observed at $z = 30$. This value is approximately the same as

the ionic conductivity of the ICC(60/10/30). This value is close to the ideal ionic conductivity of the PLLA/ICC(60/10/30) blend ($2.34 \times 10^{-7}$ S cm$^{-1}$, which is obtained by multiplying the ionic conductivity of ICC(60/10/30) by the ICC ratio of 0.3 in the blend.). Therefore, we can assume that the ionic conductive phase in this blend forms a continuous phase.
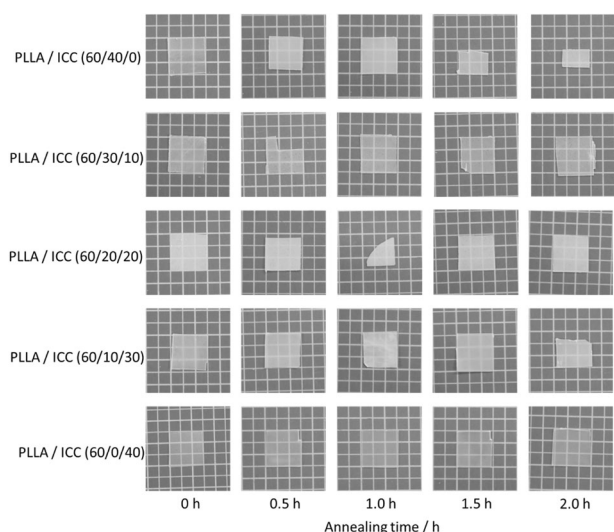
**Fig. 5** Photographs of PLLA/ICC(60/y/z) = 70/30 blend films: amorphous; annealed at 130 °C for 0.5, 1.0, 1.5, and 2.0 h

The SEM images of the cross-section of the PLLA/ICC (60/y/z) = 70/30 blend films are presented in Fig. 4. The white area in the images is the ICC (ionic conductive phase), and the other region is the matrix (insulating phase). The SEM images of the cross-section of the crystallized PLLA/ICC(60/y/z) = 70/30 blend films are also shown in Figure S2. By comparing this with Fig. 4, it can be seen that the phase structure of the PLLA/ICC blend changes negligibly before and after annealing. As seen in Fig. 4, the conductive phases in the PLLA/ICC(60/10/30) blend and PLLA/ICC(60/20/20) blend are finely dispersed within the matrix as small domains, and some connections of small domains are recognized. The ionic conductive phases in the blends that contain a large amount of the cross-linking agent (PLLA/ICC(60/30/10) blend and PLLA/ICC(60/40/0) blend) are larger than those in other blend compositions. Because of this, the ionic conductive phase is less likely to form a continuous phase. The ionic conductive phases are larger at these compositions because the cross-linked structure increases the glass transition temperature of POEGMA, making it difficult for the ICC to disperse as small domains during kneading. In contrast, the total area of the ionic conductive phases observed in the SEM image for the blend that contains no cross-linking agent (PLLA/ICC (60/0/40) blend) is less than those of other blends. This result is because the PMMA in the ICC appears easy to separate out during kneading as a result of the insufficient entanglement between the POEGMA molecular chain and PMMA molecular chain. For these reasons, except for the PLLA/ICC(60/10/30) blend and PLLA/ICC(60/20/20) blend, a continuous ionic conductive phase was not formed. Furthermore, when Figs. 3 and 4 are compared, it can be seen that the ionic conductivity of the blends in which the ionic conductive phases are finely dispersed is higher. The
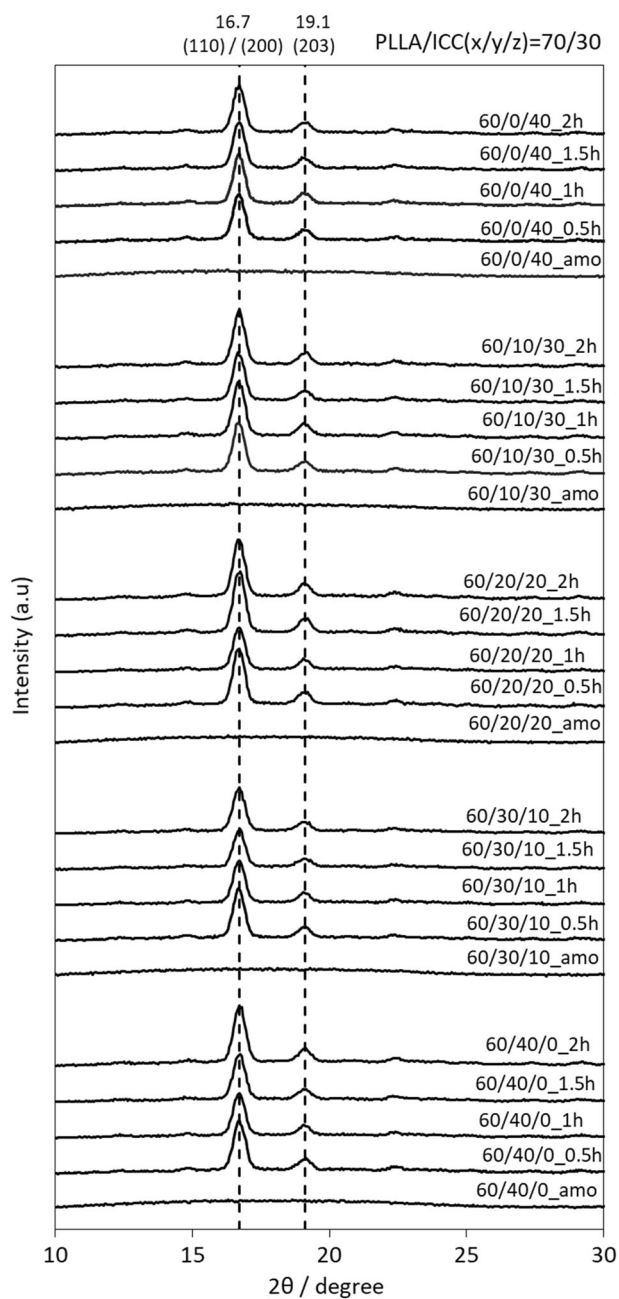


**Fig. 6** Wide-angle X-ray diffraction curves of PLLA/ICC(60/y/z) = 70/30 blends: amorphous; annealed at 130 °C for 0.5, 1.0, 1.5, and 2.0 h

DSC curves of the amorphous and crystallized (annealed for 2 h at 130 °C) PLLA/ICC (60/y/z) = 70/30 blend films are shown in Figure S3. The peaks representing the crystallization of PLLA observed ~100 °C become broader as the amount of cross-linking agent in the ICC is reduced. This finding may be because PMMA, which has separated from the ICC during kneading, is compatible with PLLA and inhibits the crystallization of PLLA.

Figure 5 shows photographs of the amorphous and crystallized PLLA/ICC blends. The amorphous blends are

transparent regardless of the composition of the ICC. The crystallized blend films are opaque because visible light is scattered by the crystallites of PLLA.

To evaluate the degree of crystallinity of the blend films, WAXD measurements were performed. Figure 6 shows WAXD curves of the amorphous and crystallized PLLA/ICC blends. All crystallized blend films formed an α-form crystal of PLLA with diffraction peaks at 16.7° and 19.1° [20, 21].

The degree of crystallinity for PLLA in the blends ($=\chi_c$) was determined from the WAXD curves in Fig. 6 via the following equation (1). The results are plotted in Fig. 7.

$$\chi_c = \frac{A_{\text{total}} - A_{\text{amo}}}{A_{\text{total}}} \times 100 \tag{1}$$

where $A_{\text{total}}$ is the total area of the WAXD pattern, and $A_{\text{amo}}$ is the area of the amorphous PLLA reflection. The degree of crystallinity of all crystallized samples increases similarly, levels off within 0.5 h, and ultimately reaches approximately 40%. Therefore, it seems that crystallization is almost complete within 0.5 h. The degrees of crystallinity for the 2-h-annealed blends calculated from Figure S3 are shown in Figure S4. They were determined via the following equation (2).

$$\chi_c = \frac{\Delta H_{m,C} - \Delta H_C}{\Delta H_C^0} \times 100 \tag{2}$$

where $\Delta H_C^0$, $\Delta H_{m,c}$, and $\Delta H_c$ are the heat of fusion of the perfect PLLA crystals (93 J/g [22]), heat of melting of PLLA crystals, and heat of crystallization of PLLA crystals, respectively. The degrees of crystallinity calculated from WAXD measurements and DSC measurements were highly correlated.

Figure 8 shows the ionic conductivity of the amorphous and crystallized blend films. In all cases, regardless of the duration of heat treatment, the ionic conductivity of the blends does not change. Hence, we can conclude that the crystallization of PLLA exerts no influence on either the phase structure of the ionic conductive phase or the ionic conduction mechanism of the conductive phases.

To explore the viscoelastic properties of the blend films, the temperature dispersion of the complex modulus was measured. Figure 9 shows the temperature dispersion of the storage modulus (Fig. 9a) and the loss tangent (Fig. 9b, c) of the blend films. In Fig. 9, all of the blends exhibit a sufficiently high storage modulus between 1.0 and 2.0 GPa at room temperature. Furthermore, unlike the amorphous blends, the large decrease in the storage modulus at approximately the $T_g$ of PLLA ($\cong 60\,°C$) is not observed in the crystallized blends. To investigate additional mechanical properties of the blended films, tensile measurements were performed (Figure S5). It was found that the yield stress is improved by crystallization but that the fracture strain is
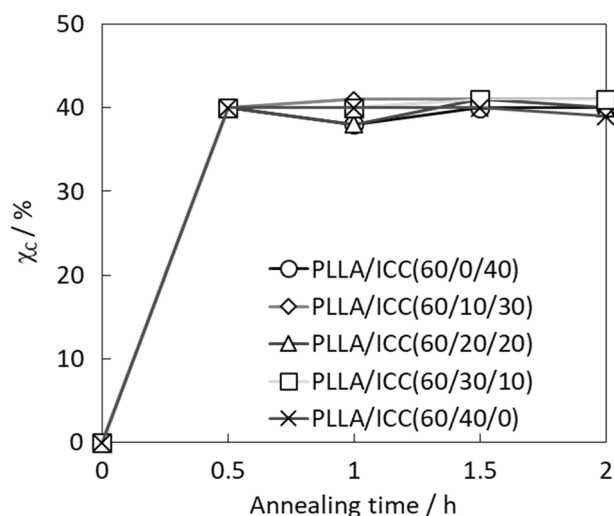


**Fig. 7** Degree of crystallinity χc as a function of annealing time for PLLA/ICC($60/y/z$) = 70/30 blends
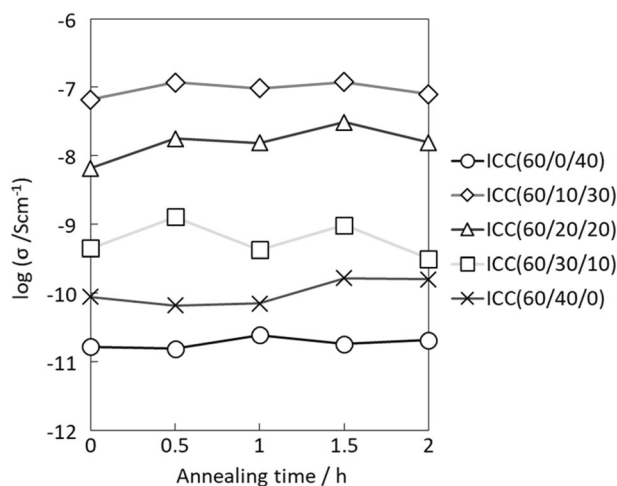


**Fig. 8** Relationship between ionic conductivity at 30 °C and annealing time for PLLA/ICC($60/y/z$) = 70/30 blends annealed at 130 °C

decreased. This finding can be attributed to the increase in hard PLLA crystallites. In Fig. 9b, two peaks appear at approximately −30 °C and 60 °C, assigned to the glass transitions of the conductive phase and insulating phase, respectively. Fig. 9c shows a magnified view of the peak of the low-temperature area in Fig. 9b. As mentioned in section 1, the segment motion of the ICP chain correlates with ionic conductivity. Therefore, it is considered that the value of $T_g$ correlates with the ionic conductivity; however, this could not be observed. This result suggests that the ionic conductivity of the blend in this study correlates not only with the mobility of the molecular chain and the amount of metal salt but also with the continuity of the ionic conduction phase. Fig. 9c also indicates that the peak temperature changes negligibly before and after the crystallization of the blended film. Thus, it appears that the phase structure and
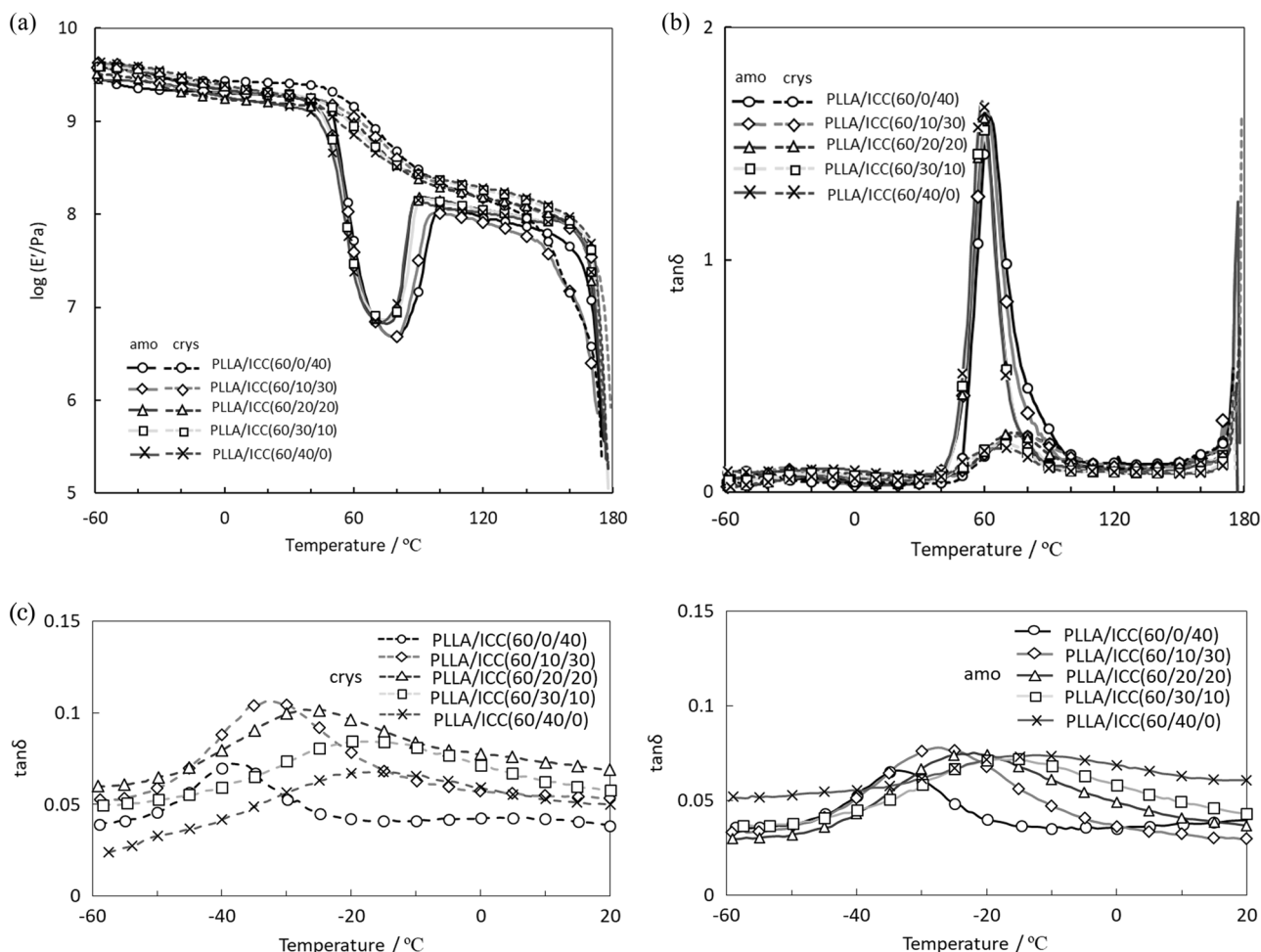
**Fig. 9** Temperature dispersion of storage modulus (E′, **a**) and loss tangent (tanδ, **b**, **c**) for PLLA/ICC(60/y/z) = 70/30 blends: amorphous; annealed at 130 °C for 1 h

mobility of the ionic conductive phase do not change even if the crystallization of PLLA in the insulating phase occurs.

## Conclusions

We manufactured a series of amorphous and crystallized PLLA/ICC blend films by melt mixing to investigate the relationships between the phase structure and the electrical and mechanical properties. The ionic conductivity of the PLLA/ICC(60/10/30) blend $(1.1 \times 10^{-7}\,\text{S cm}^{-1})$ was the highest among all compositions of the PLLA/ICC(60/y/z) = 70/30 blends. This value is close to the ideal ionic conductivity of the PLLA/ICC(60/10/30) blend $(2.34 \times 10^{-7}\,\text{S cm}^{-1})$ SEM images showed that the ionic conductive phase of this blend was finely dispersed within the matrix as small domains, and some connections of the small domains were recognized. As a result of the crystallization of the amorphous PLLA/ICC blend films, α-form crystals of PLLA were formed. In both amorphous and crystallized blend films, a storage modulus value of between 1 and

2 GPa was obtained at room temperature. In the crystallized film, the large decrease in the storage modulus at approximately 60 °C was not observed.

## Compliance with ethical standards

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