

Isothermal melt crystallization behavior of neat poly(L-lactide) (PLLA) and PLLA/organically modified layered silicate (OMLS) nanocomposite studied by two-dimensional (2D) correlation spectroscopy

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ABSTRACT

Isothermal melt crystallization behavior of neat poly(L-lactide) (PLLA) and PLLA/organically modified layered silicate (OMLS) nanocomposite was studied by using time-dependent infrared (IR) spectroscopy and transmission electron microscopy (TEM). Sets of time-dependent IR spectra reflecting the crystallization from the melt of the neat PLLA and PLLA/OMLS nanocomposite were collected at 105 °C. Fine details of the crystallization behaviors were analyzed by two-dimensional (2D) correlation spectroscopy, and significant differences in the crystallization behaviors depending on the presence of OMLS were revealed. Namely, it was found that the crystalline lamellae of the PLLA nanocomposite grow along the layered silicate, while the orientation of the neat PLLA resulted in more disordered orientation because of the absence of the OMLS. The result derived from the 2D correlation analysis of the time-dependent IR spectra of PLLA samples showed good agreement with corresponding TEM images.

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1. Introduction

In the past decade, the demand of biodegradable polymers for industry has increased considerably with more public attention paid to environmental issues. Poly(L-lactide) (PLLA) is one of the promising candidates of biodegradable polymers for practical usage [1]. PLLA is an aliphatic semicrystalline polyester that can readily be hydrolytically degraded and eventually biodegraded by bacteria in the soil under proper conditions. PLLA is usually synthesized with ring opening polymerization of lactide obtained from cyclization of lactic acid [1]. Importantly, it is possible to utilize the lactic acid derived from the fermentation of a number of naturally derived renewable materials, such as corn and sugar beet [2]. Since PLLA is made from such renewable nonpetroleum-based resources, much attention has recently been paid as an attractive carbon neutral material.

PLLA products prepared from their melt possess complex supermolecular structures consisting of crystalline lamellae embedded

in an amorphous matrix. The crystal structure of PLLA has been well investigated, and it has been reported that they have three different kinds of crystalline modifications, referred to as α , β and γ forms, depending on the preparation conditions [3–6]. The α form, which is the most common crystalline structure of PLLA, is obtained by crystallizing PLLA from solutions or melt conditions [3]. The α form has 10_3 helical chain conformation [4]. The coexistence of the rigid crystalline and more ductile amorphous phase is closely related to the physical property of PLLA. For example, appropriate crystallinity of PLLA provides the toughness required for many industrial applications.

PLLA has good mechanical properties, thermal plasticity and biocompatibility compared to many other biodegradable polymers and especially superior transparency of the processed materials [7–10]. However, more improvement in toughness, thermal resistance and hydrolytic resistance of PLLA is still required for broader practical usage. Therefore, several different approaches, e.g., blending, stereo complexation or composite formation, have been tried to improve physical properties [11–18].

Fabrication of nanocomposites is one of the ways to enhance the properties of PLLA by dispersing a small amount of nanoparticles,

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consisting of multiple layers of unit cell, into the polymer matrix [19]. A typical form of nanocomposites is intercalated nanocomposites, in which the unit cells of the nanoparticles are expanded by the insertion of polymer into the interlayer spacing. A number of papers regarding the dispersion techniques, e.g., melt mixing or in situ polymerization method, have been published [15,20]. Melt mixing method with organically modified layered silicate (OMLS) seems to be well-suited for practical preparation of nanocomposites, since the dispersion of OMLS can readily be achieved during the conventional melt-extraction process. However, this process often experiences difficulty of dispersing layered silicates into polymer matrix due to the intrinsic incompatibility between the hydrophilic layered silicates and hydrophobic polymer matrix [21]. Thus, the layered silicates are often modified with alkylammonium surfactants to decrease their surface tension and made them compatible with the hydrophobic polymer matrix.

Nanocomposites with well-dispersed OMLS often provide the improvement in the physical properties. For example, Okamoto et al. [15,16,22] reported the preparation and characterization, as well as the assessment of mechanical properties, biodegradability, melt rheology, and foam processing, of a PLLA/OMLS nanocomposite. They revealed that intrinsic properties of neat PLLA were improved after nanocomposite fabrications. However, the nature of the nanocomposite systems, such as interaction between PLLA and OMLS, has not yet been adequately investigated.

Typical approaches to probe polymer nanocomposite samples are the use of X-ray diffraction (XRD) and transmission electron microscopy (TEM). For example, XRD patterns enable one to estimate the gallery spacing of the silicate layers, and TEM can be used to detect intercalated or exfoliated structures [23,24]. Vibrational spectroscopic techniques are useful to detect molecular structures, as well as environmental change around inter- or intra-molecular interaction [25,26]. For example, time-dependent infrared (IR) spectroscopy can simultaneously monitor local structures of molecules and kinetics of crystal growth or morphology. Zhang et al. studied isothermal crystallization of neat PLLA with IR spectroscopy and two-dimensional (2D) correlation spectroscopy to sort out intermolecular interactions of the PLLA polymer through the isothermal crystallization [27]. Compared to XRD and TEM observations, a characteristic advantage of IR measurement lies in the fact that it can provide an interesting opportunity to prove transient variations in the orientation and molecular interaction through the kinetics measurement. Kinetics measurement is important for polymer nanocomposite to clarify the dynamics of crystal growth of nanocomposite, since OMLS might work as a nucleating agent [24]. The crystallization process of PLLA substantially depends on time and this behavior may be influenced by the presence of the OMLS. Thus, it becomes important to observe such dynamic variation in the system to elucidate differences induced by the presence of OMLS. Such observation may bring additional information on the nature of crystallization of PLLA, compared to the static observation based on TEM.

In this study, the difference in isothermal crystallization behavior between neat PLLA and PLLA/OMLS nanocomposite was investigated by using time-dependent IR spectroscopy and 2D correlation analysis to clarify how the presence of OMLS affects the morphology of the polymer. Fine details about the crystallization behaviors of PLLA samples were elucidated with 2D correlation analysis of time-dependent IR spectra [25,26,28–30]. More importantly, the different crystallization scheme, depending on the presence or absence of the OMLS, was clearly sorted out by 2D correlation analysis, providing penetrating insight into the nanocomposite system.

2. Experiment

2.1. Nanocomposite preparation

A commercial PLLA was supplied by Mitsui Chemicals Company (LACEA H-100: D content was 1%, $M_n = 11000$, $M_w = 65000$, $T_m = 170^\circ\text{C}$, $T_g = 70^\circ\text{C}$). Conventional layered silicates based on synthetic fluorine hectorite (syn-FH) modified by N-(cocoalkyl)-N,N-[bis(2-hydroxyethyl)]-N-methyl ammonium cations [31] was used as OMLS. Melt mixing was carried out in a miniature mixer named Mini-Max Molder (CS-183, Custom Scientific Instruments Inc.). PLLA and OMLS underwent the melt-mixing at 190°C for 5 min to complete intercalation. The content of the OMLS in the nanocomposite was 3 wt%. Extruded nanocomposite was converted into the sheet with by using a hot-press with the constant pressure of 1 MPa at 190°C for 30 s. A thin film sample for the isothermal crystallization measurement was prepared with a spin coater (3000 rpm at room temperature) by using dissolved nanocomposite matrix by chloroform of 3 wt%. A PLLA film and a nanocomposite film were cast on a CaF_2 window for the IR measurement. The thickness of each film was approximately $1.5\ \mu\text{m}$.

2.2. Time-dependent infrared spectra

Sets of time-dependent IR spectra of the neat PLA and PLA nanocomposite undergoing melt crystallization process were measured with a Nexus 470 FT-IR spectrometer (Thermo Electron Inc) equipped with a MCT detector. The IR spectra were collected in the $4000\text{--}1000\ \text{cm}^{-1}$ region with a resolution of $2\ \text{cm}^{-1}$ by co-adding 16 scans. The sample was first heated from room temperature to 210°C with the rate of $100^\circ\text{C}/\text{min}$ and held for 2 min to erase the thermal history. Then, it was cooled to 105°C by $60^\circ\text{C}/\text{min}$ for 20 min.

2.3. TEM

TEM observation (H-7100, Hitachi Co.) was conducted to investigate the morphology of the PLLA nanocomposite sample. TEM was operated at an accelerating voltage of 100 kV. After imposing the same thermal history for the PLLA nanocomposite as the time-dependent IR spectroscopic measurement, the ultra thin sections (the edge of the sample sheet was cut perpendicular to the cast phase) with thickness of $\sim 100\ \text{nm}$ were microtomed at -80°C by using a Reichert Ultra cut cryo-ultramicrotome, after suitably staining the sample with 12 tungstophosphoric acid at 80°C for 5 h.

3. Results and discussion

3.1. 2D correlation analysis of time-dependent IR spectra of neat PLLA

Fig. 1 compares (a) the time-dependent IR spectra of the neat PLLA and (b) PLLA nanocomposite measured during isothermal crystallization at 105°C . In this study, special attention is paid on the C–O stretching region, where the variation in the orientation of the crystal lamellae is readily reflected in the spectrum feature. For example, a peak observed at $1212\ \text{cm}^{-1}$ is assigned to the coupled C–O stretching vibrations aligned in the direction perpendicular to the helix axis of PLLA, while another peak at $1182\ \text{cm}^{-1}$ is assignable to the vibrations aligned parallel to the helix axis of PLLA [32].

The PLLA samples studied here undergo isothermal crystallization. This process is accompanied by a gradual development of crystalline component. Time-dependent IR spectra of the neat PLLA show obvious increase in the contribution from these two parallel and perpendicular components, suggesting the crystalline

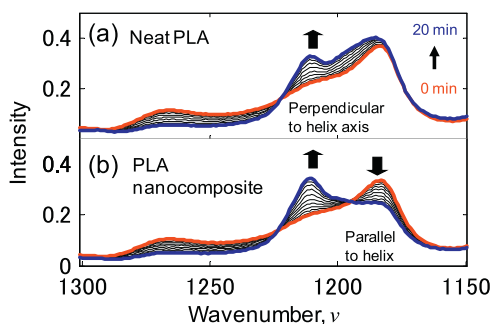


Fig. 1. Time-dependent IR spectra of neat PLLA and PLLA/OMLS nanocomposite samples measured during isothermal crystallization at 105 °C.

growth during the isothermal crystallization process. On the other hand, the IR spectra of the PLLA nanocomposite sample show the decrease in the spectral intensity associated with the crystalline structure aligned parallel to the helix axis of PLLA, while the peak assigned to the vibrations aligned perpendicular to the helix axis steadily increases. Thus, it is likely that some parts of lamellae are aligned in a preferred orientation. Consequently, it suggests the PLLA nanocomposite undergoes somewhat different crystallization scheme because of the existence of the OMLS in the system.

Variations of the spectral features are probed by 2D correlation analysis in detail. Fig. 2 shows (a) synchronous and (b) asynchronous correlation spectra generated from the time-dependent

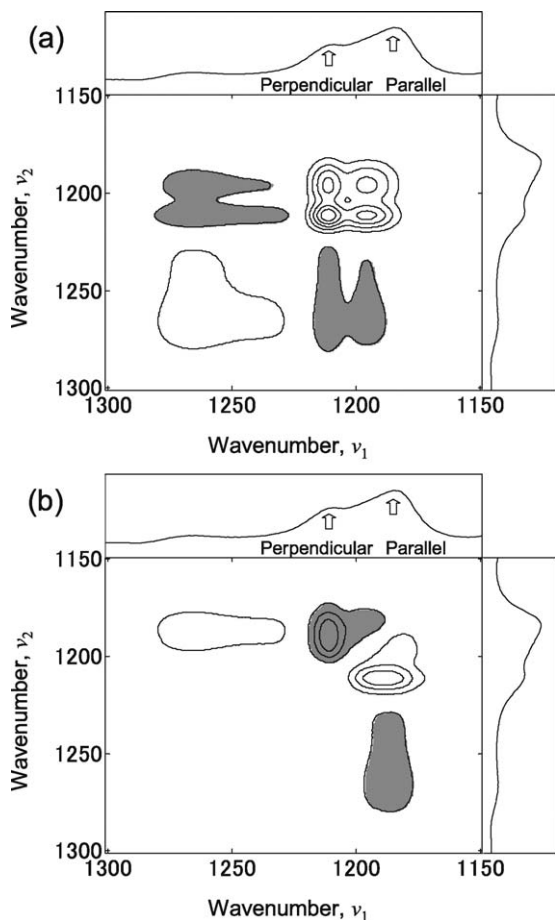


Fig. 2. (a) Synchronous and (b) asynchronous correlation spectra generated from time-dependent IR spectra of neat PLLA.

IR spectra of the neat PLLA. As expected, one can find a generation of positive synchronous cross peak between 1212 and 1182 cm^{-1} . This result indicates that the changes in these two components, both assigned to the crystalline structure of the PLLA, occur in the same direction. Such observation can be interpreted as the gradual crystalline growth with the time. From the apparent intensity variation of the peak shown in Fig. 1(a), one may expect to determine that development of the peak at 1212 cm^{-1} occurs before that of the peak at 1182 cm^{-1} . It is, however, important to point out here that the degree for the spectral intensity change does not mean that the change of the band occurs earlier than others. For example, amorphous structure of polymer often provides weak signal in IR spectroscopic measurement because of the disordered orientation. In contrast, signal contribution from crystalline structure becomes predominant. When such sample undergoes heating via the glass-to-rubber transition. Around the T_g , the relaxation predominantly occurs in the polymer chain of the amorphous region but the variation of the spectral intensity associated with the amorphous may look very small. Consequently, the difference in the degree for the spectral intensity change does not explain the difference in the sequential order of the event. Thus, that analysis of asynchronous correlation spectrum revealing so-called out-of-phase relationship becomes important.

In Fig. 2(b), it is noted that the asynchronous correlation spectrum provides cross peaks between 1212 and 1182 cm^{-1} . When the lamellae of the PLLA is developed in a totally random direction, it should result in the simultaneous development of both components aligned perpendicular and parallel to the helix axis without any sequential or successive changes in them. In other words, it should only show synchronous correlation but no asynchronous correlation. Thus, the generation of the cross peaks in both synchronous and asynchronous correlation spectra suggests that a portion of the lamellae must be preferentially aligned in a certain direction, even if a greater portion of the lamellae orients in a totally random direction. Crystal lamellae of PLLA can potentially be oriented in many directions, depending on the way they grow. For example, Meaurio et al. reported that a PLLA thin film predominantly forms edge-on or flat-on lamellar structure, depending on the way of crystallization process [32]. Namely, the lamellae growth direction is preferably oriented normal to the substrate (i.e., edge-on lamellae) when a thin film of PLLA does not undergo sufficient crystallization at a low temperature. In contrast, it becomes perpendicular to the substrate (i.e., flat-on lamellae) when it is fully crystallized at a high temperature.

The fact that the predominant variation of the peak intensity at 1182 cm^{-1} occurs before that at 1212 cm^{-1} may thus be interpreted to mean that some parts of the crystals tend to grow into the edge-on lamellae.

3.2. 2D correlation analysis of time-dependent IR spectra of PLLA nanocomposite

It is possible to probe the effect of OMLS on the isothermal crystallization behavior of the PLLA by analyzing the time-dependent IR spectra of PLLA nanocomposite undergoing seemingly similar crystallization behavior. Fig. 3 represents (a) synchronous and (b) asynchronous correlation spectra directly calculated from the time-dependent IR spectra of the PLLA nanocomposite sample. As expected, the synchronous correlation spectrum shows the development of a negative cross peak between 1212 and 1182 cm^{-1} , which turns out to be the opposite sign of the cross peak shown in Fig. 2(a). This result indicates that the change of these two peaks takes place in the opposite directions during the isothermal crystallization. In the case of PLLA nanocomposite, most of the lamellae seem to grow along the direction perpendicular to the substrate, namely flat-on lamellae.

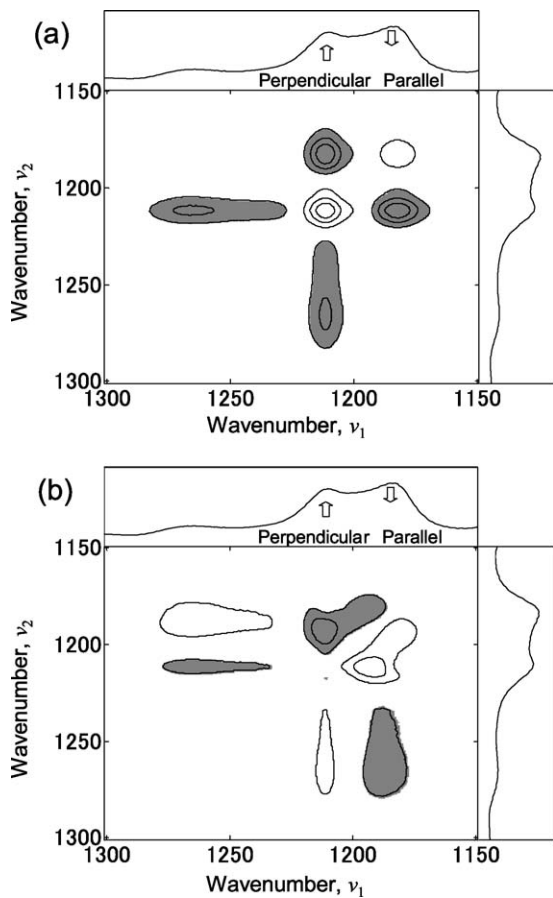


Fig. 3. (a) Synchronous and (b) asynchronous correlation spectra generated from time-dependent IR spectra of PLLA/OMLS nanocomposite.

The corresponding asynchronous correlation spectrum provides cross peaks between 1212 and 1182 cm^{-1} , revealing that the variation of the peak intensity at 1212 cm^{-1} predominantly occurs before that at 1182 cm^{-1} . It is important to point out that the sequential order derived here turns out to be opposite to that observed for the neat PLLA. Thus, the preferred development of the peak at 1212 cm^{-1} can be explained as the lamellar growth along the octahedral sheet of the silicate. Consequently, it is likely that the lamellar growth is closely related to the presence of the OMLS.

This hypothesis is clearly supported by the direct observation of superstructure of the PLLA nanocomposite sample by TEM. A TEM image of the PLLA nanocomposite sample is shown in Fig. 4. The black shadow region indicated by an arrow in the figure is a part of the OMLS dispersed over the matrix. The striped pattern observed around the OMLS indicates the lamellar structure of the PLLA. It is

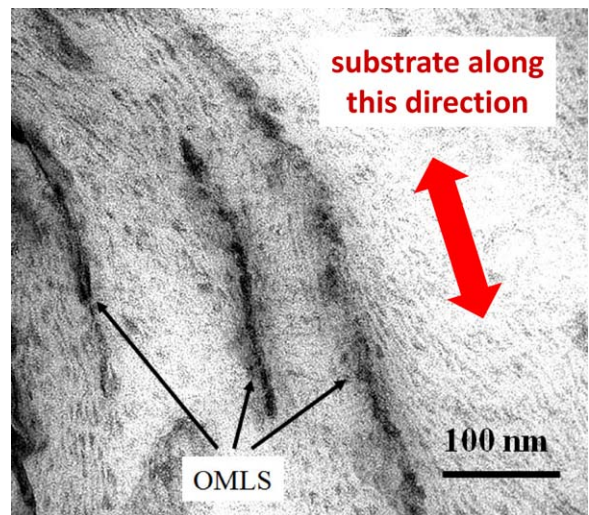


Fig. 4. A TEM image of PLLA nanocomposite sample.

important to point out that, in Fig. 4, the PLLA lamellae apparently align parallel to the octahedral sheet of the silicate. This observation can be interpreted by assuming that the clay substantially works as a nucleating agent to induce the additional crystallization of the PLLA. Since the samples are prepared by spin-casting the dissolved PLLA and clay, most of the octahedral sheets of the silicate are aligned parallel to the substrate. This condition should result in the increase in the contribution from the flat-on lamellar. Such observation agrees well with the result deduced from the 2D correlation analysis of the PLLA nanocomposite sample.

All the results put together, the 2D correlation analysis provides a very clear picture of the system. A schematic illustration for the effect of the OMLS is shown in Fig. 5. It is likely that the existence of the OMLS increases the tendency of spontaneous nucleation of the PLLA crystals around the surface of the silicate layers. It eventually leads to the development of the lamellae aligned in the direction parallel to the octahedral sheet. Consequently, by carrying out detailed analysis of the time-dependent IR spectra, it becomes possible to extract physically meaningful information concerning the variation of the crystalline structure closely associated with the nanocomposite system.

The generation of preferred orientation by the inclusion of the OMLS can also be inferred from the detailed observation of the TEM image of the PLLA nanocomposite sample. However, it is important to point out that the new IR result suggests a useful possibility to prove transient behavior of the PLLA nanocomposite system that is substantially influenced by the existence of the OMLS. It may potentially offer additional insight into the dynamics of the system that is not provided by the simple static observation based on TEM.

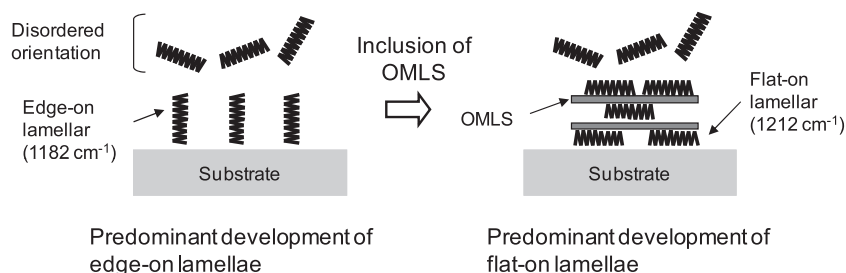


Fig. 5. A schematic illustration describing effect of OMLS.

4. Conclusion

The isothermal crystallization processes of neat PLLA and the PLLA/OMLS nanocomposite were studied by IR spectroscopy. Fine details of the variation of the IR spectral features were captured, and 2D correlation analysis clearly revealed the differences between neat PLLA and PLLA/OMLS nanocomposite during the isothermal crystallization process. Namely, the dispersed OMLS works as a nucleating agent to increase the frequency of the spontaneous nucleation of the PLLA crystals. The crystalline lamellae of the PLLA nanocomposite predominantly grow along the layered silicate, while the orientation of the neat PLLA resulted in more disordered orientations because of the absence of the OMLS. Consequently, it becomes possible to provide penetrating insight into the dynamic system undergoing the transient crystallization by the 2D correlation analysis.

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