Structural Changes in Drawn Poly(L-lactide)/Clay Hybrid Films

Naoya Ninomiya, Atsuhiro Fujimori, Toru Masuko*

Summary: The films composed of poly(L-lactide)(PLLA)/organoclay hybrids (PLACHs) have been prepared via a melt-compounding process, in which the organoclay paticles are uniformly dispersed in the PLLA matrix. The changes in PLLA crystal orientation for the uniaxially drawn films were studied by differential scanning calorimetry, X-ray diffractometry and transmission electron microscopy. Additionally, temperature dependence of the mechanical properties for these drawn films were examined by a dynamic viscoelastometer. After drawing the quenched PLACHs film at 90 °C, the orientation and crystallinity of PLLA crystal increased rapidly with increasing drawing ratio (λ) in the range more than 3 times. At the higher λ, the organoclay platelet particles in the PLACHs became parallel to the draw direction. The mechanical properties of drawn PLACHs were strongly dependent on both clay concentration and λ.

Keywords: composites; drawing; morphology; organo-modified clay; PLLA

Introduction

In this past decade, many investigators have been prepared with poly(L-lactide) (PLLA)/organoclay hybrids (PLACHs). It becomes, seemingly, popular that the PLLA chains intercalate the gallery within organo-montmorillonite particles;[1] this type of intercalation improves the physical properties of the resulting hybrids such as mechanical properties,[2–4] gas barrier features[5] and reduced flammability.[6] Especially the mechanical properties of PLACHs are strongly governed by their fine structures.

In the present study, the changes in particle orientation accompanied by drawing PLACHs films uniaxially will be studied by some structural techniques. Additionally, temperature dependence of the mechanical properties for these drawn films will also be examined by a dynamic viscoelastometer.

Faculty of Engineering, Yamagata University, Jonan 4-3-16, Yonezawa, Yamagata, 992-8510 Japan
Tel.: and Fax: +81-238-26-3073.
E-mail: fujimori@ yz.yamagata-u.ac.jp

Experimental

Materials

The polymer used was a commercial grade PLLA with M_w of 2.0×10^5, kindly supplied by Unitika Co. Ltd. The organoclay was prepared by adding Na^+-montmorillonite into a dimethyl dioctadecyl ammonium chloride aqueous solution. The hybrids with three different clay contents of 1, 3 and 6 wt% (inorganic parts), coded as Cx ($x = 1, 2, 3$), respectively, were prepared using a counter-rotating mixer (Toyo Seki Co., Japan) by mechanical kneading at 190 °C. For the purpose of comparison, the neat PLLA was processed under the same condition. The characteristics of these samples are listed in Table 1.

Preparation of Drawn Film

After melt-compounding, the collected molten materials were molded into the films of 500 μm thick between two polyimide sheets (Kapton® HN, Toray-Du Pont Co.) with a laboratory hot press at 190 °C and ca.30 MPa for 3 min, followed by quenching to room temperature. A film

Table 1.
Characteristics of the sample used in this study.

Sample	Components/ wt%		$M_w \times 10^5$	$M_w M_n$
	Clay	Organic		
PLLA	–	–	1.59	1.86
C1	1.0	1.0	1.66	1.88
C2	3.0	2.0	1.54	1.84
C3	6.0	4.0	1.46	1.86

specimen with 4 mm width and 20 mm length cut from these amorphous films was drawn by use of hand drawing apparatus in an air oven at 90 °C. The drawing speed was fixed at 20 mm/min in this study.

Characterization

To examine the thermal properties of the drawing films, a Perkin-Elmer DSC Pyris1 was utilized in the range of 40–200 °C at a heating rate of 2 °C/min under a helium purge. To obtain XRD data for the drawn films, a R-AXIS diffractometer (Rigaku Co.) was operated at 45 kV and 200 mA. The XRD photographs were taken at room temperature using graphite-monochromatized Cu$K\alpha$ radiation ($\lambda = 0.1542$ nm) focused through a 0.3 mm pinhole collimator with a cylindrical imaging plate detector.

To examine the dispersed state of clay particles in the PLLA matrix, we checked the cross-sectional slice of the drawn Cx films. Thin layers of 70 nm thick were cut from the films at room temperature by a Reichert ultra-microtome equipped with a diamond knife. The microtomed samples were then observed directly using a TEM apparatus (Philips, CM-300) operated at an accelerating voltage of 200 kV.

Rheological measurements of the drawn films were carried out by a FT-rheospectora (Rheology Co.) in an oscillating tension mode. The storage modulus (E′), loss modulus (E″) for the samples were obtained at the mechanical frequency f = 1.0 Hz with the constant strain amplitude (0.03 %) in the range from 30 °C to 160 °C at a heating rate of 2 °C/min.

Results and discussion

Changes in Fine Structure by Drawing

Figure 1 displays the DSC traces for the variously-drawn C2 films at 90 °C. The glass transition temperature (T_g) at 58 °C can clearly be observed clearly in undrawn sample; the exothermic peak at around 100 °C and the endothermic peaks at 168 °C exist. In these DSC thermograms, the exothermic enthalpy peak intensity decreases with an increase in draw ratio (λ); then it almost disappear in the range more than 3 times. These results imply that the orientation-induced crystallization occurs in the matrix prior to cold crystallization during the drawing processes.[7]

In Fig. 2, shown are the XRD fiber diagrams for the drawn PLLA and C2 films. As seen in Fig. 2, the diffraction spots on the equatorial line are observed at $2\theta = 16.5°$ for all of the drawn films, corresponding to the (110) spacing of the PLLA α-form. Upon further drawing, those diffraction spots become to be sharp with increasing draw ratio, while the broad arcs at $2\theta = 16.5°$ can be observed in XRD

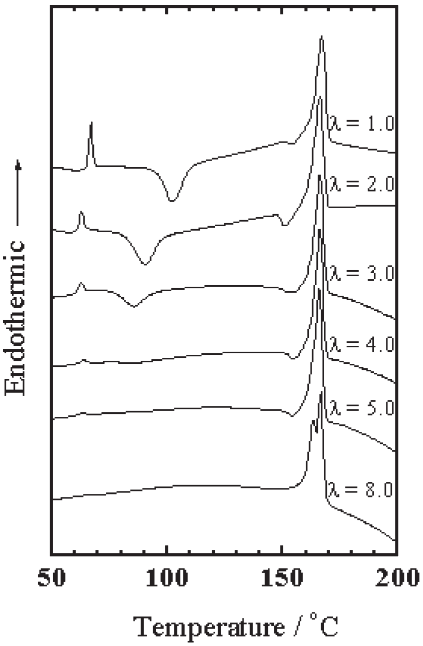

Figure 1.
DSC traces of the drawn C2 films at 90 °C.

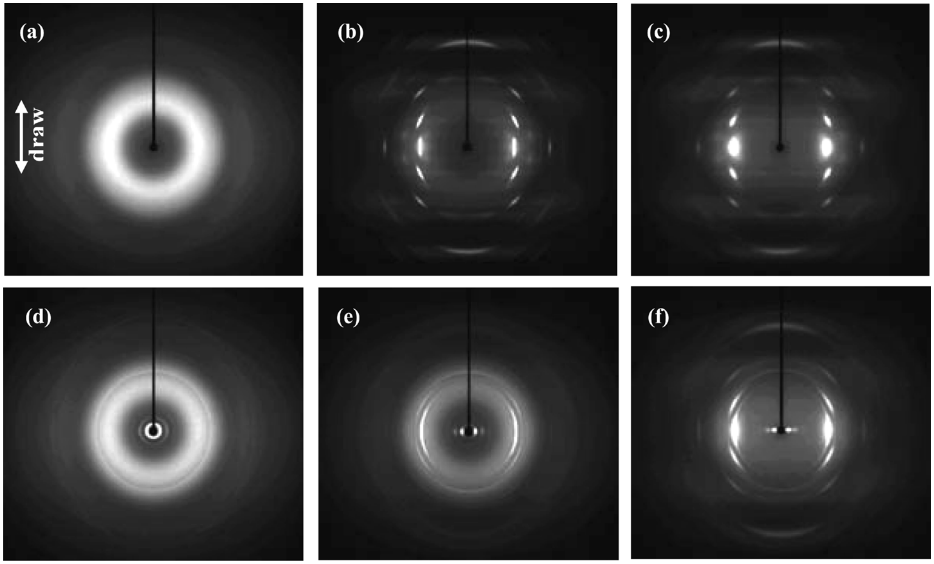

Figure 2.
XRD photographs showing for the drawn PLLA (upper) and C2 (lower) films: (a), (d) $\lambda = 1.0$ (as-drawn film); (b), (e) $\lambda = 3.0$; (c), (f) $\lambda = 8.0$.

patterns for the drawn C2 films. These XRD results suggest that the existence of organoclay in PLLA matrix might hinder the orientation of PLLA crystals during drawing processes; a less-ordered structure of oriented PLLA crystals in the hybrid system exists as compared with those of the drawn neat PLLA films.

Additionally, the reflection at $2\theta = 2.4°$ for the C2 films, corresponding to the (001) plane of the organoclay. For the initial C2 films, this reflection remains to be a Debye ring from randomly oriented organoclay particles. On drawing, the diffraction concentrate on the equator in the range more than 3 times. The existence of sharp spots on the equator indicate that the interlayer of organoclay particles in PLLA matrix orient perpendicularly to the draw direction.

Figure 3 indicates the TEM cross-sectional images for the drawn C2 films in different draw ratios. In the initial stage of

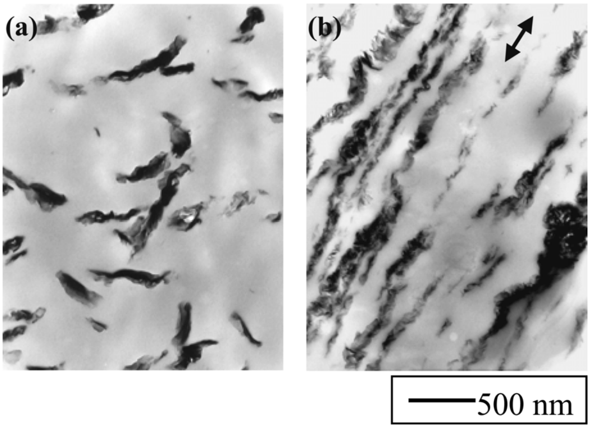

Figure 3.
TEM cross-sectional images for the C2 films: (a) $\lambda = 1.0$ (as-drawn film); (b) $\lambda = 8.0$. The arrows represent drawing direction.

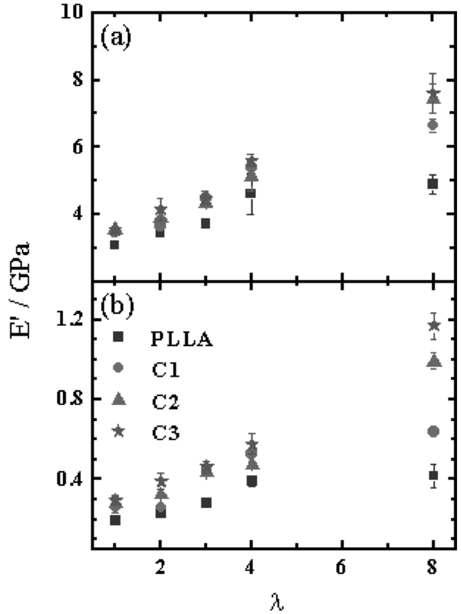

Figure 4.
Changes in storage moduli (E′) as a function of draw ratio. The marks indicated are measured at (a) 35 and (b) 100 °C for (■) neat PLLA, (●) C1, (▲) C2 and (★) C3.

the drawing, we find the randomly dispersed organoclay particles in the PLLA matrix. Upon further drawing, the organoclay platelets became to be more parallel to the draw direction.

Drawing Ratio Dependence of Dynamic Properties

The changes in storage moduli (E') measured at (a) 35 and (b) 100 °C for the drawn films are shown in Fig. 4. In the higher draw ratio range, the C1, C2 and C3 samples indicate that their E′ values at 100 °C (well above T_g) become to be about 60 %, 100 % and 200 % larger than that of neat PLLA, respectively. These results suggest that significant enhancement in E′ comes from both a larger aspect ratio and orientation of organoclay particles as shown in Fig. 3.

Conclusions

When the quenched PLACHs film were drawn at 90 °C, both the orientation and crystallinity of PLLA increased rapidly with increasing drawing ratio especially in the range more than 3 times. The XRD patterns for the drawn PLACHs film indicate that the existence of organoclay governs orientation of the PLLA crystallites in the hybrid system, thus yielding less ordered structure as compared with those in the drawn neat PLLA. At the higher drawing ratios, the organoclay particles within the PLACHs oriented their flat surface in parallel to the draw direction. The mechanical properties of drawn PLACHs were strongly dependent on clay concentration, orientation of clay particles and drawing ratio.

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