

Effects of supercritical carbon dioxide treatment on the morphology of poly(L-lactide)

Chikara Tsutsumi,¹ Ryouji Watanabe,¹ Ayaka Tokumaru,¹ Nao Kuwaoka,¹ Yuushou Nakayama,² Takeshi Shiono²

¹Department of Applied Chemistry and Biotechnology, National Institute of Technology, Niihama College, 7-1 Yagumo-cho, Niihama, Ehime 792-8580, Japan

²Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1, Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

Correspondence to: C. Tsutsumi (E-mail: tsutsumi@chem.niihama-nct.ac.jp)

ABSTRACT: Synthetic L-lactide random copolymers can be employed as controlled release materials when prepared using supercritical carbon dioxide (scCO₂), since they are biodegradable via hydrolysis. To determine the effects of thermal properties on polymer performance following scCO₂ processing, three types of poly(L-lactide) having different properties were assessed. The T_m of one poly(L-lactide) sample (H-100) was found to be approximately 170 °C over the processing pressure range from 8 to 18 MPa, while a second sample (H-440) also showed a constant value of approximately 152 °C. In contrast, the poly(L-lactide) REVODE exhibited a T_m of 146 °C prior to processing but a higher value of 147 °C following treatment at 8 MPa. Unlike the H-100 and H-440, the T_m value of the REVODE tended to decrease with increasing pressure. The T_g values increased greatly under mild conditions of 8 MPa pressure and a temperature of 40 °C. In particular, the T_g values for the H-440 and REVODE increased by 4 °C and 5 °C, respectively. All T_g values were lowest at 12 MPa and increased with increasing processing pressure, although the effect of processing temperature was minimal. The X_c DSC of the H-100 was 18% initially but increased to 20% upon scCO₂ processing at 40 °C and 14 MPa, and showed further increases at higher processing temperatures. Although the relationship between processing temperature and X_c DSC values for the H-440 showed the same trend as observed with the H-100, a different trend was seen for the REVODE. The X_c XRD values obtained from the XRD analyses differed from the values generated by DSC analysis, and showed a maximum degree of crystallinity following processing at 80 °C both with and without scCO₂ treatment. ATR FT-IR analyses identified peaks due to semicrystalline regions in poly(L-lactide) samples treated with scCO₂, even when applying low temperatures. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 44006.

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INTRODUCTION

Environmentally friendly (so-called “green”) degradable polymers can be classified based on their method of degradation, either by microbial action or through hydrolysis. The former type has been studied extensively as substitutes for general-purpose polymers,^{1–3} while the latter type has been investigated for medical applications.^{4–6} General-purpose degradable polymers are designed to disintegrate after use through processes such as composting. In contrast, degradable medical polymers have found practical usage as dissolvable sutures and in more advanced applications such as drug delivery systems (DDSs).^{7–9} Polymers used for DDSs release a water-soluble medicine incorporated uniformly into the polymer upon degradation due to hydrolysis. Recently, supercritical carbon dioxide (scCO₂) has

been used to facilitate the uniform distribution of medicine in polymers and for the production of microcapsules.^{10–12}

A compound incorporated into a degradable polymer can be spontaneously released following the hydrolysis or enzymatic degradation of the polymer, such that the polymer serves as a controlled release material. Experiments have confirmed that insecticides and antibacterial compounds can be incorporated at high concentrations into L-lactide copolymers (which are subsequently degraded by hydrolysis) using scCO₂.^{13–16} Carbon dioxide is a supercritical fluid above its critical temperature of 31.1 °C and critical pressure of 7.38 MPa. The resulting scCO₂ is relatively hydrophobic and nontoxic and, since it becomes a supercritical fluid at a relatively low temperature, can be used effectively to process biodegradable polymers with poor thermal

stability.^{17–19} For this reason, the effects of scCO₂ on the mechanical properties of polymers have been evaluated.¹⁷

Previous impregnation trials have indicated that the amount of oil that can be incorporated into a polymer is dependent on both pressure and temperature.¹³ Since solubilization depends on the density of the supercritical fluid, the dissolution of various oils in scCO₂ under different conditions must be investigated. In the present work, to evaluate the effects of the scCO₂ pressure and temperature on the structure of treated polymers, the thermal properties of polymers after treatment were examined. A change in the structure of a polymer prepared with scCO₂ is likely to affect its oil content, and therefore the present study examined the relationship between polymer structure and oil content, using differential scanning calorimetry (DSC) to assess thermal characteristics. The effects of scCO₂ on the thermal characteristics of polymers, such as the heat of fusion (ΔH_m), have been reported.^{20,21} In previous work,¹³ because the mechanism of oil incorporation was unknown, an evaluation of the thermal properties of the polymer following scCO₂ treatment was required in order to determine variations in oil incorporation under different processing conditions. The work reported herein investigated the thermal properties of poly(L-lactide) to determine the effects of processing temperature. Since DSC analysis gave a thermal damage to polymer conformation, the changes of the morphology were further observed by X-ray diffractometer (XRD) and attenuated total reflection Fourier transform infrared spectrometer (ATR FT-IR).

EXPERIMENTAL

Materials

Chloroform (industrial grade, over 99.9% of the purity) was purchased from the Tokuyama Corporation, except for the chloroform used as a solvent for gel permeation chromatography (GPC), which was high pressure liquid chromatography (HPLC) grade and was obtained from Wako Pure Chemical Industries, Ltd. Carbon dioxide (99.99%) was obtained from Takamatsu Teisan, Inc. The poly(L-lactide) used in this work (Lacea H-100, referred to as H-100, and Lacea H-440, referred to as H-440) were a gift from Mitsui Chemicals, Inc. In addition, a sample of REVODE 101 (a semicrystalline polymer similar to the H-100 and H-440) was purchased from Zhejiang Hisum Biomaterials. Poly(L-lactide) films were prepared using a solvent-cast method from chloroform solutions.

Characterization of Polymers

The number- (M_n) and weight-average (M_w) molecular weights of the poly(L-lactide) samples were determined by GPC, using a Hitachi D-2520 chromatograph equipped with Shodex GPC K-802.5 and K-804 columns, with chloroform as the eluent at 40 °C and a flow rate of 1.0 mL/min in conjunction with a refractive index (RI) detector. Molecular weights were determined by comparison with a polystyrene standard. The M_n and M_w/M_n values determined for the poly(L-lactide) specimens were: H-100 = 9.0×10^4 , 1.64; H-440 = 10.6×10^4 , 1.58; REVODE = 10.6×10^4 , 1.85.

The thermal characteristics of the polymers, including melting point, T_m , glass transition point, T_g , and heat of fusion, $-\Delta H_m$,

were obtained using a Rigaku Thermo Plus 2/DSC8230 DSC instrument. In these tests, samples (5 mg) were heated from room temperature to 200 °C at a rate of 10 °C/min in a nitrogen stream. The T_m and ΔH_m values were determined during the first heating cycle, while the T_g value was obtained during a second heating cycle. The extent of crystallinity of each poly(L-lactide) sample ($X_{c \text{ DSC}}$) was calculated using the equation^{22,23}

$$X_{c \text{ DSC}}(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100$$

where ΔH_m^0 is the heat of fusion and ΔH_c is the heat of crystallization for poly(L-lactide), using the value of 135 J/g reported by Miyata and Masuko²⁴ as ΔH_m^0 for a perfectly crystalline sample. The reported values each represent the average of three measurements. The T_m , $-\Delta H_m$, and T_g were found to be: H-100 = 169 °C, 28 J/g, 60 °C; H-440 = 151 °C, 21 J/g, 55 °C; and REVODE = 146 °C, 16 J/g, 53 °C.

Crystal structures were investigated with a Rigaku Rint 2100 X-ray diffractometer equipped with a scintillation counter, employing Cu-K α radiation (30 kV, 15 mA) over a scan region of $2\theta = 8$ to 35° and at a scan rate of 2°/min. Pretreated poly(L-lactide) specimens were each assessed three times and the average values are reported. Samples were first formed into films that were heated at a predetermined temperature for 3 h and then annealed at room temperature. The procedure used to prepare films treated with scCO₂ is described in the following section. The percent crystallinity ($X_{c \text{ XRD}}$) of each poly(L-lactide) sample was calculated based on equation²³

$$X_{c \text{ XRD}}(\%) = \frac{\int_{2\theta_1}^{2\theta_2} I_c(2\theta) d(2\theta)}{\int_{2\theta_1}^{2\theta_2} I(2\theta) d(2\theta)} \times 100$$

Each film sample was scanned at 8° ($2\theta_1$) and 35° ($2\theta_2$), and $I_c(2\theta)$ and $I(2\theta)$ are the diffraction intensities obtained from both 2θ , representing crystalline and noncrystalline domains, respectively.

The surface functional groups of polymeric film samples (approximately 10 μm in thickness) were assessed using attenuated total reflection Fourier transform-infrared spectrometer (ATR FT-IR; Thermo Scientific Nicolet iS5). Spectra were collected over the range of 4000 to 500 cm^{-1} , employing the same films prepared as samples for XRD measurements.

Treatment of Poly(L-lactide) with Supercritical Carbon Dioxide

Poly(L-lactide) films (100 μm in thickness) were treated with scCO₂ inside a high-pressure reaction apparatus made from stainless steel (0.5 L total volume) with stirring (100 rpm), applying pressures from 8 to 20 MPa at 40 °C for 3 h. The scCO₂ was prepared by first heating the container above the critical temperature of 31.1 °C, following which the atmosphere inside the container was replaced with CO₂ gas three times. The CO₂ was supplied as a liquid using a pump, with the pump head cooled to approximately 0 °C. The liquid CO₂ provided by the pump could be transitioned to a gas or a supercritical fluid by heating the stainless steel tube connecting the pump to the reaction container, such that the container was filled with CO₂ in the desired state. Since the temperature of the CO₂ was

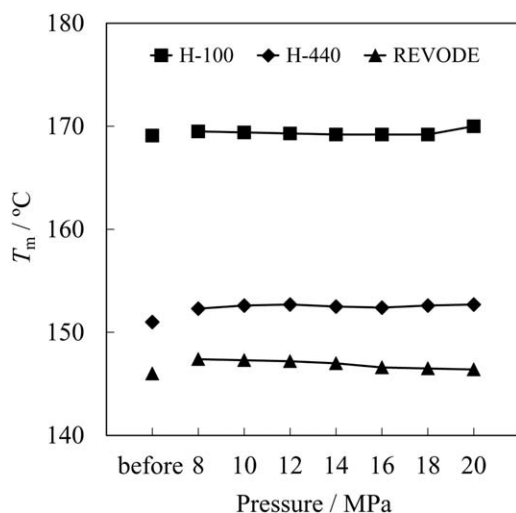


Figure 1. Effect of pressure on T_m values of poly(L-lactide) samples treated with scCO_2 at 8 to 20 MPa and 40°C for 3 h.

increased upon compression, the reaction container temperature was somewhat lower than the preset temperature during filling. After filling, the chamber temperature and pressure were adjusted to the desired values and held constant for 3 h. Following cooling from a predetermined temperature to approximately 40°C , decompression was performed gradually over 2 h, after which the sample was removed from the container. To investigate the effects of temperature, the prepared films were treated at temperatures from 40 to 100°C at 14 MPa for 3 h using the same equipment.

RESULTS AND DISCUSSION

Effect of scCO_2 Processing Pressure on the Thermal Properties of Poly(L-lactide)

Previous studies examining impregnation using scCO_2 have evaluated the amount of natural oils that can be incorporated into polymers and the results have shown that the oil content is dependent on the processing temperature and pressure, the oil feed rate and the thermal properties of the polymer.^{13–16} In this work, polymers were prepared using scCO_2 and the thermal properties of the polymers were investigated, along with the effects of these properties on the amount of oil contained in the polymers.

Figure 1 shows the T_m values of the poly(L-lactide) samples treated with scCO_2 at pressures over the range of 8 to 20 MPa at 40°C for 3 h. Although the T_m of the H-100 was 169°C before processing, this value increased slightly to 170°C after scCO_2 processing at 8 MPa and 40°C for 3 h. In contrast, the T_m of this polymer did not exhibit any further changes as the pressure rose from 8 to 18 MPa, and remained at 170°C . H-440 showed the same trend. However, the T_m of the REVODE was 146°C before processing and reached its highest value (147°C) at 8 MPa. Unlike the H-100 and H-440, the T_m of this polymer decreased slightly as the pressure increased. These results show that a polymer with a high T_m value is not readily affected by pressure. The slight increase in T_m upon processing with scCO_2 also indicates that the interactions between the polymer mole-

cules were strengthened. Because the processing temperature was low, at 40°C , the T_m values were not greatly affected even at pressures up to 20 MPa.

Figure 2 summarizes the changes in crystallinity ($X_{c\text{DSC}}$) determined from DSC measurements at various processing pressure for poly(L-lactide) samples treated with scCO_2 . The $X_{c\text{DSC}}$ variations are seen to follow different trends than those observed for T_m . In particular, the $X_{c\text{DSC}}$ values were affected by scCO_2 pressure, such that the values of all samples increased significantly after scCO_2 processing, and were dependent on pressure. The H-100 showed a maximum at 12 MPa while the other polymers had a maximum value at 14 MPa. Beyond these maximum values, $X_{c\text{DSC}}$ decreased with increasing pressure. These results can be explained as the result of the re-arrangement of the polymeric structures up to 14 MPa, producing an expansion of the folded lamellar structures. Kiran *et al.* have reported that different crystalline domains with varying lamellar thicknesses are associated with morphological changes of poly(ϵ -caprolactone) upon exposure to CO_2 at high pressures.²⁵ Research into the crystallinity of poly(lactide) in compressed CO_2 using DSC by Zhai *et al.* has demonstrated a maximum value of 27% after treatment at 6.89 MPa and 25°C , with an even higher value of 39% obtained at 100°C .²⁶ Since the crystallinity in their study was determined using a ΔH_m^0 value of 93 J/g, the results of this study are consistent with those obtained by Zhai *et al.*, although the sample thickness may have affected the degree of crystallinity, because the specimens prepared by them had a thickness of approximately 0.3 mm. Previous studies have reported that the amount of incorporated oil increased at pressures up to 14 MPa, suggesting that oil content and the crystallinity may be related,¹³ and the oil is thought to be enclosed in lamellar structures as the polymer is processed.

The T_g values of the H-100, H-440, and REVODE were 60, 55, and 53°C , respectively, as determined by DSC before scCO_2 processing. Figure 3 plots the relationship between T_g and processing pressure. The value of T_g is seen to increase significantly under mild conditions of 8 MPa and 40°C . In particular, the T_g

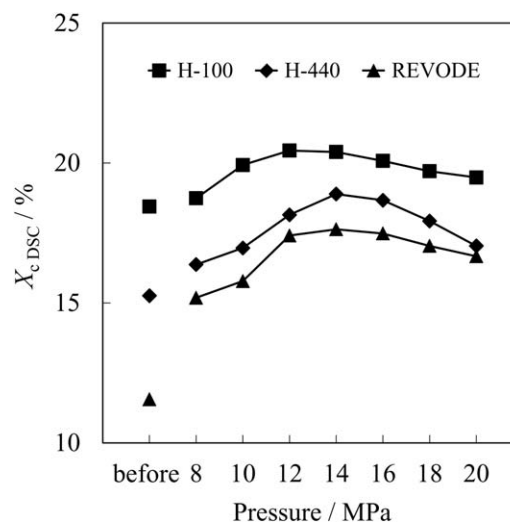


Figure 2. Effect of pressure on $X_{c\text{DSC}}$ values of poly(L-lactide) samples treated with scCO_2 at 8 to 20 MPa and 40°C for 3 h.

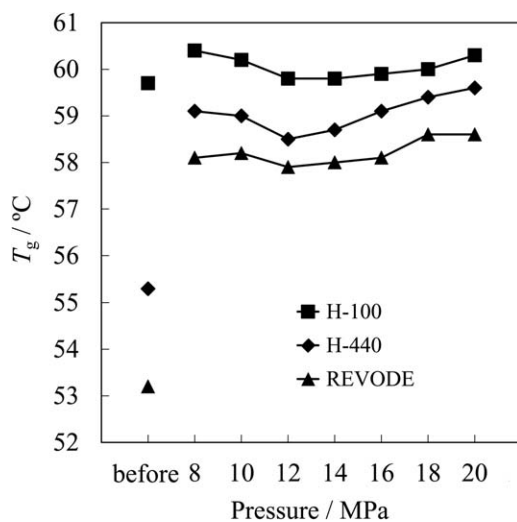


Figure 3. Effect of pressure on the T_g of poly(L-lactide) samples treated with scCO_2 at 8 to 20 MPa and 40 °C for 3 h.

values of the H-440 and REVODE were increased by 4 and 5 °C, respectively. In addition, all the T_g values reached a minimum at 12 MPa and then increased with pressure. These results show that it is easier to change the T_g compared with T_m , since T_g is closer to the processing temperature. It is possible that the intermolecular distances in the noncrystalline regions contracted by compression. Assuming the intermolecular approach by compression, the lamellar structures in the crystalline region increase, resulting in a slightly rise in T_m even at 40 °C of lower processing temperature above described.

Effect of scCO_2 Processing Temperature on the Thermal Properties of Poly(L-lactide)

To clarify the relationship between the poly(L-lactide) T_m values and the temperature applied during scCO_2 processing, the polymers were treated at a constant pressure of 14 MPa for 3 h (Figure 4). The H-100, having the highest T_m value, did not exhibit any change in this value even upon processing at 40 °C. However the T_m values of the H-440 and REVODE increased by more than 1 °C after processing at 40 °C and 14 MPa for 3 h. The T_m of the H-100 increased with increasing processing temperature up to a maximum of 170 °C at a 100 °C processing temperature. The T_m values of the H-440 and REVODE also increased with processing temperature. The T_m of the H-440 rose by approximately 1 °C on going from 40 to 100 °C, similar to that of the H-100, while the T_m of the REVODE increased significantly, from 147 to 150 °C, indicating that the processing temperature change greatly affected the interactions among polymeric chains in this sample and changed the lamellar structure.

The relationship between processing temperature and $X_{c \text{ DSC}}$ was determined simultaneously, as shown in Figure 5. Before processing, the $X_{c \text{ DSC}}$ of the H-100 was 18%, although this increased to 20% upon scCO_2 processing at 40 °C and 14 MPa. The $X_{c \text{ DSC}}$ was observed to increase at higher processing temperatures, reaching 26% at a processing temperature of 100 °C. Figure 6(a) shows the DSC thermograms for the H-100, indicating the transition in ΔH_m . Although the half-width of the peak

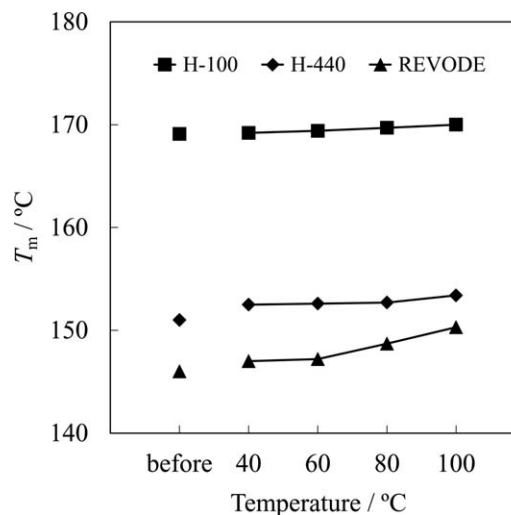


Figure 4. Effect of temperature on the T_m of poly(L-lactide) samples treated with scCO_2 at 40 to 100 °C and 14 MPa for 3 h.

was relatively narrow prior to processing, the peak extended toward the endotherm direction at 40 °C, indicating an increase in crystallinity. However, the half-width at 40 °C was wide compared to that before processing, and a small shoulder is evident at 160 °C of processing temperatures over 80 °C, indicating that lamellar structures increased upon scCO_2 processing. Furthermore, a small endotherm peak was detected near 147 °C upon processing at 100 °C, suggesting increased fragmentation of the lamellar structure. Therefore, the DSC curves demonstrate that scCO_2 processing extended the crystalline region by accelerating the conversion of noncrystalline regions to crystalline ones, or through fragmentation of the lamellar structures in the crystalline regions.

Although the relationship between processing temperature and the $X_{c \text{ DSC}}$ values of the H-440 showed the same trend as seen for the H-100, the results obtained from the REVODE differed (Figure 5). The $X_{c \text{ DSC}}$ values of the REVODE increased

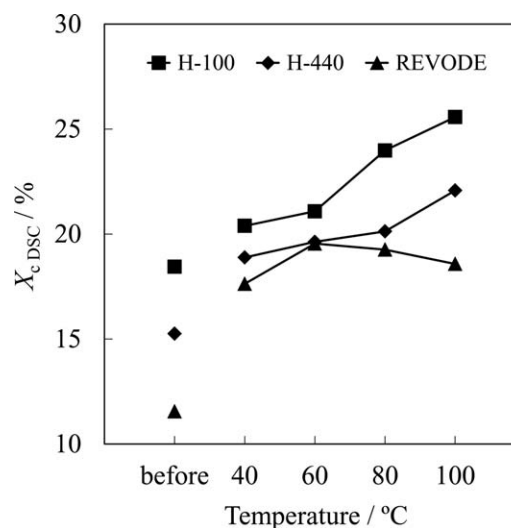


Figure 5. Effect of temperature on the $X_{c \text{ DSC}}$ of poly(L-lactide) samples treated with scCO_2 at 40 to 100 °C and 14 MPa for 3 h.

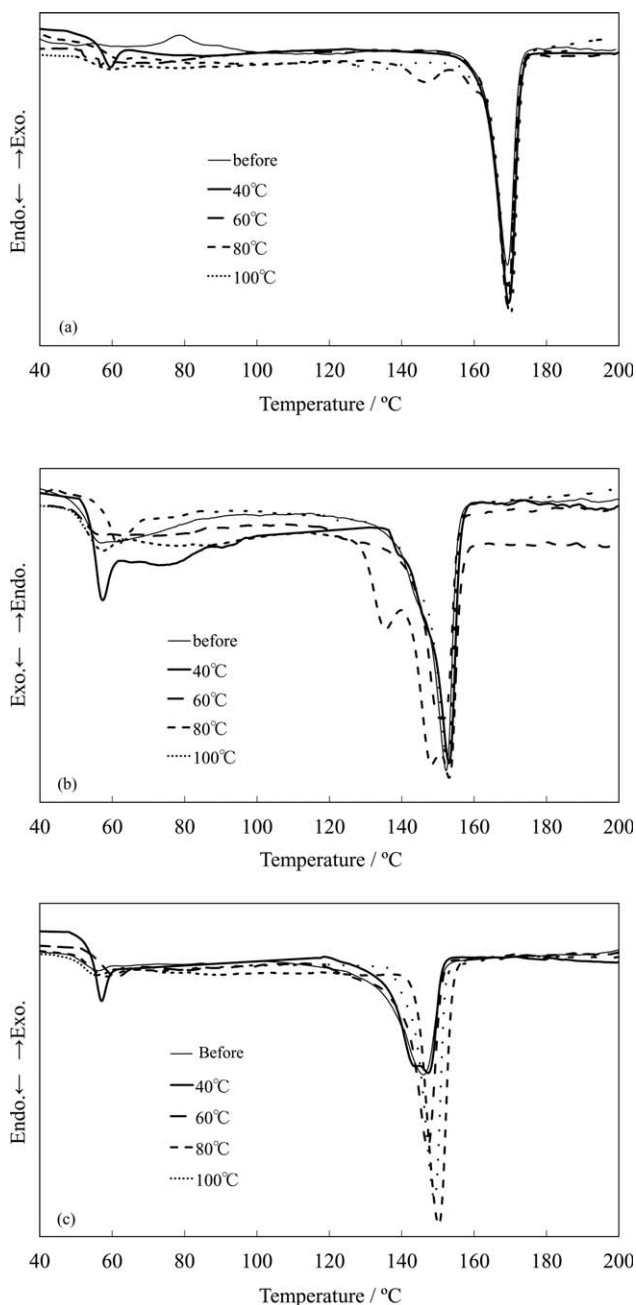


Figure 6. DSC thermograms obtained during the first heating of poly(L-lactide) samples treated with scCO_2 at 40 to 100 °C and 14 MPa for 3 h: (a) H-100, (b) H-440, and (c) REVODE.

significantly upon scCO_2 processing such that, even at 40 °C, the value was increased to 18%. Furthermore, the X_c DSC increased to a maximum of 20% at 60 °C, followed by a downward trend at temperatures over 80 °C. The data plot for the REVODE has a shape opposite to the graphs produced by the data for the other two polymers. The DSC results for the REVODE are presented in Figure 6(c). The DSC plots of the H-100 exhibited little change with processing temperature, although the half-width of the H-440 peak was increased at higher processing temperatures [Figure 6(a,b)]. In contrast, an increase in processing temperature extended the endothermic

direction of the REVODE peak in addition to moving the peak toward a higher temperature. Furthermore, the half-width of the peak narrowed as the processing temperature increased. These results suggest that the intermolecular forces between the polymer chains were strengthened within the crystalline regions of the REVODE upon scCO_2 processing. The size of the crystalline area was greatest at 60 °C, although the endothermic nature of the peak increased upon processing at 100 °C. Furthermore, since the half-width was narrow, the lamellar structures initially present at 60 °C appear to have readily aggregated as the processing temperature was increased. Consequently, a minimally crystalline polymer can evidently be converted into a highly crystalline material by scCO_2 processing.

The changes in the T_g of poly(L-lactide) specimens with variations in processing temperature are summarized in Figure 7. The T_g essentially indicates the temperature at which micro-Brownian motion begins in the noncrystalline regions. No changes in the T_g of the H-100, having a greater crystalline area, occurred upon scCO_2 processing, and the T_g showed a maximum of 60 °C upon scCO_2 processing at 80 °C. The T_g of H-440, which has lower crystallinity than the H-100, increased 3 °C upon processing at 40 °C, and the effect of processing temperature showed the same trend as observed with the H-100. The T_g of the REVODE, which exhibited low crystallinity, increased 5 °C at a processing temperature of 40 °C, and showed a maximum of 58 °C at 60 °C scCO_2 treatment. In addition, the crystalline regions of the low-crystalline polymers were evidently extended through re-arrangement of the polymer chains upon scCO_2 processing; this result agrees with the results of the T_g experiments. Although the same phenomenon occurs in the crystalline region, interactions between polymer chains are strengthened in the noncrystalline region through compression during processing. In addition, when the processing temperature was increased, polymers with a low T_g prior to processing reached their maximum T_g at a lower processing temperature. Thus, the T_g values of the polymers were dependent on the scCO_2 processing temperature and the strengthening of the

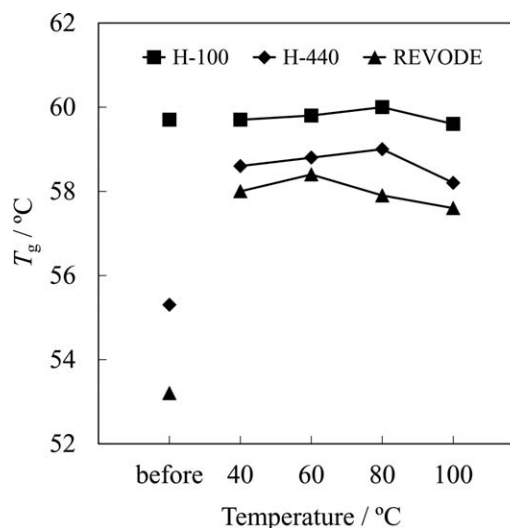


Figure 7. Effect of temperature on the T_g of poly(L-lactide) samples treated with scCO_2 at 40 to 100 °C and 14 MPa for 3 h.

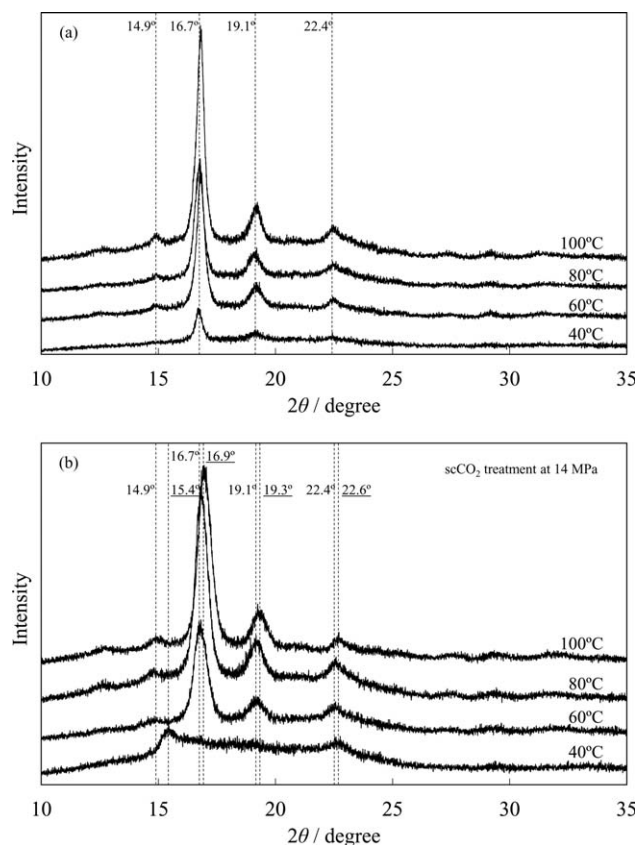


Figure 8. XRD profiles of a poly(L-lactide) (H-100) (a) heat-treated at 40 to 100 °C for 3 h and (b) treated with scCO_2 at 40 to 100 °C and 14 MPa for 3 h.

interactions between polymer chains affected the mechanical properties of the polymers.

Crystal Structure Analysis of Poly(L-lactide) Processed with scCO_2

DSC analysis has a problem of the thermal damage to polymer structure, consequently, it cannot evaluate accurate crystallinity. Therefore, the crystalline region without the thermal damage was exactly estimated by XRD and ATR FT-IR analysis. Taking advantage of the feature of these analyses, the relationship between scCO_2 processing and thermal treatment was compared and the difference was clarified. Figure 8(a) shows the XRD data for H-100 films (120 μm in thickness) heat-treated at 40 to 100 °C for 3 h. When the H-100 films were heat-treated at 40 °C, diffraction peaks were detected at $2\theta = 16.7$, 19.1, and 22.4°, similar to the pattern generated by the sample before processing. The H-440 and REVODE gave much the same results as the H-100. These films generated low intensity peaks, indicating minimal crystallinity in the specimens. The intensity of the peaks was increased at processing temperatures over 60 °C, although almost no changes were observed in peak width. Three of these diffraction peaks are attributed to α form.^{23,26,27} Zhai *et al.*²⁶ and Zhang *et al.*²⁸ have reported that the diffraction peak at $2\theta = 15.3^\circ$ suggests the presence of a new crystal structure following a reorganization of the crystals at processing conditions of 6.89 MPa and 25 °C. In this work, a similar peak

was detected at $2\theta = 14.9^\circ$ in samples processed above 60 °C, indicating that the same phenomenon has occurred.

XRD profiles of H-100 treated with scCO_2 at 40 to 100 °C and 14 MPa for 3 h are shown in Figure 8(b). The H-100 treated above 60 °C generates the same diffraction peaks as the heat-treated H-100. The peaks generated by the H-100 after treatment with scCO_2 were widened as a result of the thermal processing. Moreover, the three diffraction peaks attributed to α form were shifted by $+0.2^\circ$ after processing at 100 °C and 14 MPa, respectively. However, when the H-100 was treated with scCO_2 at 40 °C and 14 MPa, a broad diffraction peak containing peaks at 15.4° and 22.4° was subsequently evident. The appearance of this broad peak shows that there was little crystallization as a result of applying treatment without cooling. An increased value in reciprocal space ($+0.2^\circ$) means a decrease in distance between lattice planes in real space and would indicate a compressed unit cell.

Figure 9 compares the crystallinity of H-100 as determined by XRD and DSC. The $X_{c, \text{DSC}}$ was increased following scCO_2 processing and showed a tendency to increase with a rise in processing temperature, as noted above. The $X_{c, \text{XRD}}$ value was as low as 11% before treatment, and it is evident that the sample was not affected by the application of heat during the measurement process. Following processing with scCO_2 at 40 °C and 14 MPa, during which only the inclusion of CO_2 molecules takes place, the $X_{c, \text{XRD}}$ is almost the same as before processing. The $X_{c, \text{XRD}}$ of the H-100 treated at 60 °C and 14 MPa, however, increased dramatically, reaching a value of 23% (similar to the $X_{c, \text{DSC}}$ value). Although the crystallinity exhibited a maximum of 26% at 80 °C, it decreased to 25% at 100 °C.

In contrast, when the H-100 film was subjected solely to thermal treatment, the $X_{c, \text{XRD}}$ had 17%, which was high compared with that obtained from scCO_2 processing at 40 °C. The variations in crystallinity with the temperature of the film were similar to the plot obtained from scCO_2 processing, although the

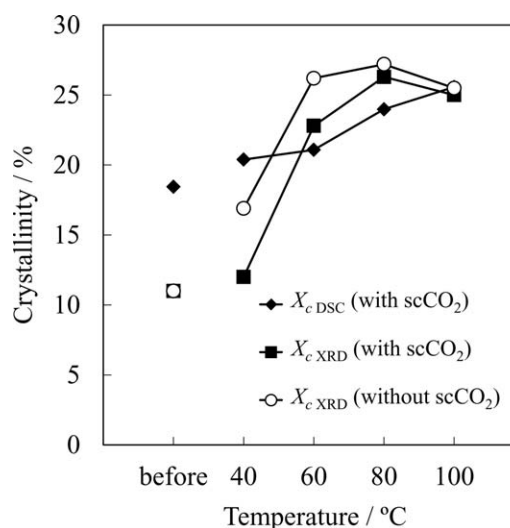


Figure 9. Change in the crystallinity of a poly(L-lactide) (H-100) following thermal treatment at 40 to 100 °C for 3 h and treatment with scCO_2 at 40 to 100 °C and 14 MPa for 3 h.

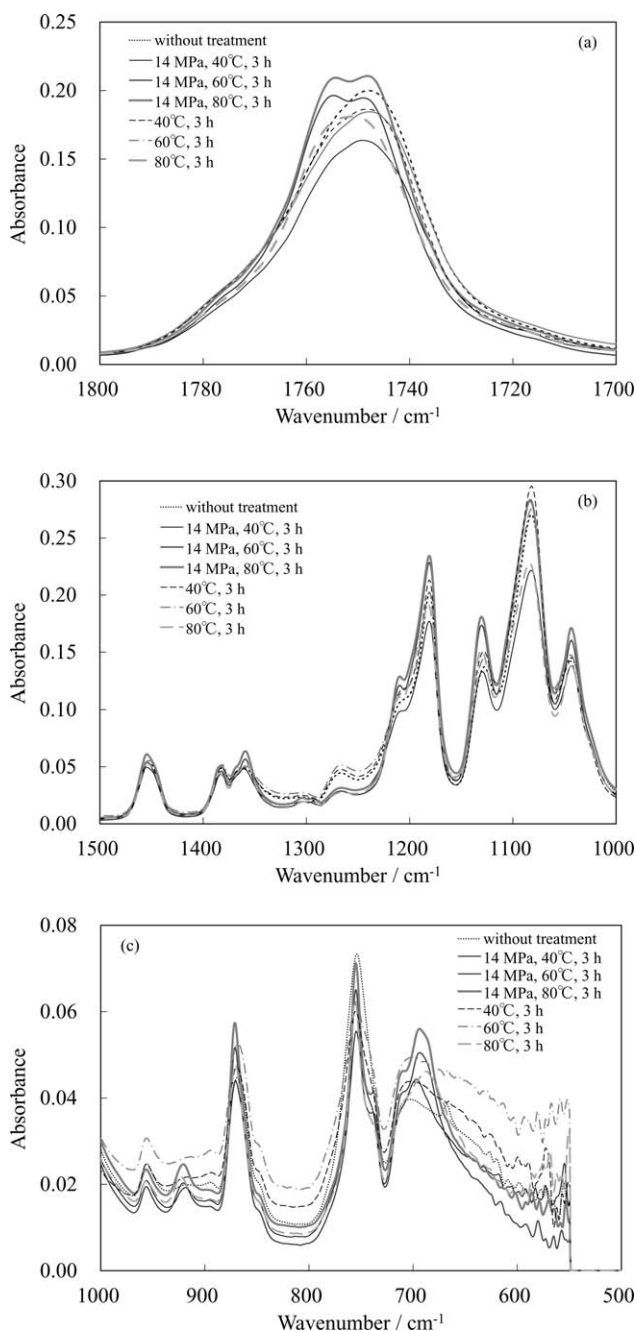


Figure 10. ATR FT-IR spectra of poly(L-lactide) (H-100) heat-treated at 40 to 80 °C for 3 h and treated with scCO₂ at 40 to 80 °C and 14 MPa for 3 h.

crystallinity was always higher for the films prepared using the thermal treatment. It is believed that only the rearrangement of polymer chains occurred in response to the thermal treatment, and therefore the inclusion and removal of CO₂ molecules affected the conformations of polymer chains during scCO₂ processing.

FT-IR spectra of H-100 treated with and without scCO₂ are shown in Figure 10 [(a) 1700–1800 cm⁻¹, (b) 1000–1500 cm⁻¹, (c) 500–1000 cm⁻¹]. These films were processed by applying the same conditions as were used to fabricate samples for XRD

analyses, although the 10 μm film could not be examined because of excess shrinkage at 100 °C. In the case of the H-100 heat-treated at 40 and 60 °C as well as the untreated sample, the C-H stretching vibrations from CH₃ groups in noncrystalline regions are observed at 2995 and 2945 cm⁻¹. The H-100 spectra also show peaks resulting from semicrystalline regions at 2997 and 2946 cm⁻¹ (data not shown). These results agree with those obtained by Zhang *et al.*²⁸

Figure 10(a) provides the FT-IR spectra obtained from H-100 treated with or without scCO₂ in the 1700 to 1800 cm⁻¹ carbonyl stretching region. The carbonyl band of the untreated H-100 shows up as a wide peak at 1748 cm⁻¹ together with shoulder peaks at 1766 and 1776 cm⁻¹. The absorbance at 1767 cm⁻¹ reveals a crystalline contribution,²⁸ while the other two are attributed to amorphous poly(L-lactide).^{28,29} The spectra are changed only minimally by thermal treatment at 40 and 60 °C or by scCO₂ processing at 40 °C. The H-100 treated with scCO₂ at 60 °C and 80 °C generated an unexpected distinctive and narrow peak at 1755 cm⁻¹. In addition, the absorbance at 1776 cm⁻¹ decreased following this processing. The shift to high wavenumbers indicates a reinforcement of the stretching vibration, suggesting that hydrogen bonds were formed by rearrangements during scCO₂ processing. The intermediate peak centered at 1752 cm⁻¹ was detected after thermal treatment at 80 °C. Since the absorption at 1776 cm⁻¹ was decreased, this new peak is attributed to a reduction in the noncrystalline regions and an increase in the crystalline regions. These results correspond to the data obtained by XRD.

The FT-IR region from 1000 to 1500 cm⁻¹ is shown in Figure 10(b). The region contains the C-H stretching and deformation vibrations of asymmetrical and symmetrical CH₃ groups, the C-O stretching vibration of asymmetrical C-CO-O and O-C-CO groups, and the C-CH₃ stretching vibration.^{28–30} The treatment with scCO₂ increased the absorbance of the asymmetric deformation at 1455 cm⁻¹, the symmetric deformation at 1382 cm⁻¹ (with a shoulder at 1386 cm⁻¹) and the symmetric mode at 1130 cm⁻¹ of the CH₃ group. Similar changes were also observed following thermal treatment at 80 °C. The presence of peaks derived from a semicrystalline α form²⁸ shows that crystallization is promoted by mild scCO₂ processing. The C-O stretching in the C-CO-O arrangement was observed as a stretching vibration at 1268 cm⁻¹, as well as asymmetrical stretching at 1210 and 1181 cm⁻¹. The absorbance centered at 1084 cm⁻¹ was assigned to the C-O asymmetrical stretching vibration in the O-C-CO arrangement. The absorbance of the noncrystalline band at 1268 cm⁻¹ decreased with increasing crystallization. When the sample was heated to 80 °C, C-O asymmetrical stretching vibration was detected at 1212 and 1182 cm⁻¹, in good agreement with previous data in the literature.^{28,30} The peak generated by the film processed with scCO₂ was shifted slightly to lower wavelengths compared to thermal treatment.

Finally, the results for the so-called fingerprint region below 1000 cm⁻¹ are shown in Figure 10(c). The out of plane and the in plane rocking deformation vibrations were observed in the region from about 600 to 800 cm⁻¹, although the sample

treated with scCO₂ generated unexpected peaks. The peak resulting from the noncrystalline regions of the polymer generated typically generally in the vicinity of 955 cm⁻¹ as a C=O stretching band.²⁸ The crystallization of the polymer also generates peaks due to the α form at 921 cm⁻¹, the α' form at 923 cm⁻¹, or the β form at 912 cm⁻¹.^{30,31} Following scCO₂ processing, although the peaks associated with noncrystalline regions were shifted from 956 to 957 cm⁻¹, the peak intensities were constant. However, a new band appeared at 921 cm⁻¹ subsequent to scCO₂ treatment at 60 to 80 °C and 14 MPa, and a band appeared at 919 cm⁻¹ following treatment at 40 °C and 14 MPa. The sample treated with scCO₂ at 40 °C and 14 MPa exhibited a gradual slope around 912 cm⁻¹ and this is believed to have resulted from a crystal structure consisting of α and β form. Thermal treatment at 80 °C evidently produced a band associated with an α' form at 923 cm⁻¹, demonstrating that scCO₂ processing and thermal treatment lead to variations in the extent of crystallization.

CONCLUSIONS

The T_m values of poly(L-lactide) samples were only slightly influenced by scCO₂ pressure or temperature. Since the T_m value of poly(L-lactide) is greater than 146 °C, this indicates that scCO₂ does not affect the T_m . In contrast, the T_g of the H-440 and REVODE changed with pressure and temperature, and those polymers with a lower T_g tended to be affected even under the mildest conditions (8 MPa, 40 °C). All T_g values were affected by pressure and temperature in a manner similar to T_m . Large changes in X_c DSC were also seen with variations in temperature or pressure. The X_c DSC indicates the extent of crystalline regions, and is dependent on both pressure and temperature. The DSC thermograms of these poly(L-lactide) samples on the first heating gave a different result for the REVODE than for the H-100 and H-440. Samples of the same polymer that differed in crystallinity were also affected differently by scCO₂ processing because of rearrangements of the lamellar structures in the crystalline regions. In addition, strengthening of the interactions between polymer chains occurred at certain temperatures during processing using scCO₂.

The T_m and X_c DSC values of the polymers, with the exception of the REVODE, were at a maximum, while T_g was at a minimum, at 100 °C. The decrease in T_g indicates that the interactions between polymer chains in the noncrystalline region were weak, allowing low molecular weight compounds to pass easily between the chains. XRD data for H-100 prepared with scCO₂ processing or heat-treated at 80 °C showed a maximum degree of crystallinity. From the results of FT-IR analyses, it was apparent that the scCO₂ processing was able to promote crystallization even under mild conditions. Although H-100 treated with scCO₂ showed crystallinity higher than the degree of crystallinity generated by thermal treatment alone on the basis of FT-IR spectra, XRD results showed the opposite. Both techniques found slight differences in 2θ or wavenumber values of peaks between scCO₂ processed and heat-treated specimens, even when applying the same temperature, suggesting variations in the degree of crystallinity. Based on all these data, we conclude

that the inclusion of CO₂ molecules during supercritical processing affects the re-arrangement of the polymer chains.

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