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Stereocomplex Formation of High-Molecular-Weight Polylactide Using Supercritical Fluid

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ABSTRACT: Stereocomplex polylactide has been known as one of the choices to enhance the properties of polylactides. Numerous studies have been carried out on stereocomplex formation and characterizations, but these have a limitation in the case of high-molecular-weight polylactides. The stereocomplex formation of high-molecular-weight polylactides was observed by supercritical CO_2 in the presence of solvent. Furthermore, the addition of solvent increased the degree of stereocomplex formation. We evaluated the degree of stereocomplex formation as a function of pressures, solvent concentration, temperature, and times. The high degree of stereocomplex formation was achieved at 30% of dichloromethane, 350 bar, and 65 °C. Compared with the solution casting method, stereocomplex formation by supercritical CO_2-solvent had a higher degree of stereocomplex formation, and dry product was obtained in situ. Significant improvements of thermal and mechanical properties have been assessed for the stereocomplex obtained by supercritical method compared with either the solution casting method or their homopolymers.

Introduction

Polylactides (poly D-lactide and poly L-lactide) are biodegradable, compostable, and producible from renewable resources. They have been used in many applications because of their biocompatibility and biodegradability. For wider applications, homopolymer polylactide has limitations because of thermal and mechanical properties. Stereocomplex polylactide (s-PLA) has been known as one of the choices to enhance the properties of polylactides.

s-PLA has been studied since its formation was discovered in the enantiomeric polymer blend of poly L-lactide (PLLA) and poly D-lactide (PDLA).[1] s-PLA has different properties than PLLA and PDLA homopolymers; the stereocomplex has a melting temperature (T_m) ~50 °C higher than the T_m of either PLLA or PDLA.[1,2] s-PLA can be used for many applications such as biodegradable films, biodegradable fibers, biodegradable microsphere, biodegradable hydrogels, nucleating agents, and others.[2]

Several reports investigated the formation of s-PLA in the presence of solvent (solution)[1,3−10] and in the absence of solvents (direct melt blending or during bulk polymerization).[11−15] The methods that are commonly used for s-PLA are solution casting and melt blending. Each method has its advantages and disadvantages. Every method must be evaluated on the basis of process ability, cost, time, and also environmental impact.

In s-PLA formation by solution casting, PLLA and PDLA homopolymers should be completely dissolved in good organic solvents (e.g., chloroform, dichloromethane). The solubility of the homopolymer was the most important factor in obtaining excellent/high degrees of s-PLA formation. This process usually requires much time to evaporate the solvent. The melt blending process is another option in making s-PLA. Direct melt blending of the PDLA/PLLA is not desirable because of the high processing temperatures required (> 230 °C), and at these temperatures, a significant degradation of the homopolymer can occur.[2] The ordinary melt blending of PDLA and PLLA produces their single polymer crystals preferentially.[16,17] By using both methods, the formation of s-PLA is difficult, particularly with the high molecular weights of PLLA and PDLA.[4,18,19] Tsuji and Ikada[19] reported that the critical value of M_w that the stereocomplex crystallites solely form is $\sim 1.0 \times 10^5$. Several researchers tried to investigate the formation of s-PLA from high-molecular-weight polylactide using melt blending, followed by a solid-state polycondensation method.[13,15] In this method, the melt blending temperature and time should be decreased so as to reduce the transesterification and depolymerization of the stereocomplex mixture.[13]

For these reasons, it is necessary to find an effective method for making s-PLA from high-molecular-weight polylactides. We were interested in studying s-PLA formation using supercritical fluids because of their unique properties, gas-like diffusivity, and liquid-like density.[20] The selection of supercritical fluid solvents to dissolve the polymers is often a challenge for processing applications because it is difficult to find a good supercritical fluid solvent that will dissolve the polymer under relatively moderate conditions.[21]

Supercritical carbon dioxide (sc-CO_2) is a viable choice for polylactide processing. Carbon dioxide has been chosen as a medium because it is environmentally friendly, nontoxic, nonflammable, and inexpensive.[22] These advantages, combined with the easily attainable critical parameters (T_c = 31.1 °C, P_c = 73.8 bar) makes CO_2 a solvent of choice for replacing a less ecological organic solvent. sc-CO_2 has been utilized extensively in basic studies, plasticization, and processing biopolymer. Kumar and coworkers have produced porous poly(DL-lactide-*co*-glycolide) by pressure quench method using sc-CO_2 as blowing agent.[23] Mooney et al. have fabricated macroporous sponges from synthetic biodegradable polymers using high-pressure CO_2 processing at room temperature.[24] Wynne investigated the swelling of polylactides in sc-CO_2 using the linear variable differential transformer (LVDT) method.[25] However, polylactides are hardly

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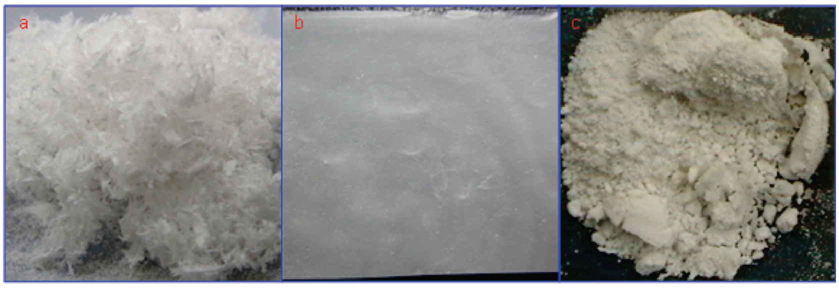

Figure 1. Material appearance: (a) PLLA and PDLA homopolymers; (b) s-PLA by solution casting; (c) s-PLA by sc-CO$_2$-dichloromethane.

dissolved in carbon dioxide, which has been used as an antisolvent when polymer particles have been formed using supercritical fluid processes, such as the supercritical antisolvent precipitation method.[26,27] Lee et al.[28] reported that poly(L-lactide) was not completely soluble in pure CO$_2$ at pressures as high as 80 MPa and at temperatures up to 373.15 K. There are several excellent solvents that can dissolve polylactide at room temperature such as chloroform, dichloromethane, dioxane, and so on. The addition of solvent to sc-CO$_2$ was predicted to increase the solubility of polylactide. The polar moment of solvent interacts favorably with the polar moment of the ester group in the polylactides.[21] The condition that can be used to determine the polymers completely dissolved in the supercritical fluid was called cloud point.

We have studied the s-PLA formation of the high-molecular-weight polylactide in the sc-CO$_2$-solvent system. To assess the s-PLA formation, we measured the degree of s-PLA formation as a function of solvent types, solvent concentrations, pressures, temperatures, and times. We also discuss thermal and mechanical properties of s-PLA and compare them with other methods.

Experimental Section

Materials. PDLA (M_n = 87 431 g/mol, M_w = 125 214 g/mol, PDI = 1.432) and PLLA (M_n = 87 287 g/mol, M_w = 153 725 g/mol, PDI = 1.761) were synthesize by bulk polymerization in Biomaterial Research Center, KIST. Chloroform, diethylether, acetone (Daejung Chemicals & Metal with a purity >99.5%), dichloromethane (JT Baker, HPLC grade), 1,4-dioxane (Sigma-Aldrich, purity ≥99%), tetrahydrofuran (Fischer ChemAlert Guide, HPLC grade), and CO$_2$ (Shin Yang Oxygen Industry, minimum purity 99.9%) were used as received.

Stereocomplex Formation. PDLA and PLLA with 1:1 weight ratio were added to a 40 mL stainless steel high-pressure reactor equipped with magnetic stirring and electrical heating mantle. The weight ratio of total polymer to total solvent (CO$_2$ and solvent) ratio was 5:100. The reactor was purged with nitrogen for 5 min and vacuumed at 40 °C for 1 h. The solvent was added by syringe, and the reactor was connected to a CO$_2$ feed system. The reactor was filled with liquid CO$_2$ to 100 bar at 30 °C and then gradually heated to 65 °C to achieve a pressure of 250 bar. s-PLA formation was allowed to proceed for the predetermined times (5 h) and the reactor was opened immediately after the reaction had finished. The solvent type, solvent concentration, pressures, temperature, and time were also varied.

Characterizations. The degree of s-PLA formation was measured by a modulated differential scanning calorimeter (modulated DSC 2910, TA Instrument). The heating rate was fixed at 10 °C/min. X-ray diffraction spectra were registered with a X-ray diffractometer Rigaku D/Max-2500 composed of Cu K$_\alpha$ (λ = 1.54056 Å, 30 kV, 100 mA) source, a quartz monochromator, and a goniometric plate. Thermogravimetric analysis (TGA) was conducted on a Hi-Res TGA 2950 (TA Instrument) under N$_2$ flow. For mechanical properties, we made a film using the pressure instrument equipped with a heating block (250 °C) and polyimide vacuum bag. The mechanical properties were measured on an Instron apparatus. The specimen size was 20 × 5 mm, and the thickness was about 170 μm. The distance between the supports was 10 mm, and the extension rate was 3 mm/min.

Results and Discussion

We investigated the s-PLA formation by the sc-CO$_2$-solvent. We tried different solvent, solvent concentration, and also processing parameters (pressures, temperatures, and times) to obtain the optimum processing condition. In our experiments, the optimum condition of sc-CO$_2$-solvent processing is sc-CO$_2$-dichloromethane at 65 °C and 350 bar for 5 h. We also compared s-PLA by sc-CO$_2$-solvent with by solution casting.

From our experiments, s-PLA by sc-CO$_2$-dichloromethane has different results compared with by solution casting. Figure 1 shows the appearance of s-PLA resulting from by sc-CO$_2$-dichloromethane compared with from solution casting. The solution casting method resulted in a solution that needs to be evaporated for a long period of time.[1-3,8,9] The final shape of the solution casting method was a thin film that was very difficult to make into a powder form for further applications. sc-CO$_2$-dichloromethane showed different phenomena. When the reactor was opened, the mixture of CO$_2$ and dichloromethane came out directly. There was no s-PLA in that mixture. By looking at these phenomena, we assumed that the homogeneous supercritical fluid became turbid, and a solid precipitated (the stereocomplex particles grow in a suspended state) and become clear again. First, homopolymers mixtures were of homogeneous state in supercritical fluid, and then the s-PLA formed was suspended. So, the final condition of sc-CO$_2$-dichloromethane containing s-PLA was heterogeneous state. The hydrogen bonding (CH$_3\cdots$O=C interaction) is the driving force for the nucleation of PLA stereocomplex crystallites.[2] The s-PLA by sc-CO$_2$-dichloromethane resulted in a dry product (powder and solid porous material) of s-PLA because the fluid was easily removed from the product. We could obtain the powder form of stereocomplex easily by using the sc-CO$_2$-dichloromethane method.

The PLLA and PDLA have left- and right-handed helical conformations. In the s-PLA structure, both PLLA and PDLA chains with opposites-hand conformation are packed side by side in parallel fashion and folded to form lamella. The helical conformation and crystal structure of PDLA and PLLA change when s-PLA crystallites are formed. It caused the X-ray diffraction pattern of s-PLA to differ from that of its homopolymers.[29] X-ray diffraction can be used to confirm the s-PLA formation from different methods.

For the PDLA and PLLA homopolymer, the diffraction peaks (Figure 2a) were observed at 2θ 16.52 and 19.08°. s-PLA by sc-CO$_2$-dichloromethane showed a single diffraction peak at 2θ 11.88° with high intensity. s-PLA by solvent casting showed diffraction peaks at 2θ 11.88, 16.78, and 19.08°, but peak intensity at 11.88° was very small compared with the peaks at 16.78 and 19.08°. It indicates that the s-PLA formation using a solution casting resulted in a small portion of s-PLA, but s-PLA using sc-CO$_2$-dichloromethane produced complete s-PLA formation.

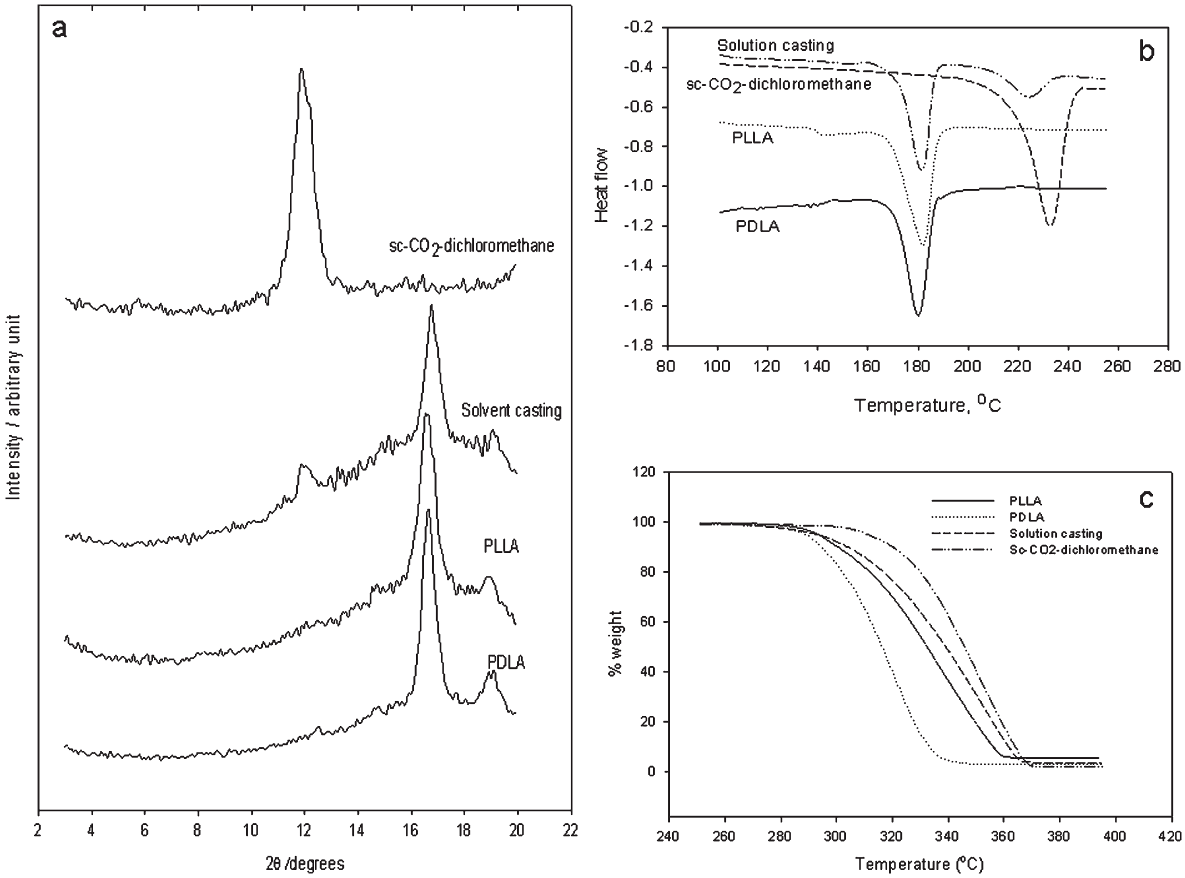

Figure 2. Comparison among PLLA, PDLA, and s-PLA using different methods: (a) X-ray diffraction patterns; (b) DSC thermogram; (c) TGA thermogram.

Table 1. Onset Temperature of Thermal Degradation and the Mechanical Properties of Homopolymers and s-PLA

materials	onset temperature (°C)	elongation at break (%)	tensile strength (MPa)	Young's modulus (GPa)
PDLA	278	2.14	14.3	1.60
PLLA	280	2.36	10.9	1.59
sc by solution casting	280	3.67[a]	36.4[a]	1.64[a]
sc by sc-CO_2-dichloromethane	305	4.31[b]	47.8[b]	2.02[b]

[a] Degree of stereocomplex after hot-pressing process: 24.4%. [b] Degree of stereocomplex after hot-pressing process: 94.7%.

From these results, it can be concluded that the s-PLA formation in sc-CO_2-dichloromethane is better than the solution casting method.

Stereocomplex can enhance the thermal properties of PDLA or PLLA homopolymers. s-PLA had a T_m at 230 °C, which was 50 °C higher than the T_m of PLLA or PDLA (Figure 2b). The T_m of these polymers was also critically dependent on the crystal size. Usually, the s-PLA crystallites formed in the mixed PLLA/PDLA samples could also nucleate the single-polymer crystals, so both single and stereocomplex crystallizations were induced simultaneously. The s-PLA were more strongly bound by the crystal network and had a slightly decreased motion compared with those in PLLA.[29] s-PLA by sc-CO_2-dichloromethane had a single peak at 230 °C, but s-PLA using the solution casting had peaks at 180 and 230 °C. The s-PLA by sc-CO_2-dichloromethane obtained 100% degree of stereocomplex, but the s-PLA by solution casting only obtained about 25.9%. This result was similar to X-ray diffraction analysis, which indicates that these methods have different degrees of s-PLA formation.

In the case of high-molecular-weight polylactide, it was very difficult to obtain a high degree of s-PLA formation by the melt blending process[16,17] and solid-state polycondensation.[15] Fukushima and Kimura[15] reported that the solid-state polycondensation process can obtain the latent s-PLA with thermal properties almost similar to those of their homopolymer.

Thermogravimetric analysis is an effective approach for evaluating the thermal properties of polymer materials. The stereocomplex has higher thermal degradation than homopolymer (Figure 2c). Table 1 shows that s-PLA has a different onset temperature of thermal degradation. The s-PLA by sc-CO_2-dichloromethane is excellent compared with the solution casting method, so it has a higher onset temperature of thermal degradation. It was caused by a strong interaction between L-lactide and D-lactide chains, which have a significant effect on reducing molecular mobility and, therefore, in disturbing the thermal degradation.[2,7]

Table 1 also shows that the mechanical properties of s-PLA improved. s-PLA using sc-CO_2-dichloromethane also had better mechanical properties compared with s-PLA by solution casting. The elongations at break and tensile strengths increased almost twice as high as neat homopolymers. The Young's modulus also increased 25% greater than neat homopolymers. This was caused by a high degree of s-PLA. In the case of s-PLA by solution casting, the increasing mechanical properties of s-PLA were ascribed to the microphase structure in which many s-PLA acted as intermolecular cross-links that connect homopolymers crystallites.[19]

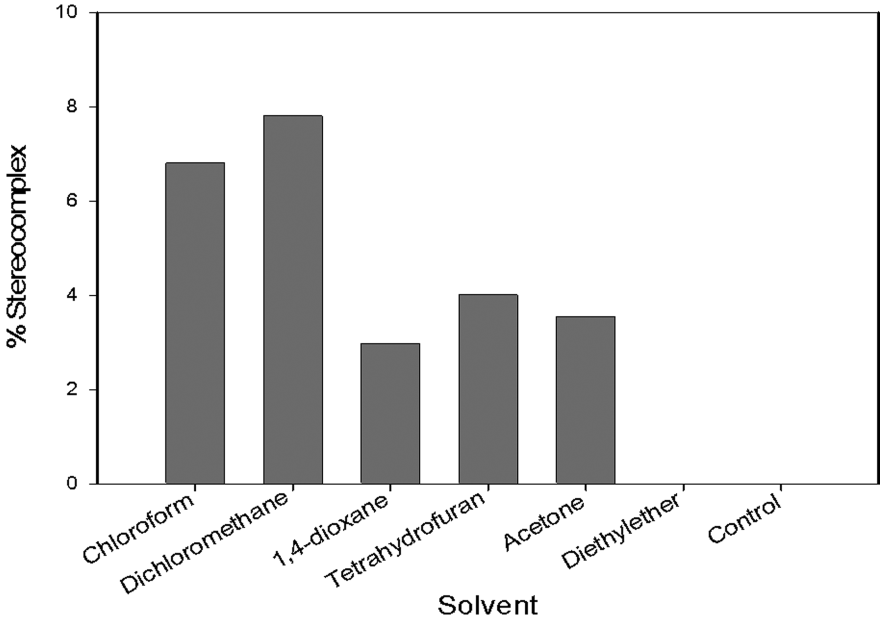

Figure 3. Degree of s-PLA formation by several organic solvents (10% w/w) in sc-CO_2-solvent at 250 bar and 65 °C for 5 h.

Table 2. Solubility Parameters of Polylactide and Solvents at 25 °C

material	δ_{d} (J/cc)$^{0.5}$	δ_{p} (J/cc)$^{0.5}$	δ_{h} (J/cc)$^{0.5}$	δ_{t} (J/cc)$^{0.5}$
polylactide[a]	17.61	5.30	5.80	19.28
chloroform[b]	17.80	3.10	5.50	18.90
dichloromethane[b]	18.20	6.30	6.10	20.20
1-4 dioxane[b]	19.00	1.80	7.40	20.50
tetrahydrofuran[b]	16.80	5.70	8.00	19.50
acetone[b]	15.00	10.40	7.00	19.60
diethylether[b]	14.50	2.90	5.10	15.60

[a] By intrinsic 3D viscosity method.[30] [b] Ref 31.

By comparing the degree of s-PLA formation and mechanical properties, it was found that sc-CO_2-dichloromethane can be used as a media to synthesize s-PLA from high-molecular-weight polylactides.

As we explained previously, the optimum conditions for s-PLA formation by sc-CO_2-solvent are determined by the effectiveness of the processing parameter (solvent type, solvent concentration, pressures, temperatures, and times).

We used high-molecular-weight polylactides to evaluate many variables related to s-PLA formation. We evaluated the degree of s-PLA formation by comparing ΔH_{m} of the melting point (T_{m}) of s-PLA (T_{m} ± 230 °C) and their homopolymers (T_{m} ± 180 °C). The solubility of polylactide homopolymers in supercritical fluid is the most important factor in making a stereocomplex. The solubility parameters can be used for predicting the solubility of polylactide. The solvent, which has solubility parameters close to those of polylactides, has better capability to dissolve polylactides. Based on the solubility parameter data of polylactide and solvents (Table 2), we understand that chloroform, dichloromethane, 1,4-dioxane, tetrahydrofuran, and acetone can be used as solvents, but diethyl ether is a nonsolvent.

The solvent effect on the degree of s-PLA formation is shown in Figure 3. Dichloromethane has a higher degree of s-PLA formation (7.81%) compared with other solvents: chloroform, 6.80%; dioxane, 2.97%; tetrahydrofuran, 4.01%; acetone, 3.55%; and diethyl ether, 0%. Different degrees of s-PLA formation resulted from the interaction of polylactide, CO_2, and solvent under a supercritical condition. Lee and Kuk[21] reported that the addition of dichloromethane to CO_2 caused an increase in dissolving power of mixed solvent because of the increase in the solvent polarity. Dichloromethane had a better interaction with CO_2 because of its lower boiling point and polarity index (3.10). The polar moment of dichloromethane can interact with the polar moment of the ester group of polylactide. These interactions make polylactide more soluble in this system compared with other solvents.

Several reports have been published on the cloud point of polylactide in supercritical fluids.[21,28,32] For example, Lee and Kuk showed that cloud point pressure was characterized as a function of temperature, solvent composition, and polymer molecular weight.[21]

We varied pressures from 200 to 350 bar to investigate the effect of pressure upon s-PLA formation (Figure 4a). At low pressure (200 bar), we obtained 4.89% s-PLA formation, which increased linearly by increasing pressure: 7.81% at 250 bar, 13.30% at 300 bar, and 19.95% at 350 bar. Lim et al.[33] reported that the increase in solubility may have been attributed to the higher pressures, which necessarily cause the solvent density to increase. These results suggest that the degree of s-PLA formation is dependent on solvent density for this system. The highest degree of s-PLA under this condition was 19.95%, indicating that PDLA and PLLA were not completely soluble.

To investigate the effect of solvent concentration on s-PLA formation, we varied the ratio of solvent to CO_2 (% w/w) from 5 to 30% with a process parameter 350 bar and 85 °C for 5 h. In the sc-CO_2-solvent system, the solubility increased in an approximately exponential fashion with increasing solvent concentration.[34] Increasing solvent concentration can increase the degree of s-PLA formation drastically (Figure 4b). At solvent concentrations of 5, 10, and 20%, the degree of s-PLA formation was 8.82, 19.13, and 52.04%, respectively. At the higher concentration of solvent (30%), the degree of s-PLA formation increased to ca. 80%. As noted earlier, carbon dioxide has an antisolvent property, and dichloromethane has a solvent property. Therefore, increases in dichloromethane concentration were followed by decreases in carbon dioxide concentration. This means that solvent properties increased and antisolvent properties decreased. Therefore, the solvation power of the sc-CO_2-solvent system increased and dissolved both homopolymers to form a stereocomplex.

As noted, the addition of 30% dichloromethane to carbon dioxide caused a significant increase in the dissolving power of mixed solvents. We continued the experiment to evaluated

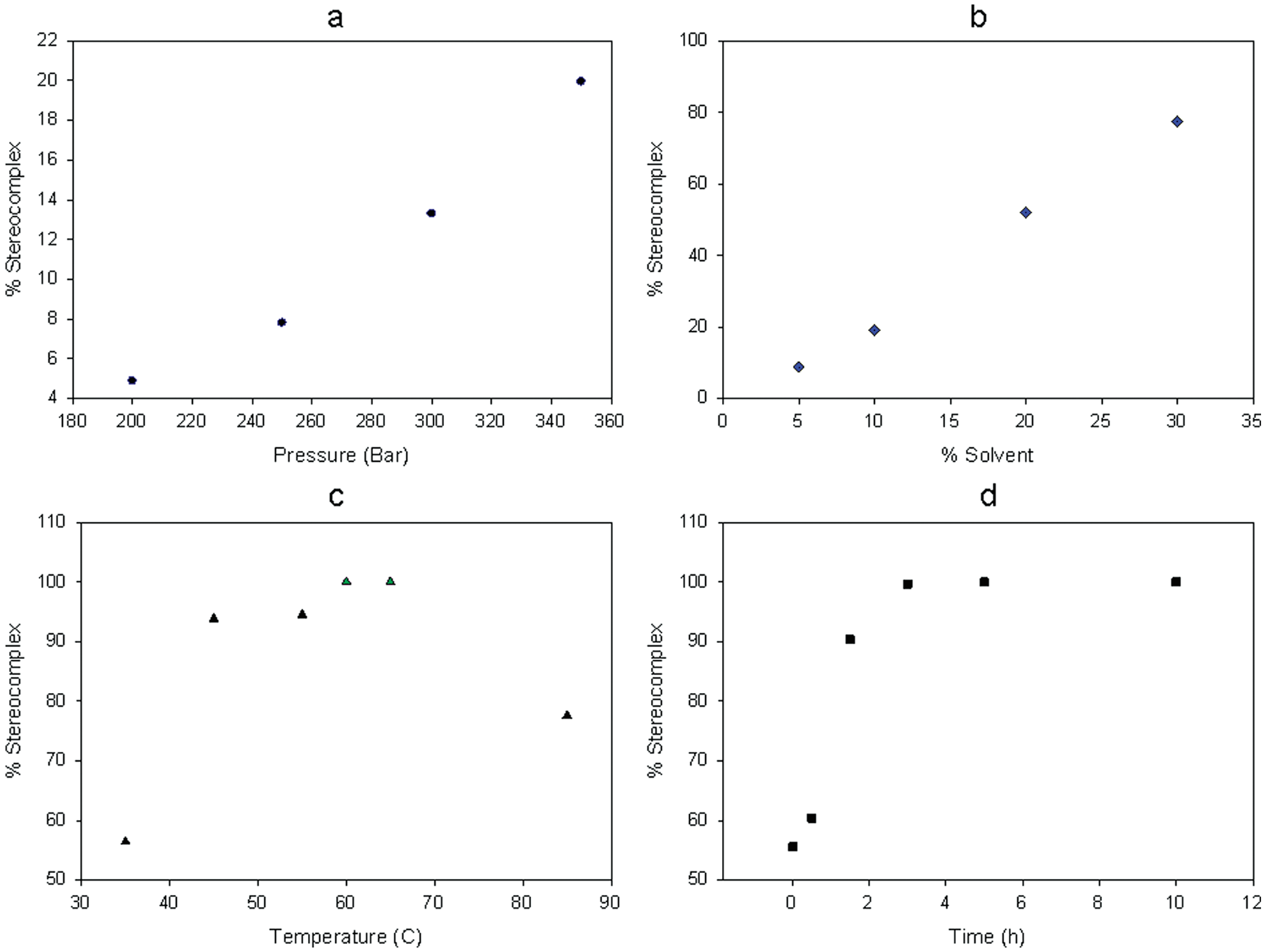

Figure 4. Processing parameter effect on s-PLA formation using sc-CO_2-dichloromethane: (a) pressure effect (dichloromethane 10%, 65 °C, 5 h); (b) solvent concentration effect (350 bar, 85 °C, 5 h); (c) temperature effect (dichloromethane 30%, 350 bar, 5 h); (d) time effect (dichloromethane 30%, 350 bar, 65 °C).

temperature effects in a series of s-PLA processing conducted at temperatures ranging from 35 to 85 °C at 350 bar, 5 h, and 30%.

Increasing temperature increased the s-PLA formation and decreased after the optimum condition (Figure 4c). Optimum conditions were reached at 60−65 °C, which resulted in 100% of s-PLA. These conditions reached cloud point; the system was single phase and completely dissolved both homopolymers. Below 60 °C (35 °C, 45 and 55 °C), the polymer was not completely dissolved. The degrees of s-PLA formation were 56.40% at 35 °C, 93.85% at 45 °C, and 94.51% at 55 °C. Lee and Kuk[21] reported that this condition was fluid to liquid−vapor phase transition (open squares). At 85 °C, the degree of s-PLA formation decreased (77.55%). This condition was below the cloud point because increasing temperature decreased the solvent density that related to solubility. Lim et al. reported that the increase in solubility may have been attributed to higher pressures that necessarily caused the solvent density to increase.[33]

As indicated in Table 3, the increasing pressure and temperature were necessary to maintain solvent density. The data suggest that the pressure necessary to maintain the solvent density and the polymer solution in the single-phase region increased as temperature increased.

Dissolving polymer requires more time than dissolving monomer because polymer is a macromolecule. By varying the processing time, we obtained a minimum time that can dissolve polymers effectively. From Figure 4d, the degree of s-PLA formation at 1 min, 30 min, 1.5 h, 3 h, 5 h, and 10 h is 55.62, 60.37, 90.35, 99.65, 100, and 100, respectively. These results suggest that increasing time will increase the degree of s-PLA formation until a maximum degree (100%) and stabilize at a maximum limit. At a processing time of 1 min, we obtained 55.62% s-PLA formation because we could not reach this processing condition directly. It required time to set up and reach the processing condition, which means some degree of stereocomplex was formed before the processing condition was reached. When pressure and temperature were increased, the homopolymer was only partially dissolved, as shown in Table 3 (pre reaction conditions).

Table 3. Prereaction Conditions and Necessity of Pressure−Temperature in s-PLA Formation by sc-CO_2-dichloromethane 30%

time	pressure (bar)	temp (°C)	% stereocomplex
0 m[a]	120	25	0
20 m[a]	240	45	12.05
30 m[a]	300	55	23.02
5 h	400	75	100
5 h	400	85	81.83
5 h	450	85	97.29

[a] Prereaction conditions to reach 350 bar 65 °C.

Conclusions

The use of the sc-CO_2-dichloromethane system offers unique opportunities for s-PLA synthesis, although the processes have to be carried out at high pressures. Specifically, we synthesized s-PLA using sc-CO_2-dichloromethane at 350 bar and 65 °C for 5 h. We succeeded in forming excellent s-PLA using high-molecular-weight polylactide homopolymers ($M_w >$ 100.000) that are difficult to prepare using conventional methods. The sc-CO_2-dichloromethane system resulted in a dry s-PLA product (powder and solid porous material) because the fluid was easily removed from the product. This method has promising applications in polymer processing. We expect that the sc-CO_2-solvent system will be used more widely in polymer processing.

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Supporting Information Available: Materials appearance, experimental data (containing: X-ray diffraction patterns, DSC thermogram, and TGA thermogram), and degree of stereocomplex measurements (solvent type effect and processing parameter effect). This information is available free of charge via the Internet at http://pubs.acs.org/.

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