Temperature-dependent Crystallization and Phase Transition of Poly(L-lactic acid)/CO$_2$ Complex Crystals

Ying Zheng$^{a,b}$, Cai-Liang Zhang$^{a,b}$, Yong-Zhong Bao$^{a,b}$, Guo-Rong Shan$^{a,b}$, and Peng-Ju Pan$^{a,b,*}$

$^a$ State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China
$^b$ Institute of Zhejiang University-Qzhou, Qzhou 324000, China

**Abstract**
Semicrystalline polymers can crystallize in the unique crystalline polymorph and show different phase behaviors under the high-pressure CO$_2$ treatment. Understanding such unique crystallization and phase transition behavior is of fundamental importance for the CO$_2$-assisted processing of semicrystalline polymers. Herein, we investigated the polymorphic crystalline structure, phase transition, and structure-property relationships of poly(L-lactic acid) (PLLA) treated by CO$_2$ at different pressures (1−13 MPa) and crystallization temperatures ($T_c$'s, 10−110 °C). PLLA crystallized in the PLLA/CO$_2$ complex crystals under 7−13 MPa CO$_2$ at $T_c$≤550 °C but the common α crystals under the high-pressure CO$_2$ at $T_c$≥370 °C. Solid-state nuclear magnetic resonance analysis indicated that the PLLA/CO$_2$ complex crystals possessed weaker interactions between the PLLA chains than the common α crystals. The PLLA/CO$_2$ complex crystals were metastable and transformed into the thermally stable α crystals via the solid-to-solid route during heating or annealing at the temperature above 50 °C. The complex crystals of PLLA produced at low $T_c$ was more ductile than the α crystals due to the lower crystallinity and the plasticizing effect of CO$_2$.

**Keywords** Poly(lactic acid); CO$_2$ Complex crystal; Phase transition

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**INTRODUCTION**
As a potential substitute of the petroleum-based polymers, poly(l-lactide) (PLLA) derived from the plant-derived chemicals has attracted increasing interests in both the scientific and technological fields due to its good biocompatibility, biodegradability, processing ability, and mechanical property.$^{[1,2]}$ As a typical semicrystalline polymer, physical properties of PLLA depend strongly on the crystalline structure, morphology, and crystallinity ($X_c$)$^{[3−8]}$. PLLA is a representative polymorphic polymer that can grow in several crystal modifications such as α$^{[9]}$, α' or Δ$^{[10]}$, α$^{[11]}$, β$^{[12]}$, γ$^{[13]}$ forms, and mesophase.$^{[14,15]}$ In addition to these polymorphs, PLLA is also able to cocrystallize in the complex crystals with CO$_2$ and some organic solvents$^{[16−19]}$ under the specific conditions. In the case of PLLA/CO$_2$ complex crystals, the CO$_2$ molecules are encapsulated in the cavity surrounded by four PLLA chains in the crystal unit cell.$^{[16]}$

Compressed and supercritical CO$_2$ has been widely used as the plasticizer and foaming agent in polymer processing, since CO$_2$ is an environmentally-friendly, removable solvent and can easily reach the critical condition (31.1 °C, 7.37 MPa)$^{[20,21]}$. Analogous to the organic solvent, CO$_2$ could permeate into the polymer matrix and act as a diluter or plasticizer to enhance the chain mobility of polymers. Therefore, the treatment by CO$_2$ can influence the crystallization kinetics, crystalline structure, morphology, and phase transition of semicrystalline polymers, depending on the treatment conditions (e.g., treatment time, temperature, and CO$_2$ pressure). The CO$_2$-influenced crystallization and phase transition have been found in many polymers such as syndiotactic polystyrene (sPS)$^{[22−24]}$, poly(ethylene terephthalate)$^{[25]}$, isotactic poly(1-butene)$^{[26,27]}$, poly(vinylidene fluoride)$^{[28]}$, polycarbonate$^{[29]}$ and PLLA$^{[15,16,18,30−32]}$.

Due to the plasticizing effect, the CO$_2$ treatment generally depresses the glass transition temperature ($T_g$) of polymers, which enables the polymers to crystallize at a low temperature below the usual $T_g^{[25,33−35]}$. Crystallization of PLLA was accelerated at low temperature while slowed down at high temperature under the high-pressure CO$_2$ treatment$^{[32,34]}$. In addition to the crystallization kinetics, CO$_2$ treatment also triggered the semicrystalline polymers to grow in the crystals having the specific unit cell structure, morphology$^{[10,15,22,31]}$ and phase transition behavior.$^{[22−24]}$ Previous studies have demonstrated that PLLA crystallized in the unique metastable polymorph under the high-pressure CO$_2$ treatment. PLLA grows in a new crystal polymorph (α$^*$ form) after the high-pressure CO$_2$ treatment at a low crystallization temperature ($T_c = 0$−30 °C)$^{[10]}$. The α$^*$ crystals of PLLA are disordered and have the looser chain packing structure compared to the thermally stable α crystals. The spherulite size of PLLA treated
by CO₂ at high pressure (3−15 MPa) is enhanced and the crystalline morphology transformed from the micro-sized spherical to the nano-sized rodlike superstructure as T_c is increased.[18] CO₂ treatment also influenced the phase transition behavior of semicrystalline polymers. For example, the unique phase transition (e.g., γ-to-β crystal transition) of sPS, which did not take place under atmospheric condition,[36,37] could be triggered by treating with high-pressure CO₂.[23,24] Therefore, control over the crystalline structure and morphology by CO₂ treatment imparts the semicrystalline polymers tunable microstructure, physical properties, and foaming behavior in polymer processing.

Despite the recent progresses in the CO₂-induced crystallization and polymorphic structure of PLLA, the formation condition, structural feature, and phase transition of PLLA/CO₂ complex crystals have been unexplored or far from well understood. In this study, we aim to elucidate the formation condition of PLLA/CO₂ complex crystals in the broad CO₂ pressure (1−13 MPa) and T_c (10−110 °C) range, as well as the thermal stability and thermally-induced phase transition of PLLA/CO₂ complex crystals in the heating and annealing processes. The solid-state structure of different crystal polymorphs of PLLA (PLLA/CO₂ complex and α crystals) were investigated and compared. The underlying mechanism for the complex-to-α crystalline phase transition was discussed. Relationships between the polymorphic crystalline structure and mechanical property of CO₂-treated PLLA materials were also elucidated.

EXPERIMENTAL

Materials and Sample Preparation

PLLA (M_w=155 kg/mol, D=1.62, optical purity>99%) was purchased from Purac Co. (Gorinchem, the Netherlands) and used as received. PLLA pellets were compression-molded into the film (thickness ~0.4 mm) after melting at 190 °C for 3 min. Subsequently, the PLLA film was quenched into liquid nitrogen to obtain the amorphous sample.

To prepare the CO₂-treated PLLA film, the amorphous PLLA film was placed into a pressure vessel and treated by CO₂ at the desired T_c (10−110 °C) and pressure (1−13 MPa) for 4 h. After the CO₂ treatment, the vessel was depressurized to the atmospheric pressure. Then, the CO₂-treated PLLA film was taken out of the vessel; this sample was marked as the as-taken sample. The as-taken sample was further aged at 20 °C in air for 48 h (marked as the RT-aged sample), where RT meant the room temperature. We note that the RT aging was conducted in air but not in vacuum; most of CO₂ resided in the PLLA/CO₂ complex crystals was desorbed in such aging process. Unless otherwise specified, the RT-aged PLLA (20 °C, 48 h, in air) but not the as-taken PLLA was used in this study.

Characterizations

Differential scanning calorimetry (DSC)

DSC analysis was conducted on a NETZSCH 214 Polyma DSC (NETZSCH, Germany) equipped with an IC70 intercooler. The sample (8−10 mg) was heated from 20 °C to 190 °C at the heating rate of 10 °C/min to measure the melting behavior.

Wide angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS)

WAXD and SAXS measurements were performed on the beam-line BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF) with the X-ray wavelength of 0.124 nm. The sample-to-detector distances were 0.16 and 2.0 m for the WAXD and SAXS analyses, respectively. For the temperature-variable measurements, the sample sandwiched by polyimide films was heated from 30 °C to 190 °C at 10 °C/min on a Linkam THMS600 hot stage. WAXD and SAXS patterns were recorded with a temperature interval of 5 °C. In the time-dependent WAXD analysis, the CO₂-treated PLLA (7 MPa, T_c=10 °C, 4 h) was annealed on the hot stage at 50 °C for 10 min, during which the diffraction pattern was recorded every 0.5 min. The collection time of each WAXD and SAXS pattern was 15 s. 2D patterns were converted to the 1D profile by integration via a Fit2D software.

Solid-state nuclear magnetic resonance (NMR) spectroscopy

Solid-state NMR was analyzed on a Bruker Avance 400 III HD spectrometer (magnetic field strength: 9.7 T) at the resonance frequency of 100.61 MHz for ²³Na using the cross-polarization (CP), magnetic-angle spinning (MAS), and a high-power ¹H decoupling. The spectra were measured on a 3.2 mm MAS probe at a spinning speed of 10 kHz, with a 2.4 µs ¹H π/2 pulse, a 2 ms CP pulse, and a recycle delay of 5 s. The methylene signal of adamantane at 38.5 ppm was used as the reference of ¹³C chemical shift.

Fourier-transform infrared (FTIR) spectroscopy

FTIR spectra were measured on a NICOLET iS550 FTIR spectrometer (Thermo Scientific, USA) equipped with an MCT detector in the transmission mode.

Uniaxial tensile test

Tensile tests were performed on a SUNS UTM2503 instrument under a strain rate of 5 mm/min at the ambient temperature. The dumbbell specimen with a length of 35 mm, a cross-section width of 3.0 mm, and a thickness of ~0.4 mm was cut from the CO₂-treated PLLA films. Seven replicated measurements were performed for each sample and the averaged results were used.

RESULTS AND DISCUSSION

Melting Behavior and CO₂ Absorptivity

Figs. 1(a) and 1(b) show the DSC heating curves of the as-taken and RT-aged (20 °C, 48 h, in air) PLLA films after CO₂ treatment at 7 MPa, T_c = 10−110 °C for 4 h. DSC results of the amorphous PLLA and corresponding aged sample (20 °C, 48 h, in air) were also included for comparison. Both the amorphous and aged PLLAs exhibited the broad cold-crystallization peak at ~130 °C and the melting peak at ~175 °C. As shown in Fig. 1(a), the as-taken PLLAs showed the similar melting behavior after treating by CO₂ at T_c = 10−110 °C. Single melting peak located at ~175 °C was seen for all the CO₂-treated PLLAs, analogous to the melting temperature (T_m) of melt-crystallized PLLAs under the atmospheric condition. Intriguingly, PLLA could even crystallize at the low T_c of 10−30 °C under high-pressure CO₂ attributable to the depression of PLLA T_m due to the plasticizing effect of CO₂.[25,33−35] The RT-aged PLLAs (20 °C, 48 h, in air) had the very similar T_m to those of the as-taken ones (Fig. 1b). However, the enthalpy relaxation peak was detected for the RT-aged PLLAs with T_c = 10−30 °C, similar to the physically-aged amorphous PLLA.[35] The occurrence of enthalpy relaxation implied the low X_s and less ordered crystalline structure for the PLLAs treated by CO₂ at low T_c.

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The CO$_2$ molecules could penetrate into PLLA under high pressure and most of the CO$_2$ was desorbed when the as-taken PLLA was stored or aged under the ambient condition. In order to quantitatively evaluate the absorptivity of CO$_2$, we calculated the CO$_2$ absorptivity (g CO$_2$/g PLLA) in the as-taken PLLA films according to the weight change of PLLA before and after CO$_2$ treatment. Fig. 1(c) shows the absorptivity of CO$_2$ in the as-taken PLLA films crystallized in 7 MPa CO$_2$ at different $T_c$’s. The absorptivity of CO$_2$ in PLLA was the highest (22.3%) at $T_c$=10 °C and dropped to 4.52% with $T_c$ increasing.
from 10 °C to 110 °C. The decrease of CO\textsubscript{2} absorptivity with T\textsubscript{c} followed a nearly linear trend at T\textsubscript{c} = 10–90 °C. However, most of CO\textsubscript{2} desorbed from PLLA after aging at the ambient conditions for 48 h. After RT-aging in air for 48 h, the CO\textsubscript{2}-treated PLLAs with T\textsubscript{c} = 10–50 °C had the slightly higher CO\textsubscript{2} absorptivity of ~1.7%, compared to the ~0.3% for the PLLAs treated at above 70 °C. This was originated from the growth of different crystal polymorphs at low and high T\textsubscript{c}'s, as elaborated in the following section.

On basis of the results of DSC and CO\textsubscript{2} absorptivity, we evaluated the X\textsubscript{c} values of CO\textsubscript{2}-treated PLLAs by comparing the melting enthalpy (∆H\textsubscript{m}) to the corresponding value of PLLA with the infinite thick lamellae (∆H\textsubscript{m} = 93.4 J/g), as shown in Fig. 1(d). ∆H\textsubscript{m} was normalized by the weight of PLLA. X\textsubscript{c} of CO\textsubscript{2}-treated PLLA increased with the increase of T\textsubscript{c}, attributed to the formation of more regular and ordered crystals at high T\textsubscript{c}. X\textsubscript{c} of CO\textsubscript{2}-treated PLLA improved from 51.4% to 54.9% as the T\textsubscript{c} increased from 10 °C to 110 °C; they slightly increased after aging at room temperature for 48 h (Fig. 1d).

The CO\textsubscript{2}-treated PLLAs with low T\textsubscript{c} (10–30 °C) were as transparent as the amorphous PLLA (Fig. 1e). The transparency of CO\textsubscript{2}-treated PLLAs dropped with the increase of T\textsubscript{c} due to the enhancement of X\textsubscript{c} and the change of crystalline morphology. It has been reported that the crystalline morphology of CO\textsubscript{2}-treated PLLAs transformed from the nanosized rod-like to usual spherulite superstructures with increasing T\textsubscript{c}.[10]

**Formation of PLLA/CO\textsubscript{2} Complex Crystals**

Crystalline structure of CO\textsubscript{2}-treated PLLAs (7 MPa, T\textsubscript{c} = 10–110 °C, 4 h) was investigated via WAXD, FTIR and solid-state NMR spectroscopy. All the PLLAs used for the following structural studies were the RT-aged sample (20 °C, 48 h, in air), in which most of CO\textsubscript{2} was desorbed. Figs. 2(a) and 2(b) show the WAXD patterns and FTIR spectra of CO\textsubscript{2}-treated PLLAs (7 MPa, 4 h) with different T\textsubscript{c}'s. The CO\textsubscript{2}-treated PLLAs crystallized at high T\textsubscript{c} (60–110 °C) exhibited the typical diffraction profiles of α crystals.[2] However, the CO\textsubscript{2}-treated PLLAs showed different diffraction profiles from the usual α and α' crystals when the T\textsubscript{c} was decreased to below 50 °C (10–50 °C); a strong diffraction peak was seen at 2θ = 12.3°, demonstrating the formation of PLLA/CO\textsubscript{2} complex crystals.[16] It has been reported that the polymers bearing electron donor groups (e.g., carbonyl) had the unique Lewis acid-base interactions with CO\textsubscript{2}.[40] Due to the PLLA/CO\textsubscript{2} intermolecular interactions and high absorptivity of CO\textsubscript{2} in PLLA, PLLA was favored to form the complex crystals with CO\textsubscript{2} at a low T\textsubscript{c} (10–50 °C). The critical transition temperature from complex to α crystals located at 50–60 °C, consistent with the T\textsubscript{c} of PLLA.

FTIR spectroscopy was further employed to investigate the T\textsubscript{c}-dependent crystalline structure of CO\textsubscript{2}-treated PLLAs. As shown in Fig. 2(b), the CO\textsubscript{2}-treated PLLAs with high T\textsubscript{c} (≥70 °C) exhibited a conformation-sensitive band at 921 cm\textsuperscript{-1}, which was a pure crystalline band corresponding to the 10\textsubscript{h} helical chains in the crystalline phase of PLLA α or α’ crystals.[8,41] However, this conformation-sensitive band shifted to 918 cm\textsuperscript{-1} at the low T\textsubscript{c} (550 °C), demonstrating that the chain conformation of complex crystals was similar to but slightly different from that of the usual α or α’ crystals (10\textsubscript{h} helix, 921 cm\textsuperscript{-1}). The conformational feature of complex crystals may be attributed to the special intermolecular interactions between CO\textsubscript{2} and PLLA. We note that the FTIR spectra of CO\textsubscript{2}-treated PLLA did not change during aging at ambient condition for 48 h, demonstrating that the RT-aging and CO\textsubscript{2} desorption at room temperature did not vary the crystal polymorph.

Fig. 3 shows the 13C CP-MAS NMR spectra for the carbonyl, methine, and methyl carbons of CO\textsubscript{2}-treated PLLA (7 MPa, 4 h) with T\textsubscript{c} = 10 and 110 °C. Crystallization at 10 and 110 °C gave the complex and α crystals, respectively. NMR spectrum of complex crystals was distinct from that of the α crystals.

**Fig. 2** (a) WAXD patterns and (b) FTIR spectra in 975–850 cm\textsuperscript{-1} wavenumber region of PLLA. PLLA was treated with 7 MPa CO\textsubscript{2} at different T\textsubscript{c}'s for 4 h and then aged at ambient condition for 48 h.

**Fig. 3** 13C CP-MAS NMR spectra of PLLA treated with 7 MPa CO\textsubscript{2} treatment at 10 and 110 °C for 4 h and then aged at ambient condition for 48 h: (a) carbonyl carbons; (b) methine carbons; (c) methyl carbons.
The α crystals exhibited dual or multiple resonance splitting for each carbon, due to the presence of crystallographically inequivalent sites in the molecular chain caused by the intermolecular interactions. However, the complex crystals showed single and broad resonance peak for each carbon, similar to the results of amorphous PLLA and α crystals. This suggests that the complex crystals possessed looser, less ordered packing, and weaker interactions between the PLLA chains, compared to the α crystals. It is understandable that the preferable interactions (Lewis acid-base interactions) between PLLA and CO₂ in the complex crystals could disrupt the interchain interactions between adjacent PLLA chains. In addition, the larger unit cell volume of complex crystals than α crystals could also weaken the interactions between PLLA chains.

We further investigated the effect of CO₂ pressure on the formation of PLLA/CO₂ complex crystals. Figs. 4(a)−4(c) show the WAXD patterns of PLLAs treated under the different CO₂ pressures (1−13 MPa) and $T_c$’s (10−110 °C) for 4 h. Three crystal polymorphs, e.g., PLLA/CO₂ complex crystals, α’ and α crystals, were detected for the PLLAs treated by CO₂ under different conditions. The diffraction peaks located at $2\theta$=13.3°, 15.2°, and 19.7° in Fig. 4(a) were assigned to the α’ crystals. At the low CO₂ pressure (1 MPa), PLLA did not crystallize at a low $T_c$ (<50 °C) below $T_g$; it crystallized in the usual α’ and α crystals at $T_c$=70 and 110 °C, respectively. Such $T_c$ dependence of crystal polymorph was the same as that found in the cold and melt crystallizations of PLLA. However, the effect of CO₂ treatment on PLLA crystalline structure became more significant at the high CO₂ pressure. Crystallization of PLLA took place even at the low $T_c$ (<50 °C) after the high-pressure CO₂ treatment (4−13 MPa) due to the strong plasticizing effect of the high-pressure CO₂.

According to the WAXD results, we proposed the crystalline phase diagram of PLLAs crystallized under different CO₂ pressures and $T_c$’s in Fig. 4(d). PLLA crystallized in the PLLA/CO₂ complex crystals under 4−13 MPa CO₂ at $T_c$=10 °C and under 7−13 MPa CO₂ at 30−50 °C, while grew in the common α crystals under 7−13 MPa CO₂ at $T_c$=70−110 °C, under 7 MPa at 60 °C and under 4 MPa CO₂ at 50−110 °C. The mixture of α and PLLA/CO₂ complex crystals was generated under 4 MPa CO₂ at $T_c$=30 °C. The $T_c$-dependent crystalline structure of CO₂-treated PLLAs was almost independent of CO₂ pressure but dominated by $T_c$ at the high CO₂ pressure.

![Fig. 4] WAXD results of PLLA treated with different CO₂ pressures and $T_c$’s for 4 h and then aged at ambient condition for 48 h: (a−c) WAXD patterns of PLLA under (a) 1 MPa, (b) 4 MPa, and (c) 13 MPa CO₂ pressure; (d) polymorphic phase diagram of PLLA treated under different CO₂ pressures and $T_c$’s.

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The crystalline structure of CO$_2$-treated PLLA at 7 and 13 MPa showed the same $T_c$ dependence. However, the $T_c$-dependent crystalline structure of CO$_2$-treated PLLA was dissimilar at the low CO$_2$ pressure (1−7 MPa). In the case of the CO$_2$-treated PLLAs under 4−7 MPa at $T_c = 30–50$ °C, the PLLA/CO$_2$ complex crystals were facilitated under the high-pressure CO$_2$ treatment due to the higher CO$_2$ absorptivity.

### Complex-to-$\alpha$ Crystal Transition

In order to explore the thermal stability of complex crystals, we investigated the phase transition and structural evolution of complex crystals during heating and thermal annealing via the WAXD and SAXS analyses. Fig. 5(a) depicts the temperature-variable WAXD patterns of complex crystals collected upon heating; the initial complex crystals were prepared through crystallization at 7 MPa CO$_2$, $T_c=10$ °C for 4 h and subsequent RT-aging for 48 h. Peak intensities for the (110) plane of complex crystals and the (110/200) plane of $\alpha$ crystals were evaluated and normalized by the maximum intensity of (110/200) plane of $\alpha$ crystals, as shown in Fig. 5(b). Diffraction pattern of complex crystals varied little upon heating to 50 °C (Fig. 5a). However, the (110) diffraction of complex crystals vanished and the (110/200) diffraction of $\alpha$ crystals appeared with heating from 50 °C to 55 °C, followed by the continuous enhancement of $\alpha$ crystal diffraction with further heating to 155 °C (Figs. 5a and 5b). The diffraction intensity of $\alpha$ crystals started to decline with heating to ≥160 °C due to the crystal melting.

Fig. 5(c) shows the Lorentz-corrected SAXS profile ($Iq^2$-$q$ plot) of complex crystals recorded upon heating from 30 °C to 190 °C. Long period ($d_{ac}$) was evaluated by $d_{ac} = 2\pi/q^*$, where $q^*$ was the $q$ value corresponding to the peak top of $Iq^2$-$q$ plot. The calculated $d_{ac}$ was plotted against temperature in Fig. 5(d). Single scattering peak was seen at all temperatures and it shifted toward the low-$q$ side during heating, corresponding to the increase of $d_{ac}$ with heating. Notably, we did not see the obvious change of scattering intensity and $d_{ac}$ for the complex crystals in the temperature range (50−60 °C) corresponding to the complex-to-$\alpha$ transition. This manifested that the complex-to-$\alpha$ transition did not involve the remarkable change of crystalline lamellae thickness. On the other hand, the increases of scattering intensity and $d_{ac}$ (from 19.1 nm to 40.4 nm) were more pronounced with heating at 150−180 °C, ascribed to the thermally-induced lamellar thickening of $\alpha$ crystals before the final melting.

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**Fig. 5** Temperature-variable WAXD and SAXS results of PLLA/CO$_2$ complex crystals (7 MPa CO$_2$, $T_c=10$ °C, 4 h) during heating from 30 °C to 190 °C: (a) WAXD patterns; (b) change of normalized intensity; (c) Lorentz-corrected SAXS profiles; (d) change of long period. The intensity was normalized by the maximum intensity of (110/200) plane of $\alpha$ crystals.
We then studied the effects of isothermal annealing process (annealing temperature and time) on the crystalline phase transition and structural evolution of complex crystals. Fig. 6(a) shows the WAXD patterns of complex crystals (7 MPa, $T_c=10\ ^\circ C$, 4 h) after annealing at various temperatures (40–80 °C) for 1 h. We detected the characteristic diffraction of $\alpha$ crystals ($2\theta=13.5^\circ$) after the complex crystals were annealed at 40 °C for 1 h, indicating the slow complex-to-$\alpha$ phase transition under this condition. As revealed by the WAXD results, the complex crystals completely transformed into the $\alpha$ crystal.

Fig. 6 WAXD results of PLLA/CO$_2$ complex crystals (7 MPa CO$_2$, $T_c=10\ ^\circ C$, 4 h) during thermal annealing: (a) WAXD patterns collected after annealing at different temperatures for 1 h; (b) time-resolved WAXD patterns collected during annealing at 50 °C for 10 min; (c) change of normalized intensity derived from panel (b). The intensity in panel (c) was normalized by the maximum intensity of (110/200) plane of $\alpha$ crystals.

Fig. 7 Tensile properties of PLLA films after treating with 7 MPa CO$_2$ at different $T_c$’s for 4 h and RT-aging for 48 h: (a) stress-strain curves; (b) tensile strength; (c) Young’s modulus; (d) breaking strain.

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tals after annealing at a high temperature of 50−80 °C for 1 h. We further investigated the structural changes of complex crystals in the annealing process by in situ WAXD. Fig. 6(b) shows the time-resolved WAXD profiles of complex crystals (7 MPa, Tc = 10 °C, 4 h) during annealing at 50 °C for 10 min. The normalized intensity changes of characteristic diffractions of α and complex crystals are depicted in Fig. 6(c). The characteristic diffraction of complex crystals (2θ = 12.3°) weakened but that of the α crystals intensified with the progress of annealing.

On the basis of these WAXD results, we concluded that the complex crystals were thermally metastable and transformed into the thermally stable α crystals during heating or annealing at a high temperature (50−80 °C). It is notable that the thermally-induced transformation from complex to α crystals was direct and did not pass through the other metastable polymorph (such as α' or α′ crystals). The thermally-induced phase transition of polymers can proceed by either the direct solid-to-solid route or the indirect melt-recrystallization route. The complex-to-α transition took place at the low temperature around the Tc of PLLA. We did not see the obvious thermal transitions corresponding to the crystal melting and recrystallization in the temperature range where the complex-to-α transition occurred (Fig. 1a). Also, the crystallization or recrystallization of PLLA could not take place at the low temperature of 40−50 °C. Therefore, we proposed that the complex-to-α phase transition proceeded through the solid-to-solid route, but not the melt-recrystallization route. Mechanism of complex-to-α transition is different from that of the heating-induced mesophase-to-α′ transition in stretched PLLA.[43] The strain-induced PLLA mesophase melted partially and transformed immediately into the α′/α crystalline phase during heating. On the other hand, we found that the sample weight retained to the initial weight after annealing at 50−80 °C for 1 h. Accordingly, the thermally-induced complex-to-α phase transition would be driven by the desorption of CO2 in the complex crystals, which triggered the rearrangement of conformation and interchain packing of PLLA chains.

**Mechanical Property of CO2-treated PLLA**

Since the physical properties of PLLA were drastically influenced by crystal polymorph, we investigated the mechanical property of PLLAs treated by CO2 under different conditions. Fig. 7(a) shows the stress-strain curves of the PLLA films treated under 7 MPa CO2 at various Tc's. Tensile strength, Young's modulus and breaking strain were evaluated from the stress-strain curves and plotted against Tc in Figs. 7(b)−7(d). The mechanical property of CO2-treated PLLAs depended strongly on the Tc and crystal polymorph. The PLLA α and α′ crystals were typically brittle and had the breaking strains lower than 3%. [44] CO2-treated PLLAs at low Tc (e.g., 10 °C) were more ductile than the melt-crystallized PLLAs, but similar to the solvent-cast and annealed PLLAs.[45] The complex crystals of PLLA developed at Tc = 10 °C showed a breaking strain of 29.6%, a tensile strength of 5.9 MPa, and a Young's modulus of 7.7 MPa. The high ductility of complex crystals generated at a low Tc was ascribed to the plasticizing effect of CO2 and the lower Xc. The CO2-treated PLLAs became more brittle and stiffer with the improvement of Tc due to the increase of Xc, the decrease of CO2 absorptivity, and the formation of ordered α crystals. The tensile strength and Young's modulus of PLLA enhanced from 5.9 and 7.7 MPa to 39.2 and 12.8 MPa, respectively, but the breaking strain decreased from 29.6% to 5.6% with Tc increasing from 10 °C to 110 °C. Therefore, control over the microstructure and crystal polymorph by CO2 treatment was a feasible way to tailor the mechanical property of PLLA.

**CONCLUSIONS**

In summary, we have elucidated the formation condition, structural feature, thermally-induced phase transition, and mechanical property of PLLA/CO2 complex crystals under different CO2 pressures and Tc's. We find that the growth of PLLA/CO2 complex crystals was facilitated at the high CO2 pressure (7−13 MPa) and the low Tc (10−50 °C). However, increasing the Tc to above 60 °C facilitated PLLA to crystallize in the common α crystals. Crystalline structure of CO2-treated PLLA was less dependent on the pressure but dominated by Tc when the CO2 pressure was higher than 7 MPa. The broad resonance peak of the solid-state NMR spectra for the complex crystals suggested the weaker interchain interaction and locally disorder chain packing in the crystal lattice. The PLLA/CO2 complex crystals transformed into the thermodynamically stable α crystals through the direct solid-to-solid route upon heating or annealing at the temperature above 50 °C. The complex crystals of PLLA had higher ductility and flexibility but lower tensile strength and modulus than the usual α crystals, attributed to the lower Xc and the plasticizing effect of CO2. These results would be essential for tuning the microstructure and physical property of PLLA in the CO2-assisted processing and also advance the current understanding on the complexation or cocrystallization between the semicrystalline polymers and solvents.

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