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Sustainable Blends of Poly(propylene carbonate) and Stereocomplex Polylactide with Enhanced Rheological Properties and Heat Resistance

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Abstract Sustainable blends of poly(propylene carbonate) (PPC) and stereocomplex polylactide (sc-PLA) were prepared by melt blending equimolar poly(L-lactic acid) (PLLA) and poly(D-lactide acid) (PDLA) with PPC to form sc-PLA crystals *in situ* in the melt blending process. Differential scanning calorimetry analysis revealed that only sc-PLA, no homo-crystallization of PLLA or PDLA, formed in the PPC matrix as the sc-PLA content was more than 10 wt%. Very intriguingly, scanning electronic microscopy observation showed that sc-PLA was evenly dispersed in the PPC phase as spherical particles and the sizes of sc-PLA particles did not obviously increase with increasing sc-PLA content. As a consequence, the rheological properties of PPC were greatly improved by incorporation of sc-PLA. When the sc-PLA content was 20 wt%, a percolation network structure was formed, and the blends showed solid-like behavior. The sc-PLA particles could reinforce the PPC matrix, especially at a temperature above the glass transition temperature of PPC. Moreover, the Vicat softening temperature of PPC/sc-PLA blends could be increased compared with that of neat PPC.

Keywords Sustainable; Polymer blends; Poly(propylene carbonate); Stereocomplex polylactide

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INTRODUCTION

Recently, an increase in carbon dioxide (CO₂) emission due to the use of fossil fuel continues to raise concerns because of its greenhouse effect that causes global warming. Furthermore, it is anticipated that the emission rate of CO₂ will continue to increase because carbon-based fossil fuels are still the main energy consumption for the next few decades.^[1] As a result, tremendous effort has been made to reduce CO₂ accumulation, such as CO₂ capture and storage, and chemical conversion of CO₂ into useful compounds. It is important to develop the products and processes for the utilization of CO₂ as a feedstock for polymers from the standpoint of sustainable and green chemistry.^[2]

CO₂ can be copolymerized with many epoxides to produce a series of alternating aliphatic polycarbonate copolymers, including poly(propylene carbonate) (PPC), poly(ethylene carbonate) (PEC), poly(butylene carbonate) (PBC), poly(cyclohexene carbonate) (PCHC), and so on.^[3–5] These aliphatic polycarbonates have a range of applications because of the combination of properties: its relatively high mechanical strength, excellent optical properties, and processability. On the contrary, due to the characteristic low molecular weight, high susceptibility to hydrolysis, and low melting point or

glass transition temperature (T_g), the widespread use of these aliphatic polycarbonates is limited.^[6] Of these, PPC is the most widely studied polymer compared to the other CO₂ derived polymers. However, its current development will not meet most of the performance needs for commercial applications as polymers due to its relatively low T_g , poor rheological properties, and rather poor heat resistance. For instance, T_g of PPC is around 35–40 °C.^[7] The thermal decomposition temperature is 180–260 °C, mainly depending on the catalyst used in the synthesis of PPC, monomer, and the co-polymer component.^[8–10] In addition, most PPCs show a wide range of polydispersity index (PDI) and amorphous morphology, so PPC is brittle below T_g , and exhibits poor dimensional stability above T_g .^[11] In order to improve performance and processability of PPC, melt blending is one of the most economical and technically simple methods for preparing polymer materials with desirable features. Many commercially successful blend systems have been prepared by traditional melt blending or extrusion processes.^[12] Among them, blending with biodegradable polymers has attracted significant attention, in line with the concept of environment protecting and sustainability. Up to now, the different binary PPC blend systems such as PPC/poly(lactic acid) (PLA),^[13–15] PPC/poly(hydroxy butyrate-co-valerate) (PHBV),^[16–18] PPC/poly(3-hydroxybutyrate) (PHB),^[19,20] PPC/poly(butylene succinate) (PBS),^[21,22] and PPC/starch^[23,24] have been studied in both academia and industries.

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Poly(lactic acid) (PLA) is a fully biodegradable thermoplastic polymer, which has a wide range of application in the biomedical and packaging fields due to its compostability and renewability.^[25] PLA can form two stereoisomeric forms: poly(L-lactic acid) (PLLA) and poly(D-lactide acid) (PDLA), due to a chiral carbon center in the lactic acid monomer. When PLLA or PDLA, not both, is present in the system, “homo-crystallization” can be formed. When both PLLA and PDLA are present in a system, and they are arranged side by side because of peculiarly strong interaction between them, “stereocomplex crystallites” can be formed.^[26–28] Therefore, stereocomplex-PLA (sc-PLA) displays a melting temperature (T_m) in a range of 220–250 °C, which is 30–60 °C higher than that of homopolymerized PLA.^[29] In addition, the rapid crystallization rate from the melt, enhanced mechanical properties, high heat resistance performance, and lower thermal degradation rates of sc-PLA make it a promising application in both biomaterials and traditional plastic substitutes.^[30,31] Sc-PLA can be formed in bulk or solid-state (polymerization or crystallization from the melt), or in solvent condition.^[32,33] Recently, Yang *et al.*^[34,35] presented a simple and novel low-temperature approach for preparing PLA stereocomplex crystallites by melt mixing or solution casting of PLLA and PDLA. A notable observation in this study was that only stereocomplex crystallites without homo-crystallites of PLA could be formed under processing temperature of 160 °C.

With regard to fully biodegradable PPC/PLA blend systems, most research has focused on blending with PLLA homopolymer, whereas there have been few investigations on the use of sc-PLA as a modifier. Therefore, in this work, we devise a simple and effective way of blending PPC with equimolar PDLA and PLLA at a low temperature to *in situ* form stereocomplex crystallites of PLA in the PPC matrix. As a consequence, the rheological properties and heat resistance of PPC will be enhanced by sc-PLA due to its high melting temperature and high modulus. In addition, the “low temperature” means that the processing temperature is much lower than T_m of sc-PLA and slightly higher than T_m of PLLA and PDLA, which also makes the processing process easier. This interesting method can help us to obtain PPC/sc-PLA blends with superior performance by simple melt processing technology, which in turn expands the application of CO₂ based aliphatic polycarbonates.

EXPERIMENTAL

Materials and Sample Preparation

PPC was synthesized by copolymerization of carbon dioxide and epoxy propane. It exhibited a weight-average molecular weight (M_w) and polydispersity by GPC analysis of 4.1×10^6 g/mol and 2.68, respectively. PLLA (4032D) with D-isomer content of 2%, supplied by Nature Works LLC (Blair, Nebraska, USA), had an M_w of 2.07×10^5 g/mol and polydispersity of 1.73. PDLA was obtained from Total Corbion company, with an M_w of 1.25×10^5 g/mol and polydispersity of 1.68.

PPC, PLLA, and PDLA were first dried in a vacuum oven for 48 h at a temperature of 50 °C. The ternary blends of PPC, PLLA, and PDLA were prepared by an internal mixer (Haake Rheomix 600, Karlsruhe, Germany) with a processing temperature of 175 °C and a screw speed of 60 r/min. First, PLLA and

PPC were melt mixed for 3 min, and then PDLA component was added to continue mixing for 4 min. The blended samples were hot pressed for 3 min at 150 °C and then cold pressed at room temperature to form thin sheets with a thickness of 1 mm. Neat PPC was also subjected to the same heat treatment process in order to have the same thermal history as its blends. In ternary blends, the weight of PLLA to PDLA was fixed at 1:1, while the sc-PLA contents of 10 wt%, 20 wt%, and 30 wt% were chosen to study the effects of sc-PLA contents on the performance of PPC. For convenience, PPC/sc-PLA blends were denoted as PPC/XSC, with X representing the weight content of sc-PLA.

Characterizations

Differential scanning calorimetry (DSC)

Melting properties of neat PPC and PPC/sc-PLA blends were analyzed using a TA Instruments DSC Q20 (USA) under nitrogen atmosphere. All samples (around 5–8 mg) were heated from 0 °C to 250 °C with a heating rate of 10 °C/min. The degree of crystallinity of sc-PLA (X_{sc}) was evaluated by using the following equation:

$$X_{sc} = \frac{\Delta H_{sc}}{\Delta H_{sc}^0} \times 100\% \quad (1)$$

where ΔH_{sc} is the melting enthalpy of sc-PLA in the PPC/sc-PLA blends occurring at ~220 °C. ΔH_{sc}^0 is the melting enthalpy of 100% crystalline sc-PLA with a value of 146 J/g.^[36] φ is the weight ratio of sc-PLA.

Scanning electronic microscopy (SEM)

A field-emission SEM (FEI Co., Eindhoven, Netherlands) was used to investigate the morphology of PPC/sc-PLA blends at an accelerating voltage of 10 kV. All samples were placed in the liquid nitrogen for 10 min, and then were immediately cryogenically fractured. After the surfaces of the specimens were sputter-coated with gold, the morphology was observed.

Rheological measurements

Rheological properties of PPC/sc-PLA blends were determined by using a rheometer (AR2000ex, TA Instruments, USA) equipped with a parallel plate of 25 mm diameter. Sample sheets with a thickness of 1 mm were heated to 160 °C for frequency scanning under N₂ atmosphere. The dynamic frequency sweep ranged from 100 rad/s to 0.05 rad/s, and the strain was fixed at 1.25%.

Dynamic mechanical analysis (DMA)

DMA measurements for all samples were carried out using a TA Instruments dynamic mechanical analyzer SDTA861e (Mettler Toledo). The test samples were the rectangular sheets with a size of 20.0 mm × 4.0 mm × 1.0 mm. The test temperature range was –20 °C up to 80 °C, the heating rate was 3 °C/min, the frequency used was 1 Hz, and the mode was in tensile.

Vicat softening temperature (VST)

VST of PPC/sc-PLA composites was determined according to GB/T1633-200 at a heating rate of 2 °C/min and 1 kg load. The temperature at which the needle is inserted into the sample at 1 mm is considered to be the VST.

RESULTS AND DISCUSSION

Stereocomplex Formation

The formation of sc-PLA crystallites *in situ* in the PPC matrix is a

major factor in determining the properties of PPC/sc-PLA blends. DSC is a simple and efficient way of monitoring PLA stereocomplexation formation. Fig. 1 shows typical DSC heating curves for neat PPC and its blends with different contents of sc-PLA. Table 1 summarizes the thermal properties of all samples based in Fig. 1.

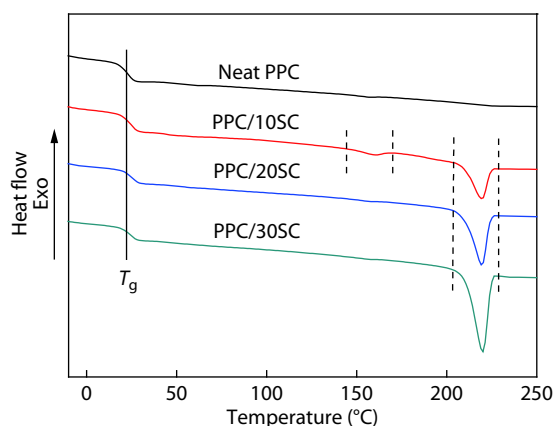


Fig. 1 DSC heating traces for neat PPC and PPC/sc-PLA blends.

Table 1 Thermal parameters of neat PPC and PPC/sc-PLA blends from heating scan at 10 °C/min.

Sample	T_g (°C)	T_m^a (°C)	T_m^b (°C)	ΔH_m^a (J/g)	X_c^a (%)
PPC	23.5	—	—	—	—
PPC/10SC	25.3	219.0	161.7	28.0	19.2
PPC/20SC	25.6	219.2	—	42.9	29.4
PPC/30SC	25.8	219.7	—	55.1	37.7

^a T_m , ΔH_m , and X_c of the sc-PLA component in PPC/sc-PLA blends. ^b T_m of the homo-crystallization of PLLA or PDLA in the blends. The values of ΔH_m were corrected for the content of sc-PLA in the blends.

It can be seen from Fig. 1 that neat PPC had no melting peak because PPC was amorphous due to its structural characteristics, namely the flexible C—O—C bonds in the skeleton, the existence of many weak polar, and weak molecular chain interaction.^[37] In all blends, the melting peaks from the stereocomplex were present around 220 °C, as reported in the literature.^[38] It was important to note that when 10 wt% sc-PLA was added to the PPC matrix, the blend exhibited a weak melting peak at 160 °C and a melting enthalpy of 0.9 J/g, which was ascribed to the melting of PLLA or PDLA homo-crystallites. At the melt processing temperature of 175 °C, PLLA and PDLA were in a molten state, and only the stereocomplex crystallites could be formed in the PPC melt. Furthermore, the formation of stereocomplex crystallites required that PLLA and PDLA molecules alternate to reach the crystal growth front.^[39] As a result, the concentration of PLLA and PDLA was the main factor affecting the formation of the stereocomplex crystallites. When the PLLA and PDLA contents were 10 wt%, respectively, PLLA and PDLA molecules had less chance to meet each other during melt blending due to the relatively low concentration in the matrix. Therefore, the homocrystallites of PLLA and/or PDLA still existed in the blends, showing a weak melting peak at around 160 °C. The melting peak of homopolymer completely disappeared when the PLLA and PDLA content increased to 20 wt%, indicating

that only the stereocomplex crystallites were formed in the PPC matrix. Moreover, the degree of crystallinity (X_c) for PPC/sc-PLA blends was in the range of 19.2%–37.7%, depending on the content of formed sc-PLA. It was also evident that the change in concentrations of PLLA and PDLA affected the contents of formed sc-PLA. Finally, compared to the glass transition temperature (T_g) of neat PPC, T_g of PPC/sc-PLA blends was slightly increased, as shown in Table 1. In an amorphous polymer such as PPC, T_g is mainly influenced by physical crosslinks. One might expect that the restrictions on the motion that the formed sc-PLA imposed on the PPC molecular chains would increase the energy requirement of the transition, thereby raising T_g .^[40]

Morphological Characterization

Since the dispersion of *in situ* formed sc-PLA in the PPC matrix plays a decisive role in affecting the physical properties of PPC, it is necessary to investigate the phase morphology of the PPC/sc-PLA blends. Fig. 2 presents the SEM micrographs of fractured surfaces of neat PPC and PPC/sc-PLA blends. The surface of neat PPC was featureless and smooth, as shown in Fig. 2(a1). In Figs. 2(b1), 2(c1), and 2(d1), it was found that all the PPC/sc-PLA blends showed characteristic “sea-island” morphology with a uniform dispersion of sc-PLA particles in the PPC matrix, indicating the phase-separated nature between the sc-PLA phase and PPC matrix. The average diameter (D) of sc-PLA particles only increased from 0.32 μm for the blend with 10 wt% sc-PLA to around 0.35 and 0.37 μm for the blends with 20 wt% and 30 wt% sc-PLA, respectively, as shown in Figs. 2(b2), 2(c2), and 2(d2). Thus, the number-average particle size of sc-PLA in the blends was shown to be weakly dependent on the content of PLLA and PDLA. In general, for the immiscible polymer-polymer blends, an increase in the content of dispersed phase is favorable for the expansion of dispersed particle size.^[41] This is because the mechanism for controlling the morphology development of the blends is the balance between breakup and coalescence of dispersed phase droplets.^[42] When the immiscible polymers are blended, the dispersed phase is stretched into threads under the shearing force, and then broken into small droplets. The small droplets will also meet and coalesce.^[43] Therefore, as the content of dispersed phase is increased, cohesiveness gradually dominates in the balance of breakup and coalescence of the droplets, and as a result, the size of dispersed phase increases remarkably.

In this study, the phenomenon that the size of dispersed phase did not change greatly with the increase of dispersed phase concentrations can be explained as follows. Winter and coworkers^[44] believed that the essence of polymer crystallization was a physical gel process. When a critical gel point was reached, a transition from liquid-like to solid-like behavior would occur. In the melt blending process, once the degree of crystallinity of sc-PLA increased to a critical point, that is, the physical gel point was reached, a transition from liquid-like to solid-like state occurred, resulting in the formation of solid sc-PLA particles embedded in the PPC matrix. The size of formed stereocomplex crystallites remained almost unchanged due to its higher melting temperature and modulus under the blending conditions. Therefore, it could be considered that the critical gel point was the key factor affecting the phase morphology of PPC/sc-PLA blends. Since there was

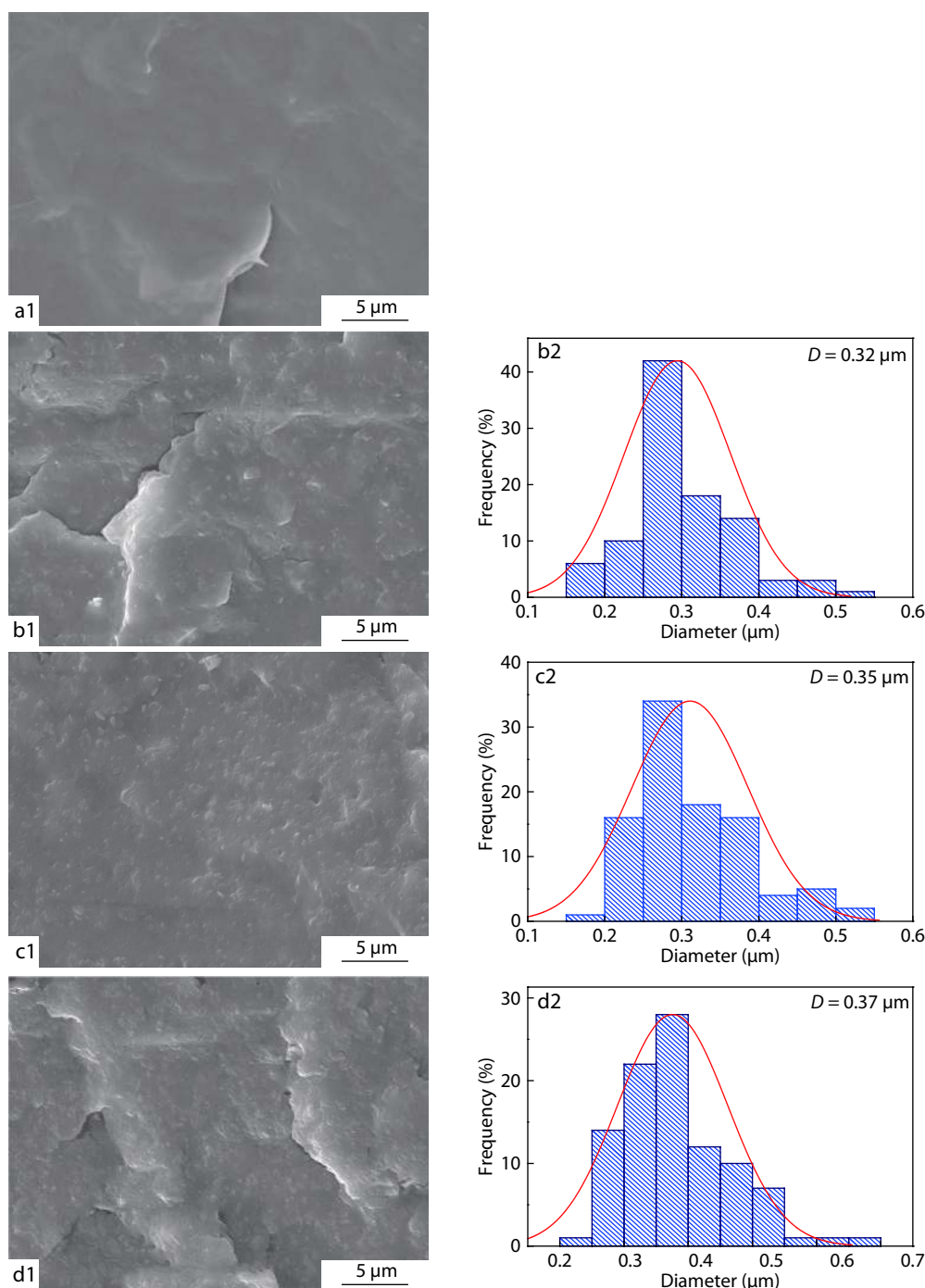


Fig. 2 SEM images of cryo-fractured surfaces for (a1) neat PPC, (b1) PPC/10SC, (c1) PPC/20SC, and (d1) PPC/30SC. (b2, c2, d2) the quantitative analyses according to the distribution of sc-PLA particle size in (b1), (c1), and (d1), respectively.

no necessary relationship between the critical gel point and the concentration of PLLA and PDLA, the size of dispersed sc-PLA did not obviously increase with the increase of PLLA and PDLA content.

Rheological Properties

Dynamic rheological properties are often used to describe the morphological structure of blends due to its high sensitivity to the structure and interaction of polymer melt.^[45] To check if sc-PLA particles can reinforce the PPC melt and the influence of sc-

PLA on the rheological properties, oscillatory shear rheological measurements were carried out at 160 °C. The effect of sc-PLA on the storage modulus (G'), loss modulus (G''), and complex viscosity ($|\eta^*|$) of PPC/sc-PLA blends are shown in Fig. 3. It was clear that G' , G'' , and $|\eta^*|$ of the blends increased significantly compared to that of neat PPC, implying that sc-PLA phase formed in the blends did not melt and enhanced the PPC melt like solid particles. The low-frequency G' of neat PPC showed a good linear relationship, indicative of typical liquid-like

behavior. However, the slopes of low-frequency G' for the blends decreased remarkably with the increase of sc-PLA content. When the sc-PLA content increased to 20 wt%, the slope of low-frequency G' became nearly independent of the frequency, indicating a pseudo-solid-like behavior. This was because the sc-PLA particles formed a network structure that enhanced the PPC melt.^[38] In addition, it was obvious that $|\eta^*|$ of neat PPC showed a Newtonian liquid behavior, while $|\eta^*|$ of the blends exhibited non-Newtonian shear-thinning behavior as presented in Fig. 3(c), which further illustrated the formation of sc-PLA network structure.

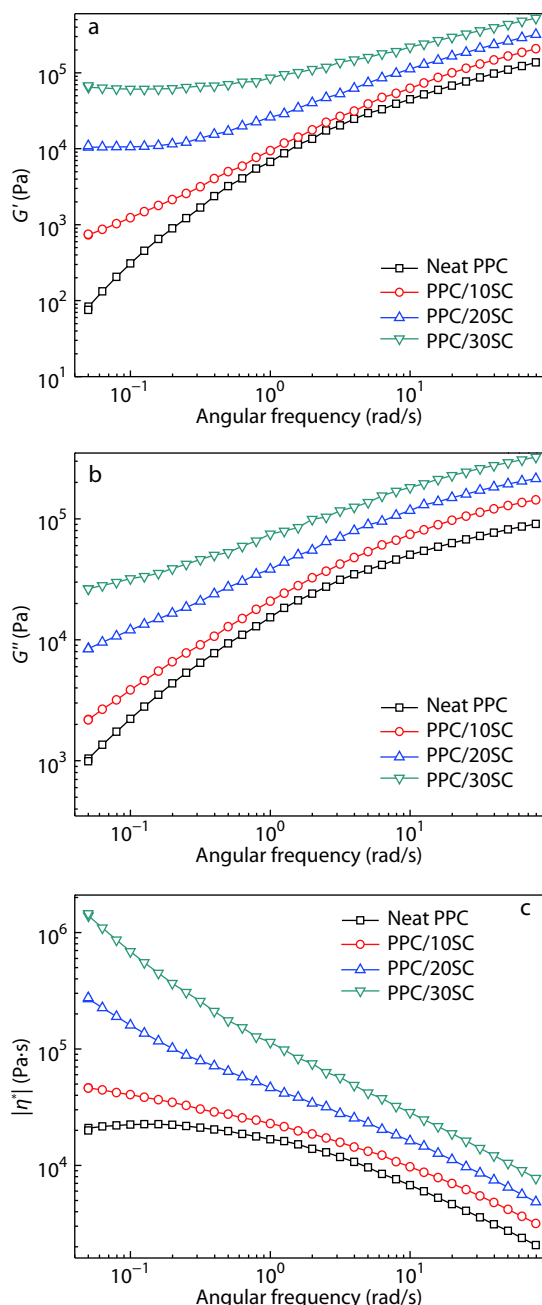


Fig. 3 (a) Storage modulus (G'), (b) loss modulus (G''), and (c) complex viscosity ($|\eta^*|$) as a function of frequency for neat PPC and PPC/sc-PLA blends at 180 °C.

Plotting G' and G'' at the frequency of 0.05 rad/s versus the sc-PLA loadings, the turning point of the resulting curves can be regarded as the percolation thresholds of the system.^[46] Fig. 4 shows that the values of percolation thresholds for the PPC/sc-PLA blends were 20 wt%. This result suggested that when sc-PLA content was increased to 20 wt%, the pseudo-solid-like network of percolated spheres was formed. Another evidence for the formation of a percolation network structure is shown in Fig. 5, which presents a comparison of the changes in G' and G'' versus frequency. For neat PPC and the blend sample with 10 wt% sc-PLA, G' was lower than G'' over the whole frequency range, suggesting the occurrence of viscous deformation. For the blend sample with 20 wt% sc-PLA, there was a crossing point between G' and G'' curves, demonstrating the viscoelastic behavior owing to buildup of the network structure.^[47] For the blend sample with 30 wt% sc-PLA, G' surpassed G'' in the all-frequency range. This result should be due to the fact that microphase structure is predominated more sensitively from the elastic modulus over the viscous modulus, indicating a pseudo-solid-like rheology behavior of the blend. The same rheology behaviors were also observed in poly(ϵ -caprolactone) nanocomposites.^[48] Schematic representation of network structure of solid sc-PLA in the PPC matrix is illustrated in Fig. 6.

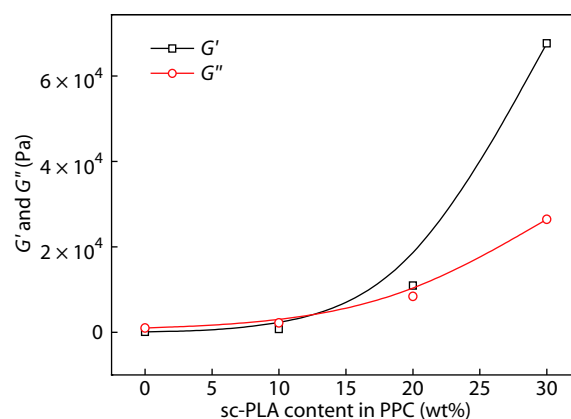


Fig. 4 Plots of G' and G'' versus sc-PLA content in the blends. The values of G' and G'' were obtained directly from Figs. 3(a) and 3(b), respectively, at the frequency of 0.05 rad/s.

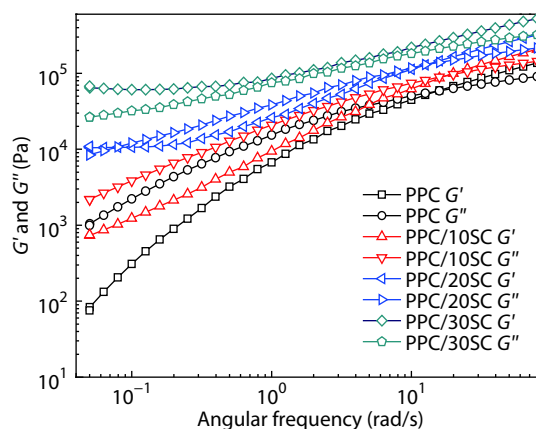


Fig. 5 Plots of G' and G'' as a function of frequency for neat PPC and PPC/sc-PLA blends.

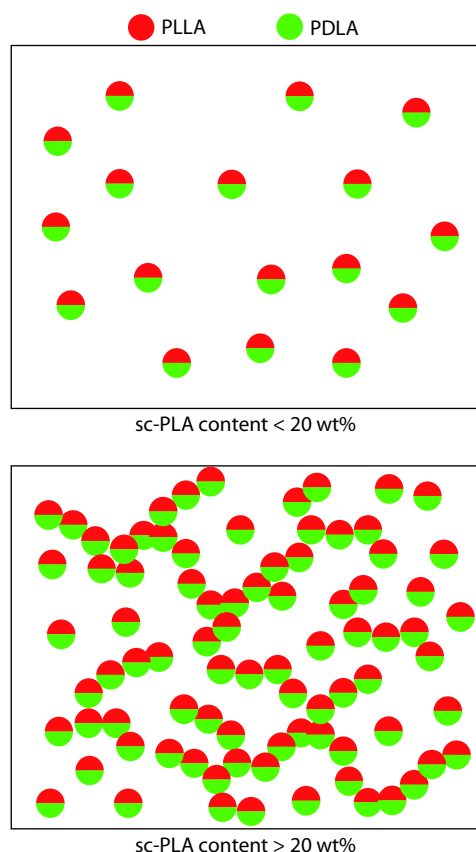


Fig. 6 Schematic illustration of sc-PLA network structure in the PPC matrix.

Since sc-PLA was formed *in situ* in the PPC melt, there was a strong physical entanglement between the dispersed sc-PLA phase and the PPC matrix. As soon as the sc-PLA particles formed a percolation network structure, the large-scale relaxations of polymer chains might be highly restrained by the percolated sc-PLA network. Fig. 7(a) shows the Han plots of plotting G' against G'' for neat PPC and its blends.^[49] The reduced slopes of PPC/sc-PLA blends with increasing sc-PLA content indicated that the blends became more heterogeneous. In addition, the inflection point at which the slopes changed moved toward higher modulus direction as the sc-PLA content in the blends increased, indicating that more energy was required to change the degree of heterogeneity due to the increased physical association in the blends at higher sc-PLA loading.

The physical association between sc-PLA and PPC matrix would change the relaxation (λ) of PPC chains, and the calculated formula is as follows:^[50]

$$\lambda = G' / (\eta^* \times \omega^2) \quad (2)$$

where ω is scanning frequency. The ratio of calculated relaxation time of blends to that of neat PPC ($\Delta\lambda$) for neat PPC, PPC/10SC, PPC/20SC, and PPC/30SC blends were 1, 4.2, 10.8, and 11.5, respectively. It was clear that $\Delta\lambda$ increased gradually with increasing sc-PLA loadings, suggesting that the role of sc-PLA to make the PPC chains need longer time to relax became stronger with the increase in the sc-PLA loading. In other words, the addition of sc-PLA greatly restricted the mobility of PPC

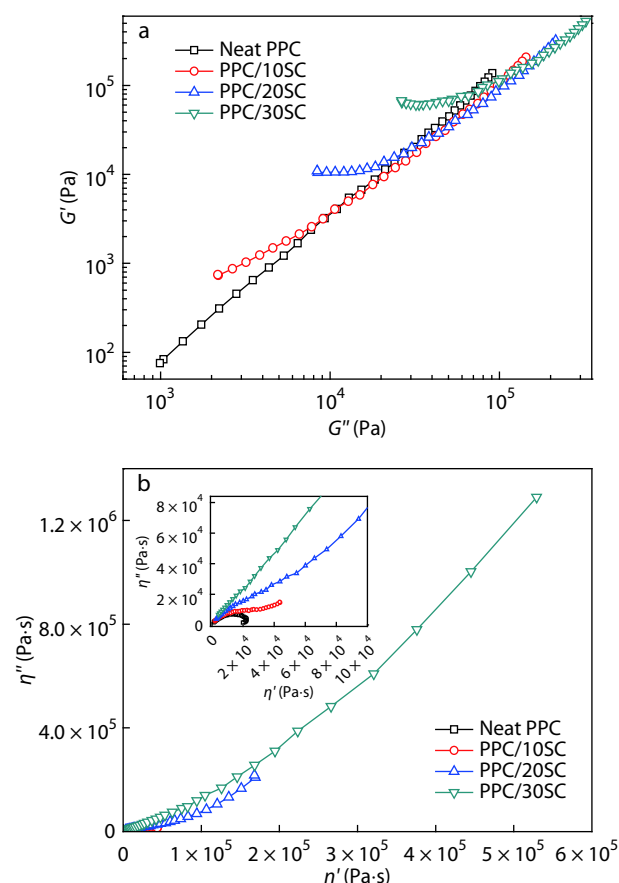


Fig. 7 (a) Han plots of G' versus G'' and (b) Cole-Cole plots of imaginary viscosity (η'') versus real viscosity (η') for the neat PPC and PPC/sc-PLA blends at 180 °C.

chains once a percolation network structure was formed.

The Cole-Cole curves shown in Fig. 7(b) can be used to further confirm this strong restriction effect, which is generally suitable for describing viscoelastic properties (viscosity and modulus) of polymer systems with a relaxed time distribution.^[51] The single arc of neat PPC shown in inset images represented the relaxation process with a relaxation time distribution. The rigid tails that appeared in the high viscosity region after incorporation of sc-PLA indicated long-term relaxation of the constrained PPC chains. When the sc-PLA content was 10 wt%, the local relaxation arc of PPC and the rigid tail representing long-term relaxation of constrained PPC chains could be observed at the same time. As sc-PLA loading reached up to 20 wt%, the local relaxation arc of PPC almost disappeared, suggesting that the long-term relaxation of the restrained PPC chains dominated the entire relaxation process of the blends, which also confirmed that the percolation network structure of sc-PLA formed at present sc-PLA content, and the long-range motion of PPC chains was highly restrained consequently.

Thermomechanical Properties

DMA was carried out to study the effect of sc-PLA on the thermomechanical properties of PPC. Figs. 8(a) and 8(b) show the variation of storage modulus (E') and loss factor ($\tan\delta$) with temperature for the neat PPC and its blends, respectively. As

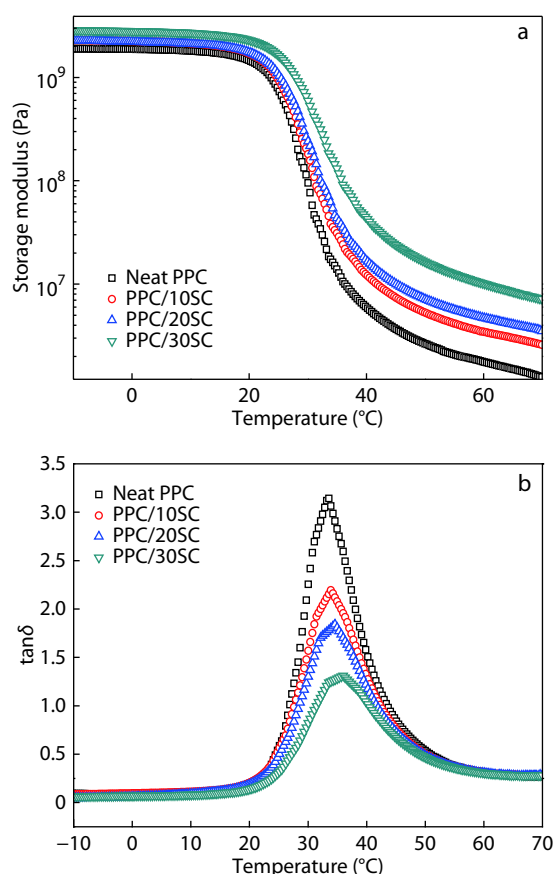


Fig. 8 Plots of (a) storage modulus and (b) $\tan\delta$ for neat PPC and PPC/sc-PLA blends.

expected, the higher the sc-PLA content, the larger the value of E' over the temperature range of -10 °C to 70 °C. This suggested that sc-PLA with high modulus and T_m did enhance E' of the PPC matrix over a wide temperature range, which was consistent with the results of aforementioned studies on the rheological properties.

It is well known that E' of a polymer drops sharply at T_g because the transformation from glass state to viscoelastic state occurs. Table 2 summarizes the values of measured E' at 15 and 45 °C in order to more intuitively compare the effect of sc-PLA phase on E' of the PPC matrix before and after glass transition. Obviously, before and after glass transition of PPC, the incorporation of sc-PLA exhibited different influences on the E' of PPC. For example, E' of the neat PPC at 15 °C was 1704 MPa, and E' of the blend with 30 wt% sc-PLA was increased to 2565 MPa. Compared with neat PPC, E' of the blend was increased by 50.5% below T_g of the PPC matrix. However, after the glass transition of PPC, the improvement

Table 2 Storage modulus of neat PPC and PPC/sc-PLA blends from DMA at different temperatures.

Sample	Storage modulus at 15 °C (MPa)	Storage modulus at 45 °C (MPa)
PPC	1704	3.6
PPC/10SC	2009	7.4
PPC/20SC	2035	10.0
PPC/30SC	2565	23.9

of E' was significant. For instance, at 45 °C, E' was increased from 3.6 MPa for neat PPC to 23.9 MPa for the blend containing 30 wt% sc-PLA. A remarkable increase in E' of 563.8% was achieved for the blend compared to neat PPC. This result indicated that sc-PLA formed *in situ* was an effective reinforcing agent for PPC. Such reinforcement effect was particularly obvious above the T_g of PPC. This was because the addition of sc-PLA with higher stiffness caused a stress interface to be introduced into the blends, which provided better stress transfer capabilities, resulting in an increase in E' of the blends.

Vicat Softening Temperature (VST)

VST tests were performed to confirm the heat softening characteristics of PPC/sc-PLA blends. The value of VST is particularly important for evaluating the heat resistance and thermodynamic properties of a thermoplastic polymer.^[52] Fig. 9(a) depicts the VST profiles of neat PPC and its blends and Fig. 9(b) shows the characteristics of VST for the blends with the sc-PLA content. It can be seen from Fig. 9 that the VST values of the blends were higher than that of neat PPC. Moreover, there was an increase in the VST values of blends as their sc-PLA content increased. For example, adding 30 wt% sc-PLA resulted in an increase in the VST value of PPC/sc-PLA blend from 32.3 °C to 39.2 °C. This indicated that the sc-PLA particles effectively improve the heat resistance of the PPC matrix. The VST value of a polymer is related to the flexibility of segments or chains

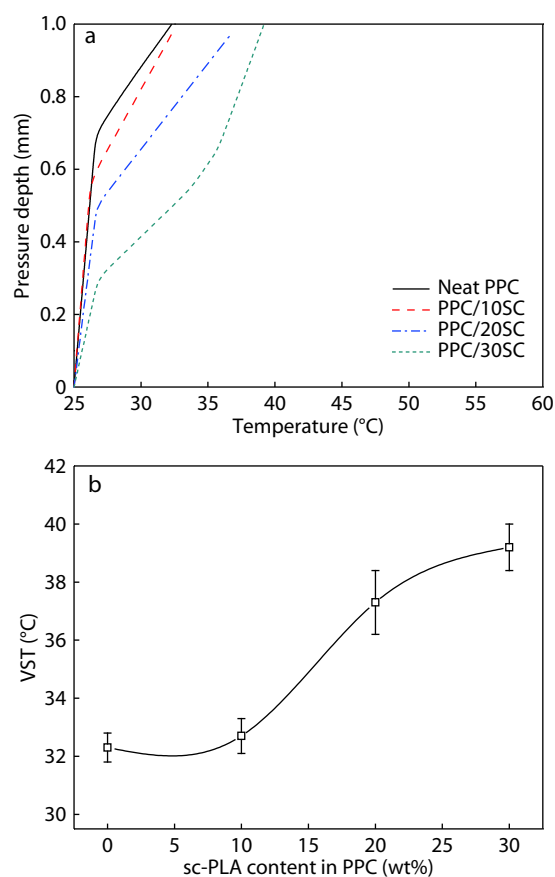


Fig. 9 (a) Deformation-temperature plots and (b) Vicat softening temperature of PPC and PPC/sc-PLA blends versus sc-PLA content.

to a certain extent and hence, methods that could reduce the ability of segmental and molecular motions would increase the heat resistance of polymers, such as increasing the degree of crystallinity or T_g and reinforcement. In the case of our study, the sc-PLA particles formed *in situ* played an enhancing role, thus increasing the VST value of PPC. On the other hand, the network structure composed of sc-PLA particles also hindered the movement of PPC chains and segments, resulting in an increase of VST value. Additionally, sc-PLA particles, due to their formation *in situ* in the PPC/PLLA/PDLA blend melt, could be regarded as physical cross-linking points, which increased the intermolecular forces and decreased the chain mobility of PPC, increasing thereby the heat resistance of PPC. The higher the VST value of a polymer, the better the dimensional stability when heated, and the smaller the thermal deformation. Improved heat resistance of PPC helps to promote its practical application in large-scale production and in a sustainable way.

CONCLUSIONS

Sustainable blends of PPC and sc-PLA were prepared by blending equimolar PLLA and PDLA with PPC at a temperature lower than T_m of sc-PLA and higher than that of PLLA and PDLA. DSC measurement revealed that there were only stereocomplex crystallites *in situ* formed in the PPC matrix as the PLLA and PDLA content increased to 20 wt%. Uniform dispersion of sc-PLA particles with a size of around 0.35 μm in the PPC matrix was observed by SEM. It was found that the size of sc-PLA aggregates did not increase significantly with the increase of PLLA and PDLA content. The effect of sc-PLA phase and its content on the rheological properties of PPC/sc-PLA blends were systematically studied by means of G' , G'' , $|\eta^*|$, relaxation time, and Cole-Cole curves. The results indicated that the sc-PLA phase improved the rheological properties of blends, and G' , G'' , and $|\eta^*|$ got rise with increasing sc-PLA content. A transformation from liquid-like to solid-like response of blends took place once the percolation network structure of sc-PLA was formed at a concentration of 20 wt% sc-PLA. Meanwhile, the long-range motion of PPC chains was also restrained by the percolation network structure. DMA analysis showed that the sc-PLA particles could reinforce the PPC matrix, and the reinforcement effect was more obvious when the temperature was higher than T_g of the PPC matrix. Finally, it was found that sc-PLA could improve the heat resistance of PPC.

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REFERENCES

1 Muthuraj, R.; Mekonnen, T. Recent progress in carbon dioxide

- (CO₂) as feedstock for sustainable materials development: copolymers and polymer blends. *Polymer* **2018**, *145*, 348–373.
- 2 Yang, Z. Z.; He, L. N.; Gao, J.; Liu, A. H.; Yu, B. Carbon dioxide utilization with CN bond formation: carbon dioxide capture and subsequent conversion. *Energy Environ. Sci.* **2012**, *5*, 6602–6639.
- 3 Williams, C. K.; Hillmyer, M. A. Polymers from renewable resources: a perspective for a special issue of polymer reviews. *Polym. Rev.* **2008**, *48*, 1–10.
- 4 Honda, S.; Mori, T.; Goto, H.; Sugimoto, H. Carbon-dioxide-derived unsaturated alicyclic polycarbonate: synthesis, characterization, and post-polymerization modification. *Polymer* **2014**, *55*, 4832–4836.
- 5 Darensbourg, D. J.; Wei, S.; Yeung, A. D.; Ellis, W. C. An efficient method of depolymerization of poly(cyclopentene carbonate) to its comonomers: cyclopentene oxide and carbon dioxide. *Macromolecules* **2013**, *46*, 5850–5855.
- 6 Xu, J. W.; Feng, E.; Song, J. Renaissance of aliphatic polycarbonates: new techniques and biomedical applications. *J. Appl. Polym. Sci.* **2014**, *131*, 39822.
- 7 Udipi, K.; Gillham, J. K. Poly(ethylene carbonate) and poly(propylene carbonate): transitions and thermomechanical spectra. *J. Appl. Polym. Sci.* **1974**, *18*, 1575–1580.
- 8 Phillips, O.; Schwartz, J. M.; Kohl, P. A. Thermal decomposition of poly(propylene carbonate): end-capping, additives, and solvent effects. *Polym. Degrad. Stab.* **2016**, *125*, 129–139.
- 9 Bahramian, B.; Ma, Y.; Rohanizadeh, R.; Chrzanowski, W.; Dehghani, F. A new solution for removing metal-based catalyst residues from a biodegradable polymer. *Green Chem.* **2016**, *18*, 3740–3748.
- 10 Zhuo, C. W.; Qin, Y. S.; Wang, X. H.; Wang, F. S. Steric hindrance ligand strategy to aluminum porphyrin catalyst for completely alternative copolymerization of CO₂ and propylene oxide. *Chinese J. Polym. Sci.* **2018**, *36*, 252–260.
- 11 Tao, Y. H.; Wang, X. H.; Zhao, X. J.; Li, J.; Wang, F. S. Double propagation based on diepoxide, a facile route to high molecular weight poly(propylene carbonate). *Polymer* **2006**, *47*, 7368–7373.
- 12 Muthuraj, R.; Misra, M.; Mohanty, A. K. Biodegradable compatibilized polymer blends for packaging applications: a literature review. *J. Appl. Polym. Sci.* **2018**, *135*, 45726.
- 13 Yao, M. Modification of poly(lactic acid)/poly(propylene carbonate) blends through melt compounding with maleic anhydride. *Express Polym. Lett.* **2011**, *5*, 937–949.
- 14 Zhou, L. Y.; Zhao, G. Y.; Jiang, W. Effects of catalytic transesterification and composition on the toughness of poly(lactic acid)/poly(propylene carbonate) blends. *Ind. Eng. Chem. Res.* **2016**, *55*, 5565–5573.
- 15 Qin, S. X.; Yu, C. X.; Chen, X. Y.; Zhou, H. P.; Zhao, L. F. Fully biodegradable poly(lactic acid)/poly(propylene carbonate) shape memory materials with low recovery temperature based on *in situ* compatibilization by dicumyl peroxide. *Chinese J. Polym. Sci.* **2018**, *36*, 783–790.
- 16 Corre, Y. M.; Bruzard, S.; Grohens, Y. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and poly(propylene carbonate) blends: an efficient method to finely adjust properties of functional materials. *Macromol. Mater. Eng.* **2013**, *298*, 1176–1183.
- 17 Peng, S. W.; An, Y. X.; Chen, C.; Fei, B.; Zhuang, Y. G.; Dong, L. S. Miscibility and crystallization behavior of poly(3-hydroxyvalerate-co-3-hydroxybutyrate)/poly(propylene carbonate) blends. *J. Appl. Polym. Sci.* **2003**, *90*, 4054–4060.
- 18 Li, J. H.; Lai, M. F.; Liu, J. J. Control and development of crystallinity and morphology in poly(β -hydroxybutyrate-co- β -hydroxyvalerate)/poly(propylene carbonate) blends. *J. Appl. Polym. Sci.* **2005**, *98*, 1427–1436.
- 19 El-Hadi, A. M. Improvement of the miscibility by combination of poly(3-hydroxy butyrate) PHB and poly(propylene carbonate) PPC with additives. *J. Polym. Environ.* **2017**, *25*, 728–738.
- 20 Yang, D. Z.; Hu, P. Miscibility, crystallization, and mechanical

- properties of poly(3-hydroxybutyrate) and poly(propylene carbonate) biodegradable blends. *J. Appl. Polym. Sci.* **2008**, *109*, 1635–1642.
- 21 Chen, G. J.; Wang, Y. Y.; Wang, S. J.; Xiao, M.; Meng, Y. Z. Orientation microstructure and properties of poly(propylene carbonate)/poly(butylene succinate) blend films. *J. Appl. Polym. Sci.* **2013**, *128*, 390–399.
 - 22 Pang, M. Z.; Qiao, J. J.; Jiao, J.; Wang, S. J.; Xiao, M.; Meng, Y. Z. Miscibility and properties of completely biodegradable blends of poly(propylene carbonate) and poly(butylene succinate). *J. Appl. Polym. Sci.* **2008**, *107*, 2854–2860.
 - 23 Zeng, S. S.; Wang, S. J.; Xiao, M.; Han, D. M.; Meng, Y. Z. Preparation and properties of biodegradable blend containing poly(propylene carbonate) and starch acetate with different degrees of substitution. *Carbohydr. Polym.* **2011**, *86*, 1260–1265.
 - 24 Ge, X. C.; Li, X. H.; Zhu, Q.; Li, L.; Meng, Y. Z. Preparation and properties of biodegradable poly(propylene carbonate)/starch composites. *Polym. Eng. Sci.* **2004**, *44*, 2134–2140.
 - 25 Chen, L.; Hu, K.; Sun, S.; Jiang, H.; Huang, D.; Zhang, K. Y.; Pan, L.; Li, Y. S. Toughening poly(lactic acid) with imidazolium-based elastomeric ionomers. *Chinese J. Polym. Sci.* **2018**, *36*, 1342–1352.
 - 26 Tsuji, H. Poly(lactide) stereocomplexes: formation, structure, properties, degradation, and applications. *Macromol. Biosci.* **2005**, *5*, 569–597.
 - 27 Wang, M.; You, L. C.; Guo, Y. Q.; Jiang, N.; Gan, Z. H.; Ning, Z. B. Enhanced crystallization rate of poly(L-lactide)/hydroxyapatite-graft-poly(D-lactide) composite with different processing temperatures. *Chinese J. Polym. Sci.* **2020**, doi: 10.1007/s10118-020-2374-1.
 - 28 Shao, J.; Liu, Y. L.; Xiang, S.; Bian, X. C.; Sun, J. R.; Li, G.; Chen, X. S.; Hou, H. Q. The stereocomplex formation and phase separation of PLLA/PDLA blends with different optical purities and molecular weights. *Chinese J. Polym. Sci.* **2015**, *33*, 1713–1720.
 - 29 Bouapao, L.; Tsuji, H. Stereocomplex crystallization and spherulite growth of low molecular weight poly(L-lactide) and poly(D-lactide) from the melt. *Macromol. Chem. Phys.* **2009**, *210*, 993–1002.
 - 30 Wang, G.; Zhang, D. M.; Li, B.; Wan, G. P.; Zhao, G. Q.; Zhang, A. M. Strong and thermal-resistance glass fiber-reinforced polylactic acid (PLA) composites enabled by heat treatment. *Int. J. Biol. Macromol.* **2019**, *129*, 448–459.
 - 31 Li, W.; Sun, Q. S.; Mu, B. N.; Luo, G. Q.; Xu, H. L.; Yang, Y. Q. Poly(L-lactic acid) bio-composites reinforced by oligo(D-lactic acid) grafted chitosan for simultaneously improved ductility, strength and modulus. *Int. J. Biol. Macromol.* **2019**, *131*, 495–504.
 - 32 Tsuji, H.; Horii, F.; Hyon, S. H.; Ikada, Y. Stereocomplex formation between enantiomeric poly(lactic acid)s. 2. Stereocomplex formation in concentrated solutions. *Macromolecules* **1991**, *24*, 2719–2724.
 - 33 Tsuji, H.; Ikada, Y. Stereocomplex formation between enantiomeric poly(lactic acid)s. 6. Binary blends from copolymers. *Macromolecules* **1992**, *25*, 5719–5723.
 - 34 Bao, R. Y.; Yang, W.; Jiang, W. R.; Liu, Z. Y.; Xie, B. H.; Yang, M. B. Polymorphism of racemic poly(L-lactide)/poly(D-lactide) blend: effect of melt and cold crystallization. *J. Phys. Chem. B* **2013**, *117*, 3667–3674.
 - 35 Bao, R. Y.; Yang, W.; Jiang, W. R.; Liu, Z. Y.; Xie, B. H.; Yang, M. B.; Fu, Q. Stereocomplex formation of high-molecular-weight polylactide: a low temperature approach. *Polymer* **2012**, *53*, 5449–5454.
 - 36 Tsuji, H.; Horii, F.; Nakagawa, M.; Ikada, Y.; Odani, H.; Kitamaru, R. Stereocomplex formation between enantiomeric poly(lactic acid)s. 7. Phase structure of the stereocomplex crystallized from a dilute acetonitrile solution as studied by high-resolution solid-state carbon-13 NMR spectroscopy. *Macromolecules* **1992**, *25*, 4114–4118.
 - 37 Qin, Y. S.; Sheng, X. F.; Liu, S. J.; Ren, G. J.; Wang, X. H.; Wang, F. S. Recent advances in carbon dioxide based copolymers. *J. CO₂ Util.* **2015**, *11*, 3–9.
 - 38 Li, Y.; Han, C. Y.; Yu, Y. C.; Huang, D. X. Morphological, thermal, rheological and mechanical properties of poly(butylene carbonate) reinforced by stereocomplex polylactide. *Int. J. Biol. Macromol.* **2019**, *137*, 1169–1178.
 - 39 Tsuji, H.; Tashiro, K.; Bouapao, L.; Hanesaka, M. Synchronous and separate homo-crystallization of enantiomeric poly(L-lactic acid)/poly(D-lactic acid) blends. *Polymer* **2012**, *53*, 747–754.
 - 40 Han, C. Y.; Ran, X. H.; Su, X.; Zhang, K. Y.; Liu, N. A.; Dong, L. S. Effect of peroxide crosslinking on thermal and mechanical properties of poly(ϵ -caprolactone). *Polym. Int.* **2007**, *56*, 593–600.
 - 41 Liu, H. Z.; Chen, F.; Liu, B.; Estep, G.; Zhang, J. W. Super toughened poly(lactic acid) ternary blends by simultaneous dynamic vulcanization and interfacial compatibilization. *Macromolecules* **2010**, *43*, 6058–6066.
 - 42 Chen, F.; Zhang, J. W. A new approach for morphology control of poly(butylene adipate-co-terephthalate) and soy protein blends. *Polymer* **2009**, *50*, 3770–3777.
 - 43 Sundararaj, U.; Macosko, C. W. Drop breakup and coalescence in polymer blends: the effects of concentration and compatibilization. *Macromolecules* **1995**, *28*, 2647–2657.
 - 44 Horst, R. H.; Winter, H. H. Stable critical gels of a copolymer of ethene and 1-butene achieved by partial melting and recrystallization. *Macromolecules* **2000**, *33*, 7538–7543.
 - 45 Shenoy, A. V. in *Rheology of filled polymer systems*, Springer, Netherlands, **1999**, p. 90.
 - 46 Wu, D. F.; Wu, L.; Zhang, M.; Zhao, Y. L. Viscoelasticity and thermal stability of polylactide composites with various functionalized carbon nanotubes. *Polym. Degrad. Stab.* **2008**, *93*, 1577–1584.
 - 47 Kota, A. K.; Cipriano, B. H.; Dueterberg, M. K.; Gershon, A. L.; Powell, D.; Raghavan, S. R.; Bruck, H. A. Electrical and rheological percolation in polystyrene/MWCNT nanocomposites. *Macromolecules* **2007**, *40*, 7400–7406.
 - 48 Bouakaz, B. S.; Habi, A.; Grohens, Y.; Pillin, I. Effect of combinations of nanofillers on rheology-structure relations in biodegradable poly(ϵ -caprolactone) nanocomposites. *Appl. Clay Sci.* **2018**, *161*, 35–47.
 - 49 Han, C. D.; Kim, J. K. On the use of time-temperature superposition in multicomponent/multiphase polymer systems. *Polymer* **1993**, *34*, 2533–2539.
 - 50 Li, Y.; Han, C. Y.; Bian, J. J.; Han, L. J.; Dong, L. S.; Gao, G. Rheology and biodegradation of polylactide/silica nanocomposites. *Polym. Compos.* **2012**, *33*, 1719–1727.
 - 51 Cole, K. S.; Cole, R. H. Dispersion and absorption in dielectrics: alternating current characteristics. *J. Chem. Phys.* **1941**, *9*, 341–351.
 - 52 Li, H. B.; Li, Q.; Yan, M. L. Influence of operation procedures on Vicat softening temperature of thermoplastic materials. *Adv. Mater. Res.* **2011**, *291-294*, 1820–1824.