

Thermal, Rheological and Mechanical Properties of Biodegradable Poly(propylene carbonate)/Epoxidized Soybean Oil Blends

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Abstract Biodegradable poly(propylene carbonate) (PPC)/epoxidized soybean oil (ESO) blends with different component ratios were prepared by melt blending to improve the performance of PPC. The phase morphology, thermal properties, rheological properties and mechanical properties of the blends were investigated in detail. SEM examination revealed good interfacial adhesion between PPC matrix and ESO. According to DSC and DMA, as the content of ESO increased, the glass transition temperature of the PPC component increased, indicating that there was a strong interfacial interaction between the PPC matrix and ESO. The interfacial interaction may be caused by ring-opening reaction between the hydroxyl end groups of PPC and the epoxy groups of ESO, which restricted the chain movement of PPC matrix. The disappearance of the epoxy groups in FTIR indicated that the interfacial interaction between the two phases was due to the ring-opening reaction between PPC and ESO. With the addition of ESO, the thermal stabilities were enhanced. With the increasing ESO content, the modulus gradually decreased. However, the strength at yield, the strength at break and the elongation at break were increased for the PPC/ESO blends, suggesting that the enhancement of the strength and toughness of PPC was achieved by the incorporation of ESO. The rheological measurement revealed that the complex viscosity, storage modulus and loss modulus of PPC were increased with the increasing ESO content at low frequency, which indicated that the addition of ESO enhanced the melt strength of PPC instead of plasticizing PPC.

Keywords Poly(propylene carbonate); Epoxy soybean oil; Compatibility; Mechanical properties

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INTRODUCTION

The white pollution caused by petroleum-based polymers has become more and more serious to the global ecological environment. The development of petroleum-based polymers has made petroleum resources scarce in the meantime.^[1] Therefore, the development of biodegradable and renewable resource-derived polymers to replace the conventional non-degradable petroleum-based polymers has become a hot issue in today's society.^[2] As early as the 1980s, biodegradable polymers with biodegradability, biocompatibility, environmental protection and other advantages, have been widely used in plastic packaging industry, thin films, molded products and sheets, medical scaffolds, automobile and other fields.^[3,4] Currently, carbon dioxide is considered to be a major contributor to global warming due to its greenhouse effect. Since carbon dioxide is abundant, inexpensive, safe, non-flammable and non-oxidant, Food and Drug Administration

(FDA) approved for food related use and renewable, a large number of researchers have synthesized CO₂-based polymers using a technology that can fix and harness carbon dioxide.^[5] Using carbon dioxide as a feedstock for synthetic polymers can not only reduce the dependence on petroleum but also be conducive to reducing large amounts of carbon dioxide emissions.^[6] Poly(propylene carbonate) (PPC), as a kind of biodegradable thermoplastic aliphatic polycarbonate, has aroused extensive interest in academia and industry due to its high value-added fixation of CO₂, biodegradability, biocompatibility and excellent oxygen barrier ability.^[7] PPC, an alternating copolymer of propylene oxide (PO) and carbon dioxide (CO₂), was first synthesized under a heterogeneous catalysis system by Inoue in 1969.^[8,9] Fig. 1 displays the synthesis process and chemical structure of PPC. The synthesis of PPC fixes and recycles the greenhouse gas carbon dioxide in the environment, which reduces the consumption of petroleum-based resources and a large amount of CO₂ emissions.^[10] Meanwhile, PPC can be degraded into H₂O and CO₂ without causing white pollution and damage to the ecosystem.^[11] However, PPC is an amorphous polymer with flexible polymer chain skeleton structure and weak interchain interaction,

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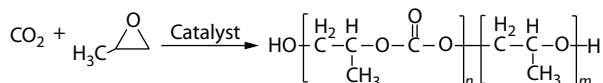


Fig. 1 Synthesis process and chemical structure of PPC.

resulting in a low glass transition temperature (T_g : 20–40 °C), low thermal decomposition temperature and poor mechanical properties.^[12] It is precisely because of the above-mentioned shortcomings that the processability and application of PPC were largely restricted. Many efforts have been made to improve the properties of PPC by blending PPC with a diverse array of polymers so as to expand the extensive use of PPC. In order to modify the properties of PPC, some people used chemical modification methods, that is, terpolymerization of carbon dioxide, propylene oxide and another monomer.^[7] However, the physical blending of PPC and other polymer was more favored due to its simplicity and cost-effective advantages. Hao *et al.*^[13] blended PPC with a plasticizer of poly(diethylene glycol adipate) (PDEGA) to improve the flexibility of PPC. Wu *et al.*^[14] used poly(1,2-propylene succinate) (PPSu) to plasticize PPC, which resulted in enhanced toughness and melt fluidity of PPC. Research by Peng *et al.*^[15] showed that melt blending of corn starch and PPC can effectively improve the modulus and T_g of PPC. Chen *et al.*^[16] used low-molecular-weight carbamate to plasticize, toughen and strengthen PPC by melt blending. The elongation at break of PPC was greatly improved and a certain mechanical strength was maintained.

Epoxidized soybean oil (ESO) is an epoxidized derivative of soybean oil which is a mixture of esters of glycerol with various saturated and unsaturated fatty acids.^[17,18] The structure of ESO is shown in Fig. 2. In recent years, ESO which belongs to epoxidized vegetable oils has attracted much attention because it is environmentally friendly, biodegradable, renewable, highly available and non-toxic.^[19] In the chemical industry, ESO was widely used as lubricant, reinforcing agent, plasticizer, etc., and at the same time exhibited an advantage in the preparation of biodegradable materials, such as resin, adhesive, coating, and composites.^[20] The epoxidation reaction of the unsaturated bonds on the chains of ESO produces more reactive oxirane groups, resulting in providing a more energetically favorable site for reaction.^[21] In general, ESO has been usually used as a plasticizer and stabilizer for poly(vinyl chloride) (PVC) films to improve thermal stability and flexibility by Bueno-Ferrer *et al.*^[22] Poly(lactic acid) (PLA) was plasticized by ESO to obtain a film with fascinating melt strength and rheological properties.^[21] Yang *et al.* found that ESO was first used as a plasticizer for ethyl cellulose (EC) film with preferable mechanical properties and thermal stability, as well as non-flammability.^[20] Choi reported that ESO, as a plasticizer, reduced the T_g of poly(3-hydroxy butyrate-co-3-hydroxyvalerate) (PHBV) and increased the elongation at break and impact strength of PHBV.^[23] However, using ESO to improve the physical properties of PPC by melt-blending has not been reported.

At present, polymer blending modification was not only a simple but also an effective method to attain polymer materials with satisfactory properties. In addition, the miscibility between different components could generally affect the properties of polymer blends. The poor miscibility between

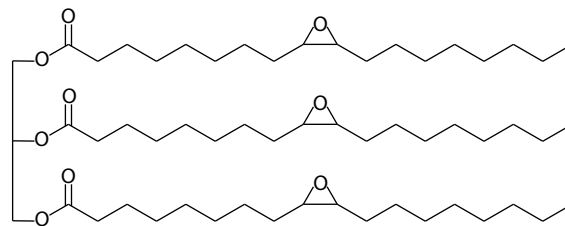


Fig. 2 Chemical structure of ESO.

the components led to phase separation in the polymer composite. Its performance was not only related to the performance of individual component, but also closely related to phase morphology.^[24] In the present work, the environmental-friendly ESO was used to improve the thermal and mechanical properties of PPC. And the PPC/ESO blends were prepared by melt blending. The phase morphology and miscibility, thermal, rheological and mechanical properties were studied by SEM, DSC, DMA, TGA, the rotational rheometer, and static tensile tests. The melt blending of PPC and ESO is expected to improve the thermal and mechanical properties of PPC, which will broaden the practical application of PPC. For example, PPC/ESO blown film has broad application prospects in environmentally friendly packaging materials such as food preservation film. Due to its good gas barrier properties, PPC can be widely used in barrier materials and food packaging materials.

EXPERIMENTAL

Materials

PPC was supplied by the research group of Researcher Xianhong Wang, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. It was prepared by the copolymerization of carbon dioxide and propylene oxide under a catalyst according to the method disclosed in the authorized Chinese invention patent CN101402726B. The weight-average molecular weight and poly-dispersity index (PDI) of the neat PPC determined by GPC was 3.0×10^5 g/mol and 2.1, respectively. ESO was provided by Nantong Hairma Group Co. (Jiangsu, China). The epoxy value of ESO, which was HN-01AD, was 6.6 according to ASTM D 1652-04.

Preparation of the Blends

In order to blend fully, before processing, the PPC granules were first frozen in liquid nitrogen for about 20 min, and then the frozen PPC granules were put into a high-speed blender for rapid stirring. The PPC powder obtained by stirring was sifted through a sieve to obtain the powder with a particle size of about 20 mesh. Finally, the PPC powder was dried in a vacuum drying oven at 30 °C for 12 h. The weight ratios of PPC powder to ESO were 100/0, 97/3, 95/5 and 93/7, respectively. Before melt blending, PPC powder and ESO were mixed uniformly by stirring. By using a torque rheometer (XSS-300, Shanghai Kechuang Rubber Plastic Mechanical Equipment Co., Ltd., China), the blends were melt-blended at 150 °C with a screw speed of 60 r/min for approximately 8 min. Then all the blends were chopped into small pieces for compression molding. But during the melt processing, it was found that more ESO was attached to the surface of the PPC/ESO blend with an ESO

content of 10 wt%, and there was more ESO around the cavity wall of the internal mixer. This made it difficult for ESO to be completely mixed into the PPC matrix. Therefore, the ESO content only increased to 7 wt% in this experiment. The small pieces were hot-pressed for 3 min at 160 °C and 10 MPa, followed by cold-pressed to room temperature at 10 MPa, and finally made into thin slices with a thickness of 1 mm. The small pieces were hot-pressed into free sheets for 3 min at 160 °C, followed by cold-pressed to room temperature at 10 MPa. The thickness of the final free sheets was about 50 µm. In order to ensure that the effects of the processing process on the thermal history of each sample were the same, all samples were subjected to the same processing conditions. The samples were finally sealed in a sealed bag for subsequent experimental measurement.

Scanning Electron Microscopy

The morphology of the samples was observed by a field emission scanning electron microscopy (FESEM) (Merlin Zeiss, Germany) at an accelerating voltage of 1 kV. The samples were soaked in liquid nitrogen for about 5 min, and then it was broken. Before SEM experiment, a thin layer of gold should be sprayed on the cryo-fractured surfaces of the sample, so that the morphology of the cryo-fractured surfaces of the samples could be observed more clearly. Then the dispersion state of ESO in PPC matrix was observed under SEM.

Differential Scanning Calorimetry

The thermal analyses of neat PPC and PPC/ESO blends were performed on TA Instruments differential scanning calorimeter (DSC) Q20 with a Universal Analysis 2000. Specimens were sliced from small pieces after melt-blending. The weight range of samples was approximately 5–8 mg, and then they were placed and sealed in aluminum pans. The whole experiment was carried out under nitrogen atmosphere (flow rate of 50 mL/min). In the first heating scan, the temperature of the samples rose first from room temperature to 165 °C at the rate of 30 °C/min to eliminate the thermal history, and then cooled to 0 °C at the rate of 45 °C/min. The samples were heated from 0 °C to 165 °C at a heating rate of 10 °C/min on the second heating scan. T_g was determined from the second heating curve.

Dynamic Mechanical Analysis

Dynamic mechanical analyses (DMA) of the neat PPC and PPC/ESO blends were measured by a dynamic mechanical analyzer (DMA, Q850, TA Instruments, USA) in the tensile mode. The size of the dumbbell shaped specimens was 20 mm × 4 mm × 1 mm. First, kept the experiment at 0 °C for 3 min, and then the temperature of the experiment ranged from 0 °C to 80 °C at a heating rate of 3 °C/min. The dynamic mechanical parameters of the samples, such as the storage modulus (E') and the dynamic loss factor ($\tan\delta$), were determined as a function of temperature at a fixed frequency of 1 Hz and the oscillation amplitude of 10 µm.

Thermal Stability Properties

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA-7 simultaneous thermal analysis instrument (USA). The weight of all samples was 10±0.2 mg. The temperature of the whole experiment was heated from room temperature to 500 °C at a heating rate of 10 °C/min in a nitrogen environment with a flow rate of 50 mL/min.

Fourier Transform Infrared Analysis

Fourier transform infrared (FTIR) spectroscopic analysis was performed on a Thermo-Niclet 6700 FTIR spectrometer. The FTIR spectra were acquired by 16 scans in the wavelength range between 4000–400 cm⁻¹, and the resolution was 2 cm⁻¹. The samples were thin films with a thickness of approximately 50 µm.

Rheological Properties

The rotational rheometer (AR2000EX, TA Instruments-Waters LLC, USA) was used to detect the rheological properties of neat PPC and PPC/ESO blends. The sample was a round piece with a diameter of 25 mm and a thickness of 1 mm. Oscillatory frequency sweep was performed at frequency between 0.05 and 100 rad/s. The temperatures were set at 145, 150 and 155 °C throughout the experiment. The storage modulus (G'), loss modulus (G'') and complex viscosity ($|\eta^*|$) of neat PPC and PPC/ESO blends were determined as a function of frequency. The small amplitude oscillatory shear (SAOS) was adapted to the strain level of 1.25%, mainly to avoid the nonlinear response at low frequency, so as to obtain reasonable signal strength.

Mechanical Property Test

The tensile tests were carried out on a universal testing machine (WSM-2KN, Changchun Intelligent Instrument and Equipment Co., Ltd., China) equipped with a high-low temperature environmental chamber according to GB/T1040.1-2006. The specimens with dumbbell shape (20 mm × 4 mm × 1 mm) were cut from the previous compressed molded sheets. The mechanical property parameters of the samples were tested at 20 °C and a cross-head speed of 10 mm/min. Five specimens were selected from each sample for testing and the average value was obtained.

RESULTS AND DISCUSSION

Morphology Analysis

The mechanical properties of blends are related to their microstructure, and the dispersion of components in the matrix is directly related to the properties of the blends. The morphology of cryogenically fractured surfaces of PPC/ESO blends with various amounts of ESO can be observed in Fig. 3. The cryo-fractured surface of neat PPC was relatively flat, smooth and without holes. When ESO was added to the PPC matrix, the microvoids of PPC/ESO blends were observed indicating that phase separation appeared in PPC/ESO blends, which was caused by the accumulation of ESO in PPC matrix.^[25] With the increase of ESO content, the morphology of PPC/ESO blends showed a significant change. The size of the microvoids increased and the cryo-fractured surface of the PPC/ESO blends became gradually uneven. When the ESO content increased to 7 wt%, there were uneven microvoids distributed in the PPC/ESO blend. Meanwhile, a dark phase could be clearly observed around the ESO phase when the ESO content was 7 wt%, which indicated that PPC and ESO were partially compatible. It was speculated that the partial compatibility between PPC and ESO may be caused by the chemical reaction between the terminal hydroxyl groups of PPC and the epoxy groups of ESO.^[26] The chemical reaction process between PPC and ESO is shown in Fig. 4. Moreover, the formation of ESO-g-PPC (marked by the yellow arrow in Fig. 3d) indicated that there was an interfacial

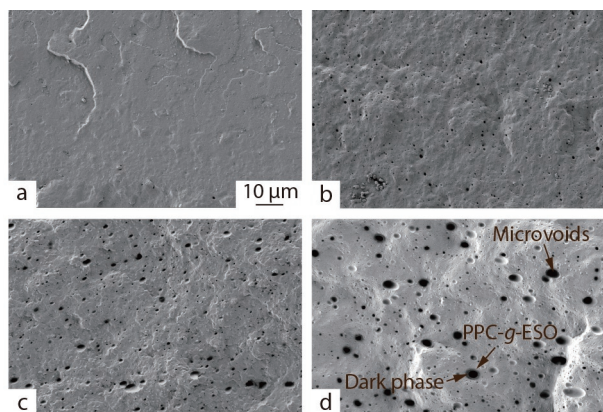


Fig. 3 SEM micrographs of cryo-fractured surfaces of PPC/ESO blends with various ESO contents: (a) 100/0, (b) 97/3, (c) 95/5, (d) 93/7.

interaction between ESO and PPC matrix, which may improve the mechanical properties of the blend.

Thermal Behaviors

DSC is one of the common methods for characterizing the T_g of polymer. T_g is closely related to the segment motion of the polymer, which determines the application temperature range of polymer materials. The DSC heating thermograms of the neat PPC and PPC/ESO blends on the second heating step are shown in Fig. 5. The T_g of PPC/ESO blends is listed in Table 1. Because neat PPC was amorphous, there was only a T_g in DSC thermograms, which was 26.3 °C. It could be seen that T_g of PPC in the blends increased with the increase of ESO content. Compared with the T_g of neat PPC, the T_g of PPC in blend containing 7 wt% ESO was 27.5 °C, which increased by about 1 °C.

In previous study,^[27] ESO usually acted as a plasticizer in the blend, thereby reducing the T_g of the polymer. However, in our work, the T_g of PPC in the blend increased instead of

decreasing, indicating that there was a certain interaction between PPC and ESO. The increase of T_g may be due to the ring-opening reaction between the hydroxyl end groups of PPC and the epoxy groups of ESO, which limited the segmental movement of PPC molecular chains.

Dynamic Mechanical Analysis

DMA is an important method to measure the T_g and investigate the miscibility of polymer blends under a dynamic condition. Fig. 6 shows the curves of E' and $\tan\delta$ of neat PPC and PPC/ESO blends as a function of temperature. The T_g of neat PPC and PPC/ESO blends tested by DMA is also listed in Table 1. As shown in Fig. 6(a), the E' of the PPC/ESO blends decreased when the ESO content increased. The decrease of E' was caused by the elastomeric effect of ESO. According to Fig. 6(b), it was understood that with the addition of ESO content, the peak of the PPC/ESO blends shifted to the high temperature direction. Compared with neat PPC (33.2 °C), the T_g of the PPC/ESO blend with a content of 7 wt% was 35.2 °C. The above results further indicated that there was an interfacial interaction between the PPC matrix and ESO, which hindered the movement of the PPC molecular chain. This result is in good agreement with DSC result.

Thermal Stability

Thermal stability parameters play an important role in polymer melt processing and molding, and it determines the choice of the upper temperature limit in polymer melt processing. The TGA and DTG curves of neat PPC and PPC/ESO blends reflected the improvement of the thermal performance of neat PPC, where the weight loss was measured as a function of temperature due to the thermal decomposition of the degradation product. The TGA and DTG curves of neat PPC and PPC/ESO blends under nitrogen are shown in Fig. 7, and the corresponding characteristic temperatures are listed in Table 2. The temperature corresponding to the onset temperature of decomposition (T_{onset}) is a very crucial parameter for considering

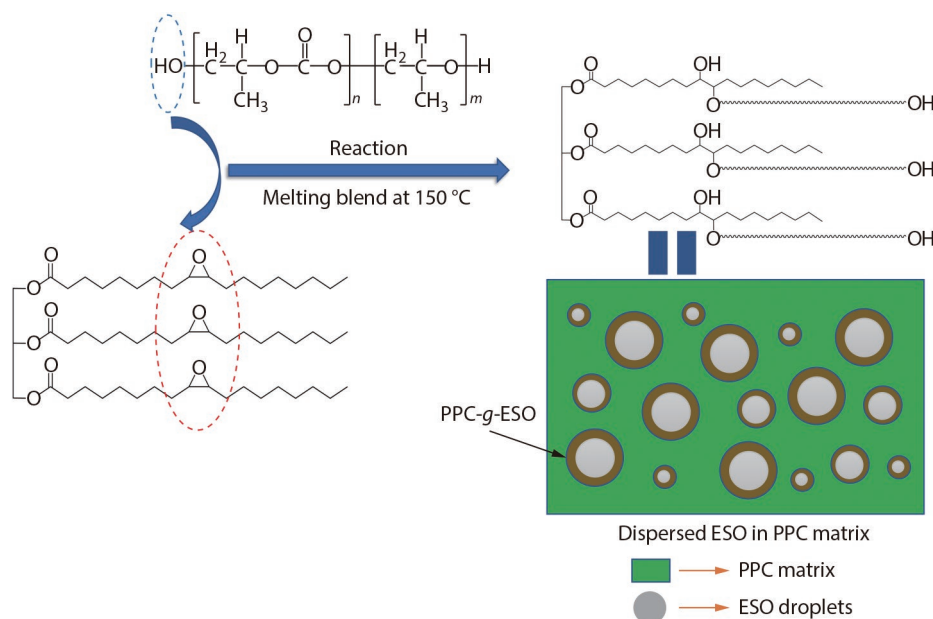


Fig. 4 The possible chemical reaction diagram in PPC/ESO blends during melt blending process.

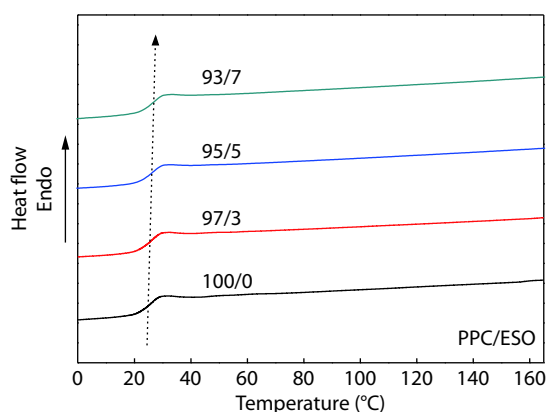


Fig. 5 DSC thermograms of PPC/ESO blends from the second heating rate.

Table 1 Glass transition temperatures of PPC in PPC/ESO blends.

PPC/ESO (W/W)	T_g (°C)	
	DSC	DMA
100/0	26.3	33.2
97/3	26.5	33.5
95/5	26.9	34.5
93/7	27.5	35.2

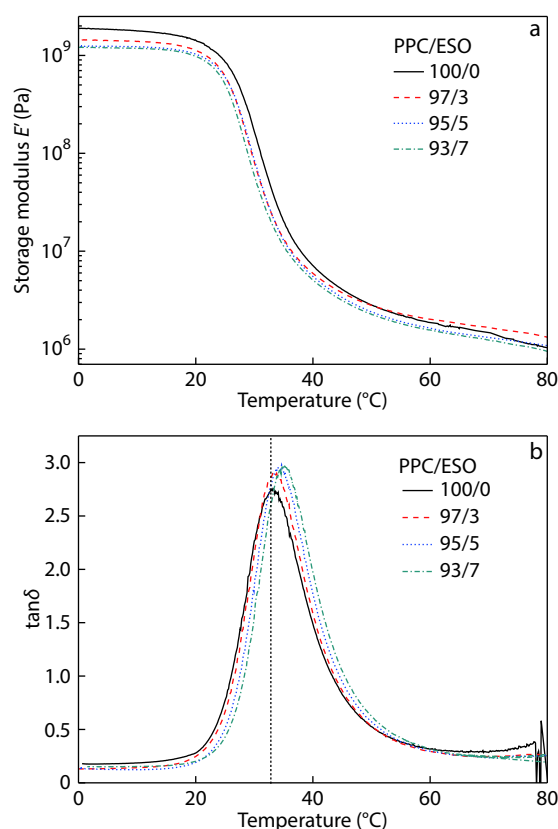


Fig. 6 The dynamic mechanical curves of neat PPC and PPC/ESO blends: (a) storage modulus (E') versus temperature curves; (b) $\tan\delta$ versus temperature curves.

the thermal stability and melt processing of polymers. It could be seen that T_{onset} of neat PPC was 264.2 °C, followed by a quick

weight loss from the Fig. 7(a). When ESO was added to the PPC matrix, the T_{onset} of the PPC/ESO blends was increased. Compared to neat PPC, the T_{onset} of PPC/ESO blend with ESO content of 7 wt% was 271.8 °C, which increased by about 7 °C. This result showed that the thermal stability of the PPC/ESO blend had been enhanced after ESO was incorporated into the PPC matrix.

The temperature corresponding to the maximum rate of weight loss (T_{max}), which is defined as the peak value of DTG curves, is also important thermal stability characteristic parameter for polymers. From Fig. 7(b), it could be observed that the T_{max} value of the PPC/ESO blend with ESO content of 7 wt% was 289.0 °C, which was higher than that of neat PPC (280.5 °C). The reason that the T_{max} moved to the high temperature direction may be due to the interfacial interaction between PPC and ESO. Moreover, in the DTG curves of neat PPC and PPC/ESO blends, two peaks could be observed, indicating that the thermal degradation mechanism of PPC/ESO blends was relatively complicated. According to the previous work,^[28,29] there were two main thermal degradation mechanisms of PPC, namely, the unzipping reaction at low temper-

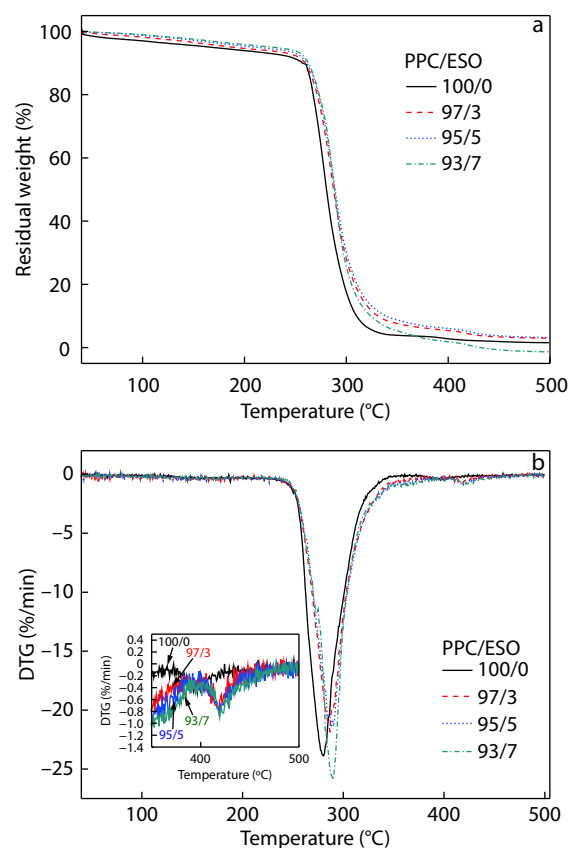


Fig. 7 (a) TGA and (b) DTG curves of neat PPC and PPC/ESO blends.

Table 2 Thermal properties of neat PPC and PPC/ESO blends.

PPC/ESO (W/W)	T_{onset} (°C)	T_{max} (°C)
100/0	264.2	280.5
97/3	268.8	286.3
95/5	270.4	288.3
93/7	271.8	289.0

ature ($\sim 280^\circ\text{C}$) and the random chain scission reaction ($>400^\circ\text{C}$) at high temperature. The effective ring-opening reaction between the terminal hydroxyl groups of PPC and the epoxy groups of ESO limited the backbiting process and depress the unzipping reaction. Hence, the addition of ESO could enhance the thermal stability of PPC.

FTIR Analysis

FTIR is one of the commonly used methods to characterize the reaction and interfacial interaction between polymer blends. Fig. 8 shows the infrared spectra of neat PPC, ESO and PPC/ESO blends at room temperature. The characteristic absorption peak of the epoxy groups at 823 cm^{-1} for ESO was clearly shown in Fig. 8(b). When ESO was added to the PPC matrix, it was found that the characteristic absorption peaks of the epoxy groups in the PPC/ESO blends disappeared, indicating the occurrence of the chemical reaction between the PPC and ESO during melt blending. According to Fig. 8(a), in the neat PPC and PPC/ESO blends, the stretching vibration bands of $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ could be observed at 1736 and 1222 cm^{-1} , respectively, while those of ESO were located at 1741 and 1155 cm^{-1} . However, as observed in Figs. 8(c) and 8(d), as the ESO content increased, the stretching vibration bands of $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ in the PPC/ESO blends became gradually narrow, which was mainly caused by the chemical reaction between PPC and ESO.^[30] The stretching vibration peak of the hydroxyl group in the region of $3700\text{--}3100\text{ cm}^{-1}$ is shown in Fig. 8(a). Since the end of the PPC molecular chain contained a small amount of $\text{O}-\text{H}$ groups, the hydroxyl stretching vibration peak of the neat PPC and PPC/ESO blends could be ignored.

At the same time, it is observed that the intensity of the peak was also changed. Compared with neat PPC, when the ESO content was 3 wt%, the band intensity of $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ was slightly higher than that of neat PPC. When the ESO content exceeded 3 wt%, the band intensity of $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ gradually decreased with the increase of ESO content. The above results indicated that there may be interfacial interaction between the PPC matrix and ESO.

It is generally believed that when the additive is added to the matrix material, the infrared spectra does not change, indicating that there is no interaction between the thermoplastic and the additive.^[31] However, when there is a change of the peak (*i.e.*, band shifts, narrowing peaks, intensity change of the peak), it is considered that there may be an interaction between the components.^[32] We believe that the interaction between PPC and ESO may be formed by the ring-opening reaction between the terminal hydroxyl groups of PPC and the epoxy groups of ESO.^[26]

Rheological Properties

Rheological analysis is a significant measurement to evaluate the melt processing parameters and the interaction between two phases in the blends. The effects of the ESO on the rheological behavior of PPC were investigated at 145 , 150 and 155°C , respectively. Fig. 9 exhibits G' , G'' and $|\eta^*|$ of neat PPC and PPC/ESO blends as a function of oscillatory frequency.

The $|\eta^*|$ values of neat PPC and PPC/ESO blends are presented in Figs. 9(a), 9(a') and 9(a''). At the beginning, the viscosity of neat PPC remained unchanged, which meant that in a relatively narrow low frequency range, neat PPC displayed a typ-

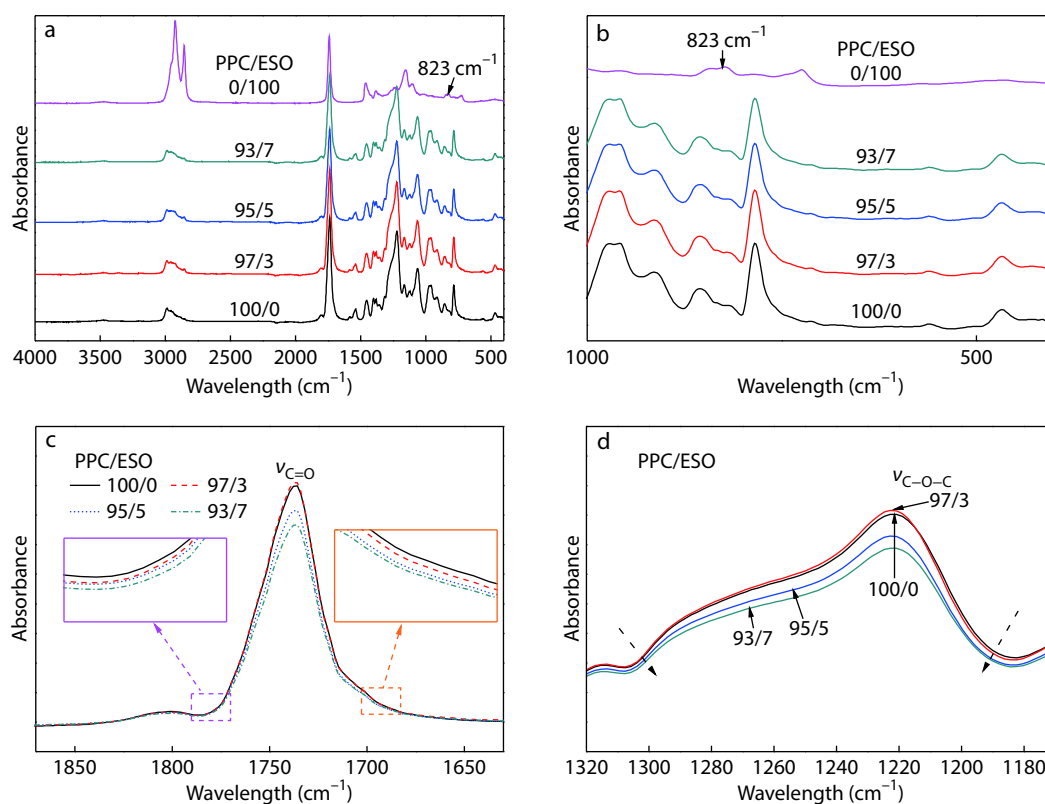


Fig. 8 FTIR spectra of neat PPC, ESO and PPC/ESO blends: (a) from 4000 cm^{-1} to 400 cm^{-1} , (b) from 1000 cm^{-1} to 400 cm^{-1} , (c) from 1870 cm^{-1} to 1630 cm^{-1} , (d) from 1320 cm^{-1} to 1170 cm^{-1} .

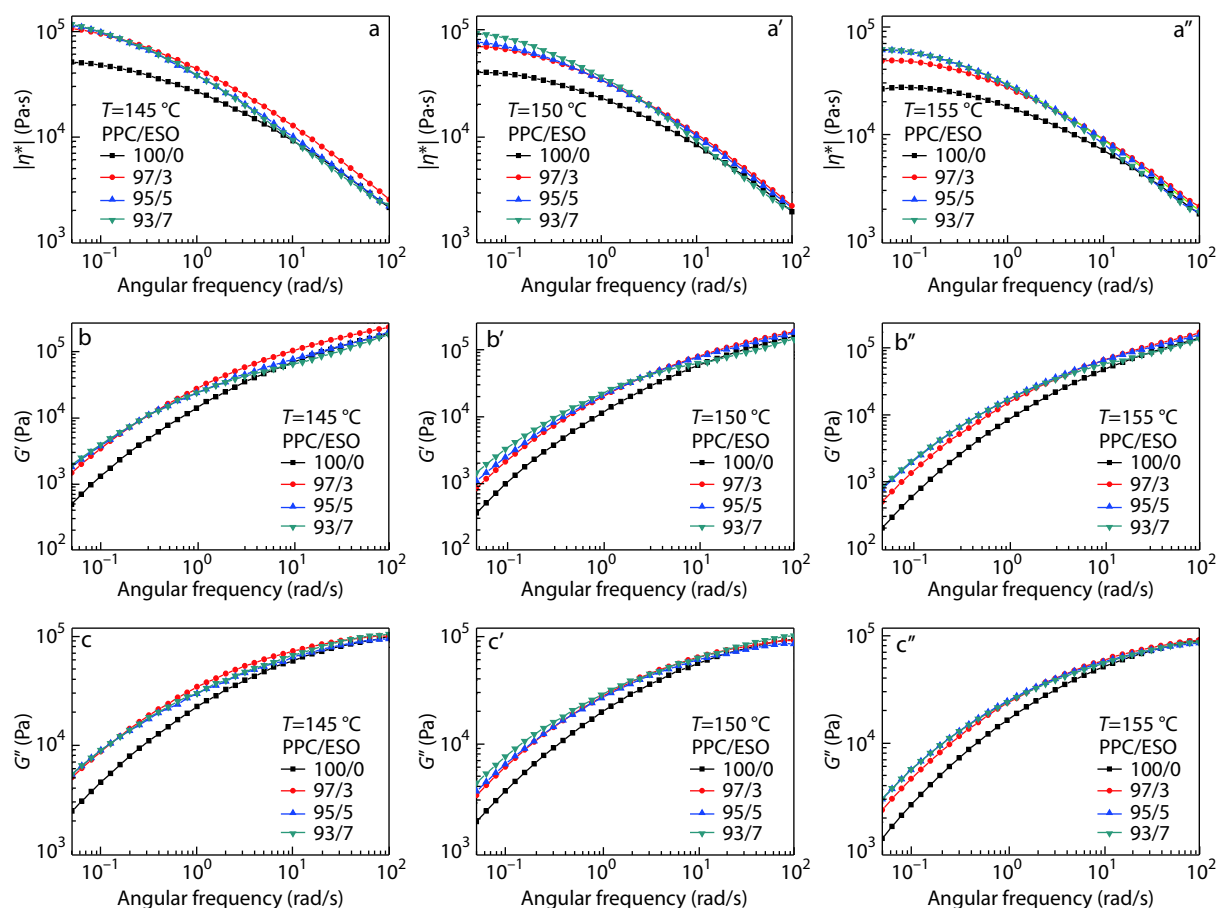


Fig. 9 Rheological properties of neat PPC and PPC/ESO blends: (a, a' and a'') complex viscosity ($|\eta^*|$); (b, b' and b'') storage modulus (G'); (c, c' and c'') loss modulus (G'') versus frequency at 145 °C, 150 °C and 155 °C, respectively.

ical Newtonian fluid behavior. After that, the $|\eta^*|$ of neat PPC decreased and showed pseudoplastic shear thinning behavior with the increase of frequency, indicating that the entanglement of PPC molecular chain was untangled due to the increase of shear rate. For the PPC/ESO blends, the viscosity platform of PPC moved to the low frequency direction, and with the increase of ESO content, the viscosity platform of PPC/ESO blends at low frequency became gradually unclear. The blends tended to show shear thinning at lower angular frequencies with the increasing ESO content. It could be observed from Figs. 9(a), 9(a') and 9(a'') that the low-frequency complex viscosity of the PPC matrix had a significant increase in the presence of ESO. On the one hand, the increasing complex viscosity in the low frequency region was related to the deformed droplet.^[33] On the other hand, the interfacial interaction between PPC and ESO was also the main reason for the further increase in low-frequency complex viscosity. Meanwhile, it could also be observed from Fig. 10 that as the temperature increased, the $|\eta^*|$ of neat PPC and PPC/ESO blends decreased in the low frequency region. This was because as the temperature increased, the random thermal motion of the molecular chain intensified, the molecular distance increased, and more energy caused more "holes" to form inside the polymer, which makes the molecular chain easier to move.

The G' and G'' of the PPC/ESO blends versus frequency are shown in Figs. 9(b)–9(c''). It could be seen that in the low frequency region, the G' and G'' of the PPC/ESO blends increased and were higher than those of neat PPC as the ESO content increased. In the low frequency region, as the content of ESO increased, more energy was stored due to the relaxation of the deformed ESO droplets, which increased the G' and G'' of the blend. With the increase of ESO content, the binding effect of the interface between PPC matrix and ESO increased, so higher shear stress and a longer relaxation time were required.^[34] When the temperature increased, it was observed that the G' and G'' of the neat PPC and PPC/ESO blends decreased. This was because as the temperature increased, the movement of PPC molecular chains was enhanced, and the rheological responses were mainly dominated by the viscous PPC matrix.^[35]

Mechanical Properties

The stress-strain curves of neat PPC and PPC/ESO blends are displayed in Fig. 11. The Young's modulus, strength at yield, strength at break and elongation at break of neat PPC and PPC/ESO blends are listed in Table 3. It was very obvious that neat PPC first underwent a yield stage, followed by a subsequent plastic deformation and strain hardening, indicating that neat PPC was a fairly ductile material. It could be seen from Fig. 11 that the elongation at break of the PPC/ESO

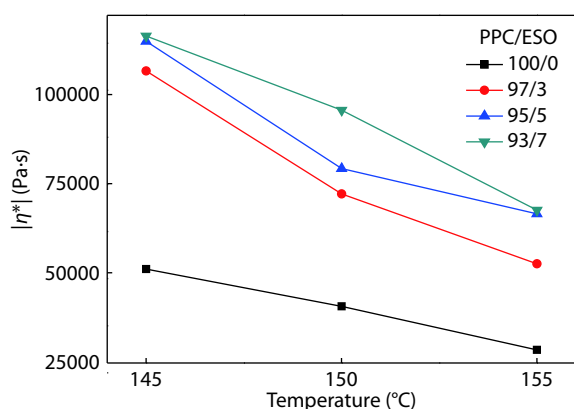


Fig. 10 The plots of $|\eta^*|$ at 0.05 rad/s versus temperature at various ESO contents.

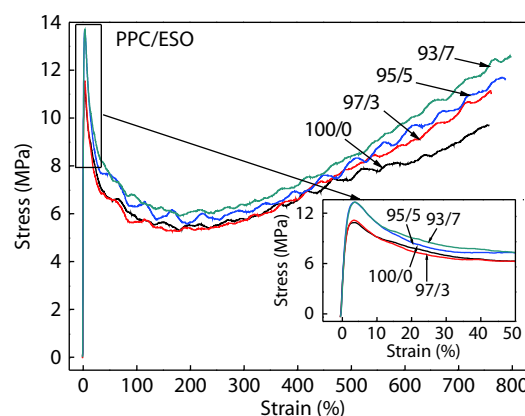


Fig. 11 Stress-strain curves of neat PPC and PPC/ESO blend.

Table 3 Mechanical properties of neat PPC and PPC/ESO blends.

PPC/ESO (W/W)	Young's modulus (MPa)	Strength at yielding (MPa)	Strength at break (MPa)	Elongation at break (%)
100/0	556.4±18.1	11.8±0.5	10.1±0.3	746.5±36.3
97/3	461.7±52.2	12.2±0.3	11.1±0.5	788.3±13.7
95/5	424.7±8.1	13.5±0.2	11.5±0.7	800.9±10.2
93/7	387.5±25.2	13.8±0.7	12.7±0.3	848.9±27.5

blends showed an increase. The elongation at break of the PPC/ESO blend with a ratio of 93/7 was 848.9%, which was approximately 14% increase compared to that of neat PPC. The reason for the increase in the elongation at break of the PPC/ESO blends may be due to the local plasticization by micro-droplets of the low molecular weight ESO dispersed in the PPC matrix. With the addition of ESO, the Young's modulus of PPC/ESO blends gradually decreased due to the elastomeric effect of ESO. However, with the increasing ESO content, an improvement in the strength at yield and strength at break of the PPC/ESO blends was achieved. This may be due to the improved interfacial interaction between PPC and ESO.^[21] It was speculated that there was the ring-opening reaction between the hydroxyl end groups of PPC and the epoxy groups of ESO. The addition of ESO efficiently changed the tensile behavior of PPC, especially the increase in strength at yield, strength at break, and elongation at break. The above results indicated that the introduction of ESO can effectively improve the mechanical properties of PPC.

CONCLUSIONS

Fully biodegradable ESO was used to modify PPC and the PPC/ESO blends were prepared by melt blending. The effect of ESO on the phase morphology, thermal behavior, rheological behavior and mechanical properties of PPC/ESO blends was investigated by SEM, DSC, DMA, TGA, rheometry and static tensile tests in detail. SEM revealed the two-phase structure with the ESO droplet dispersed in the PPC matrix. However, the interface between PPC and ESO was not so clear, indicating PPC and ESO were not highly incompatible and the interfacial adhesion was existent. DSC and DMA results further indicated that there was a strong interfacial interaction between the PPC matrix and ESO since the T_g of PPC increased with the increasing ESO content in the blends. With the introduction of ESO, the thermal stability properties of PPC/ESO blends were gradually

improved. The disappearance of the band of epoxy groups in FTIR indicated that the interfacial interaction between the two phases was caused by the ring-opening reaction between the terminal hydroxyl groups of PPC and the epoxy groups of ESO. Tensile testing showed that the strength at yield and break and elongation at break of PPC/ESO blends were enhanced simultaneously with the increase of ESO content, suggesting that the enhancement of the strength and toughness of PPC was achieved by the incorporation of ESO. Compared with neat PPC, at the low frequency range, the storage modulus, loss modulus and complex viscosity of PPC/ESO blends had a significant improvement. The addition of ESO will promote the application of PPC-based biodegradable materials in food packaging materials, food preservation films and barrier materials.

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