

Rheological, Thermal and Mechanical Properties of Biodegradable Poly(propylene carbonate)/Polylactide/Poly(1,2-propylene glycol adipate) Blown Films*

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Abstract Poly(propylene carbonate) (PPC) was blended with polylactide (PLA) and poly(1,2-propylene glycol adipate) (PPA) using a twin screw extruder. Then the PPC/PLA/PPA films were prepared using the blown film technique. DMA results showed that PPA could act as a plasticizer and improve the miscibility between PPC and PLA. Crystal morphology displayed that blending PLA with the amorphous PPC led to a decrease of the spherulite size of PLA. The results of mechanical tests indicated that PPC-rich films showed high elongation at break and PLA-rich films showed high tear strength and good optical properties. The content of PPC and PLA significantly affected the physical properties of the films. With increasing PPC content, the melt strengths of the PPC/PLA/PPA films were enhanced. These findings contributed to the biodegradable materials application for designing and manufacturing polymer packaging.

Keywords: Poly(propylene carbonate); Polylactide; Plasticizer; Blown films.

INTRODUCTION

Poly(propylene carbonate) is a kind of linear aliphatic polyester first synthesized by Inoue *et al.* via the copolymerization of carbon dioxide and propylene oxide^[1, 2]. Furthermore, PPC is a biodegradable aliphatic polycarbonate that can be degraded to H₂O and CO₂, and its synthesis can fix and recycle CO₂ in the environment which not only reduces dependence on petroleum but also decreases the massive emission of CO₂, which can mitigate the greenhouse effect^[1, 3, 4]. PPC has good properties such as compatibility, translucence *etc*^[5–7]. The versatility of PPC has found utilization in one-off packaging materials, dishware and board materials^[8]. However, PPC is an amorphous polymer and its thermal stability, viscosity and biodegradability still need to be improved. Moreover, PPC exhibited poor thermal and mechanical properties due to its relatively lower glass transition temperature (T_g). The low T_g has limited the application of PPC. Therefore, many approaches to improve these properties of PPC have been considered^[4, 7–15]. The blending of different polymers is a simple and economical method to enhance the properties of a polymer matrix. Numerous works has been devoted to improve the thermal and mechanical properties of PPC by blending it with other polymers or inorganic fillers.

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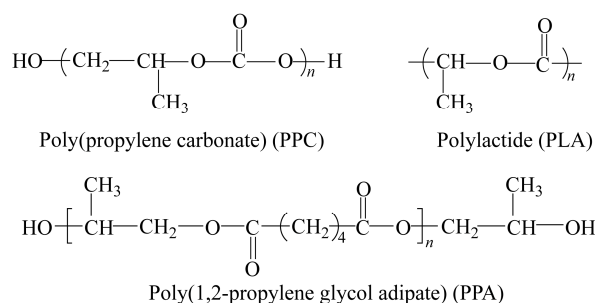
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Poly(lactide (PLA) is commonly known for its biocompatible, biodegradable, and renewable characteristics. It is accepted as an environmentally friendly material and can be used for manufacturing blown film and injected commodity products. While the biodegradable aspect of PLA is important for the biomedical applications due to the fact that PLA can be derived from renewable resources makes it even more attractive from an environmental standpoint. PLA films for packaging applications are commonly made through a blown-film process. The packaging applications included food packaging, trashcan liners, shrink films, stretch films, and merchandise packaging. In most applications, packaging films are required to possess high clarity and high strength. Unfortunately, incorporation of different kind of filler decreases the clarity of the film. However, PLA is a brittle polymer with low elongation at break^[16–18], and is difficult for film blowing, especially for high tear strength blown films. The processing ability of film blowing and the mechanical properties of the PLA resin can be improved through copolymerization or blending with other polymers or plasticizers^[19–27]. The addition of plasticizers usually reduces the glass transition temperature and the melting temperature of PLA. Further, the addition of plasticizers may also increase the elongation at break of PLA, while decrease the modulus and tensile strength.

The polyester plasticizers in this research are a kind of additives for PLA with good characters. They have the excellent performances of low toxicity, low volatility and solvents withstanding. The polyester plasticizers are called the “permanent plasticizers” and are now being studied as replacements for traditional plasticizers. Poly(1,2-propylene glycol adipate) (PPA) is a biodegradable plasticizer, which is synthesized *via* polyesterification reaction using adipic acid and 1,2-propylene glycol as raw materials. In addition, tetra-*n*-butyl titanate and isooctanol were used as a catalyst and a chain-ending reagent for the reaction, respectively^[26]. The use of environmentally-benign plasticizers is a way to improve the health and environmental issues concerning plasticizers. The growing public concern about environment and potential risks to health in the polymer and plasticizer industry promises to increase the market for a safer alternative plasticizer such as PPA. The content of the plasticizer is an important factor to obtain a desired blend with excellent mechanical properties. The degradable plasticizer content of the film is most preferably to be in the range from 8 wt% to 15 wt%. The main purpose of the incorporation of plasticizer is to enhance the flexibility and the processability of the PLA blown film.

Much work has been devoted to improve the thermal and mechanical properties of PPC by blending it with PLA^[28, 29]. In this study, PPC was blended with PLA and PPA. PPC, PLA and PPA are biodegradable aliphatic polyesters. PPA is an amorphous polymer and has a chemical structure similar to those of PLA and PPC. Their chemical structures are shown in Scheme 1. PPA could plasticize both PPC and PLA to improve the miscibility between PPC and PLA. PLA is aliphatic polyester with semi-crystalline structure and biodegradable nature. Because of its high crystallinity and crystalline structure, it exhibits excellent mechanical properties and thermal stability. The PLA presents good mechanical properties but poor elasticity, while PPC exhibits good elasticity but poor mechanical strength^[30–32]. Therefore, PPC in the PLA-rich blends can toughen PLA, while the PLA in the PPC-rich blends is expected to reinforce PPC on the other hand. The tensile and tear strength of PPC can be



Scheme 1 Chemical structures of PPC, PLA and PPA

effectively improved by simple blending with PLA in the presence of polyester plasticizer. The rheological behavior, miscibility, crystallization behavior, mechanical properties and optical properties of the PPC/PLA/PPA films were investigated.

EXPERIMENTAL

Materials

PPC was supplied by Taizhou Bangfeng Plastic Co., Ltd. (China). The number average molecular weight (M_n) and polydispersity index (PDI) of the purified PPC were determined by GPC as 1.50×10^5 g/mol and 4.32, respectively. Semi-crystalline PLA Grade 2003D (specific gravity is 1.24 g/cm³, melt flowing rate is 6.0 g/10 min) was obtained from NatureworksTM in pellet form. Poly(1,2-propylene glycol adipate) (PPA), was synthesized *via* polyesterification reaction using 1,2-propylene glycol and adipic acid as raw materials by our laboratory. In addition, tetra-*n*-butyl titanate and isooctanol were used as a catalyst and a chain-ending reagent for the reaction, respectively. They were purchased from the Sinopharm Chemical Reagent Co., Ltd. PPA has weight-average molecular weight (M_w) of 3.10×10^3 g/mol and polydispersity index of 1.5.

Blown Film Preparation

PPC and PLA were dried at 50 °C for 24 h and 70 °C for 8 h in a vacuum oven, respectively. PPC/PLA/PPA blends were prepared by melt mixing with a twin-screw extruder at a rotating speed 100 r/min at 150–175 °C. The mixing compositions of the PPC/PLA/PPA blends are summarized in Table 1. Then, all the samples and pure PLA were compression molded into sheets with thicknesses of 1.0 mm at 175 °C for rheological measurements and dynamic mechanical analysis. All the PPC/PLA/PPA blown films were prepared by using a 64.5 mm smooth-bore single-screw extruder having an aspect ratio of 25:1 and fitted with a 6-inch-diameter blown film die using external cooling air with a temperature of 15 °C. The barrel temperature profile in different zones ranged from 140 °C to 180 °C and the screw speed was kept at 38 r/min.

Table 1. The mixing compositions of the PPC/PLA/PPA blends

PPC/PLA/PPA (W/W/W)	PPC content (wt%)	PLA content (wt%)	PPA content (wt%)
0/91/9	0	91	9
73/18/9	73	18	9
55/36/9	55	36	9
36/55/9	36	55	9
18/73/9	18	73	9

Characterization

Rheological measurements of the films were conducted with a rheometer (TA Instruments Co., AR 2000ex, USA). Frequency sweep for the PPC/PLA/PPA samples was carried out under nitrogen using 25 mm plate-plate geometry. The gap distance between the parallel plates was 0.8 mm for all tests. The sheet samples were about 1.0 mm in thickness. A strain sweep test was initially conducted to determine the linear viscoelastic region of the materials. The angular frequency range used during testing was 0.1–100 rad/s. The temperature was plotted at 170 °C.

Miscibility of the films were studied by dynamic mechanical analysis (DMA) (TA Instruments Co., DMA, Q800, USA). The compression-molded PPC/PLA/PPA samples were sized 20 mm × 4 mm × 1 mm. The experiment was carried out in tension mode at a constant heating rate of 3 K/min and a frequency of 3 Hz, from –80 °C to 120 °C.

Crystallization behavior of the PPC/PLA/PPA films was studied by differential scanning calorimetry (DSC) (TA Instruments Co., DSC, Q20, USA) on the specimens sliced from blown film samples. The samples (about 5–8 mg) were heated first from –65 °C up to 185 °C at 10 K/min and held at 185 °C for 3 min to eliminate their previous thermal history. Subsequently, they were cooled to –65 °C at the same rate. Then the second heating scans were heated from –65 °C to 185 °C at 10 K/min to observe the cold crystallization temperature (T_{cc}) and

the melt temperature (T_m). As there were no crystals of PPC and PPA, only the contribution of the PLA was considered. The degree of crystallinity of the samples was evaluated from the heat evolved during crystallization by the following relationship:

$$x_c = \frac{\Delta H_f}{w_{\text{PLA}} \times \Delta H_f^0} \times 100\% \quad (1)$$

where x_c is the degree of crystallinity of the samples, ΔH_f is the heat of fusion of the PLA in the blend, ΔH_f^0 is the heat of fusion for 100% crystalline PLA (93 J/g)^[33] and w_{PLA} is the weight fraction of PLA in the blend.

The crystallite morphology of PPC/PLA/PPA films was observed with a Leica DMLP polarized microscope (POM) equipped with a Linkam TM600 hot stage and a computer-controlled charged-coupled-device camera. A small amount of samples with the thickness of approximately 0.05 mm was sandwiched between two microscopic cover glasses and then placed on the hot stage. The samples were heated from room temperature to 185 °C at a rate of 30 K/min, held there for 5 min to eliminate any thermal and mechanical history, and then quenched to 110 °C at a rate of 30 K/min for isothermal crystallization and held for 60 min. The morphology changes were recorded during the crystallization process.

The uniaxial tensile tests were carried out at (23 ± 2) °C on an 1121 testing machine (Instron Corporation, USA). Specimens ($20 \text{ mm} \times 4 \text{ mm} \times 0.05 \text{ mm}$) were cut from the previously blown films into a dumbbell shape in the machine direction (MD) and transverse direction (TD), respectively. The measurements were conducted at a cross-head speed of 50 mm/min at room temperature according to ASTM D882-2010. At least five runs for each sample were measured, and the results were averaged.

The right angle tearing strength was measured at (23 ± 2) °C on an 1121 testing machine (Instron Corporation, USA). The measurements were conducted at a cross-head speed of 200 mm/min at room temperature according to QB/T 1130-91 in the machine direction (MD) and transverse direction (TD), respectively. The size of the samples is shown in Fig. 1. At least five runs for each sample were measured, and the results were averaged.

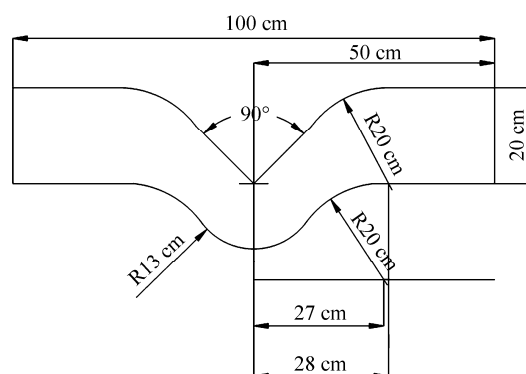


Fig. 1 The size of tear specimen

Transmittance and haze of the PPC/PLA/PPA blown films were measured in an Optical Hazemeter WGT-S system (Shanghai Precision and Scientific Instrument Co. Ltd, China). The thickness of the samples is about 40 μm. The values obtained are averages of at least six determinations.

The tear-fracture surfaces of PPC/PLA/PPA films were characterized with a scanning electron microscope (XL-30 ESEM FEG, FEI Co., USA). A layer of gold was sputter-coated uniformly over all the fractured surfaces before SEM observations.

RESULTS AND DISCUSSION

Rheological Properties

The dynamic rheological experiments were carried out for the PPC/PLA/PPA films with the different compositions. Figures 2 and 3 show the storage modulus (G') and loss modulus (G'') curves for the PPC/PLA/PPA films. There was a well developed dependence of the dynamic modulus on the PPC content: both the G' and G'' gradually increased with increasing of PPC content. At high angular frequencies, the qualitative behaviors of G' and G'' were essentially similar and not affected obviously by existence of PPC content. However, G' and G'' increased monotonically with increasing PPC content. As PPC content increased up to 36 wt%, the slopes of the modulus curves changed significantly. It indicated that PPC could improve the formation of entanglements between PLA and PPC macromolecular chains. Meanwhile, the frequency dependence of G'' also exhibited the same tendency as G' .

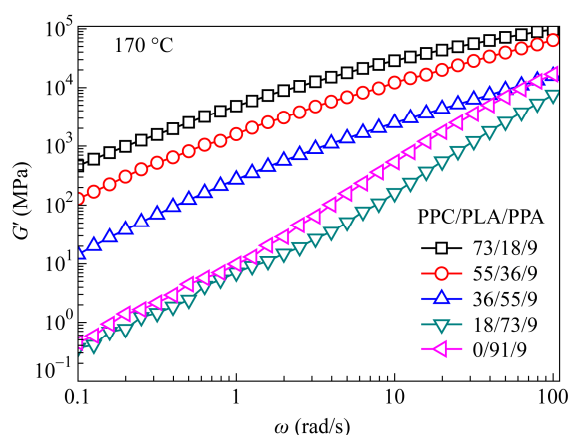


Fig. 2 Plots of storage modulus versus angular frequency for the PPC/PLA/PPA blends

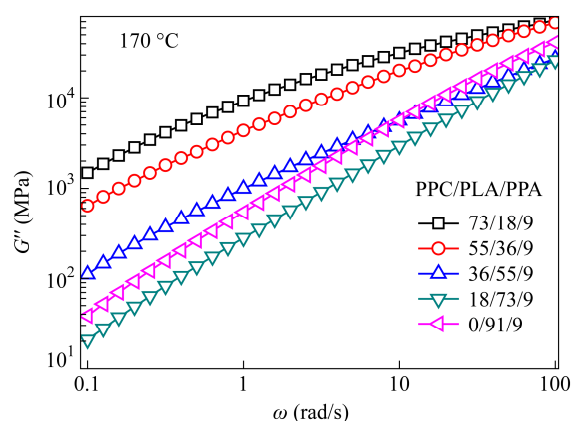


Fig. 3 Plots of loss modulus versus angular frequency for the PPC/PLA/PPA blends

The relationship between complex viscosity (η^*) and angular frequency of the PPC/PLA/PPA films at 170 °C is shown in Fig. 4. It can be clearly seen that the existence of PPC had a dramatic effect on the complex viscosity of the blends. The 18/73/9 PPC/PLA/PPA film displayed the Newtonian fluid plateau at high angular frequencies. However, with increasing PPC content up to 36 wt%, the viscosity curve of the film displayed non-Newtonian shear thinning behaviors, and no plateau region was observed during the whole angular frequency range. In particular, the 73/18/9 PPC/PLA/PPA film showed a value a few orders of magnitude greater than that of 18/73/9 PPC/PLA/PPA film. The increase of complex viscosities of the PPC/PLA/PPA films further demonstrated that the entanglements between PLA chains and PPC chains were formed. This significantly enhancement in the melt viscosity of PPC/PLA/PPA blends led to an increase in melt strength, which was favorable for the processing of blown films. Overall, both complex viscosity and storage modulus suggested gradual change from liquid-like behavior to pseudo-solid-like behavior with increasing PPC content.

Dynamic Mechanical Analysis

Figure 5 shows the dependence of loss factor ($\tan\delta$) versus the temperature for PPC/PLA/PPA blends. In general, $\tan\delta$ is the ratio of loss modulus to storage modulus, useful for determining the occurrence of molecular mobility transitions such as glass transition temperature (T_g). In Fig. 5, it can be observed pure PLA displayed a single high temperature peak for T_g around 70 °C. With the addition of PPA content, T_g was shifted to lower temperatures due to the fact that PPA served as plasticizer in this film. There was only one T_g close to the T_g of PLA phase for the 18/73/9 PPC/PLA/PPA blend and there was only one T_g close to the T_g of PPC phase for the 73/18/9 PPC/PLA/PPA blend, as shown in Fig. 5. However, there were two glass transition temperatures for 55/36/9 and 36/55/9 PPC/PLA/PPA blends. One was about 35 °C, close to the T_g of PPC phase. The other was

about 50 °C, close to the T_g of PLA phase. As seen in Fig. 5, two glass transition temperatures shifted closer towards each other, which suggested that PPC and PLA were partially miscible. In addition, PPA could significantly decrease the glass transition temperature of PLA and enhance the miscibility between PLA and PPC.

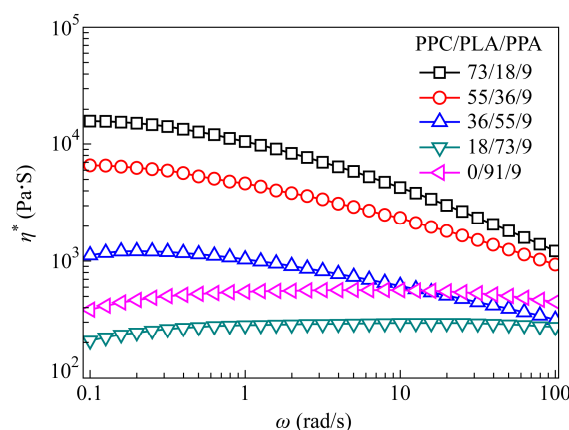


Fig. 4 Plots of complex viscosity versus angular frequency for the PPC/PLA/PPA blends

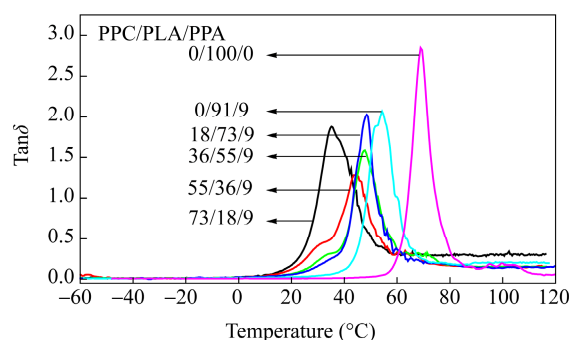


Fig. 5 The loss factor ($\tan\delta$) as a function of temperature for the PPC/PLA/PPA blends

Melting and Crystallization Behaviors

In this study, DSC was carried out to investigate the melting and crystallization behaviors of these blends. Figure 6 shows the DSC results of PPC/PLA/PPA films from the second heating scan at a rate of 10 K/min. The parameters for the melting and crystallization behaviors obtained from the heating run are listed in Table 2. The exothermic peaks could be correlated to the crystallization of PLA due to the amorphous nature of PPC and semi-crystalline nature of PLA. As the processed PLA was heated upon testing, some of the molecular chains in the amorphous regions gain enough mobility to rearrange into an ordered crystalline phase, giving out energy and forming an exothermic re-crystallization peak. It could be observed that the cold crystallization temperature of the films was significantly different from that of pure PLA, as shown in Fig. 6. The cold crystallization temperature of the pure PLA was clearly decreased with the addition of PPC and PPA contents, indicating an enforced cold crystallization ability of PLA. The increased cold crystallization ability in the films probably resulted from the presence of PPC and the PPA enhanced mobility of PLA chains. Correspondingly, the ΔH_{cc} (the enthalpy of cold crystallization of the PLA in the blend) values significantly increased with the addition of PPC and PPA contents, as listed in Table 2. For example, the ΔH_{cc} values of the 18/73/9 PPC/PLA/PPA film were 25.5 J/g, which increased by about 26 times compared with that of pure PLA.

Furthermore, pure PLA and 73/18/9 PPC/PLA/PPA film showed only one melting peak, as seen in Fig. 6. However, the other blends displayed two melting peaks. This bimodal melting peak was induced during slow

DSC scan while the less perfect crystals had enough time to be melted and reorganized into crystals with higher structural perfection, and re-melted at higher temperatures^[34, 35]. For PLA/PPA film, the decrease in the second peak temperatures (T_{m2}) suggesting more less perfect crystals were nucleated. The decrease in melting temperature was observed which agreed with the above results that PPA served as plasticizer in the films. With increasing of PPC content, there was no obvious effect on the T_{m1} and T_{m2} , suggesting that the lamellar thickness of the PLA crystals was unchanged. The observed two melting peaks indicated that more defective PLA crystals formed with increasing PPC content. The defective crystals experienced melting-recrystallization process during the heating scan, and these would melt again at the higher melting temperature (T_{m2}). This result could be explained by the fact that the enhanced cold-crystallization of PLA may result in more and more defective crystals due to the lower cold-crystallization temperature. The similar phenomenon was also reported in other PLA blends^[36, 37]. Eventually, from the data listed in Table 2, the ΔH_f and X_c values significantly increased with the addition of PPC and PPA content. It might be that the PPC and PPA enhanced the mobility of PLA macromolecular chains during the growth process of the crystals, which increased the final crystallinity. However, a further increase in PPC content led to a further decrease in ΔH_f and X_c values.

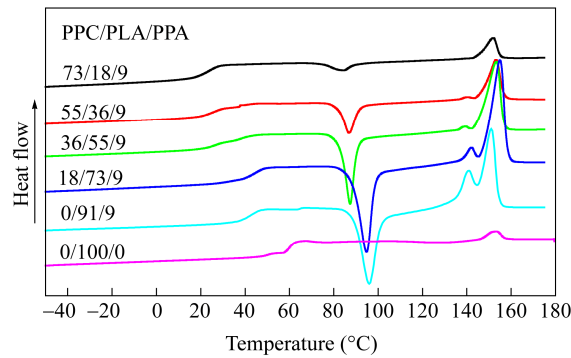


Fig. 6 DSC thermograms for PPC/PLA/PPA blends during the second heating runs

Table 2. Crystallization properties of PPC/PLA/PPA films

PPC/PLA/PPA (W/W/W)	Second heating run					
	T_{cc} (°C)	ΔH_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_f (J/g)	X_c (%)
73/18/9	87.4	2.9	—	152.6	4.0	23.9
55/36/9	90.8	8.7	140.5	153.7	10.6	31.7
36/55/9	90.6	15.8	139.9	153.7	20.6	40.3
18/73/9	95.0	25.5	141.8	154.8	29.6	43.6
0/91/9	96.1	22.8	140.0	151.0	18.8	22.2
0/100/0	132.3	0.94	—	153.7	1.67	1.8

ΔH_f^0 of PLA is 93 J/g

Crystal Morphology

Figure 7 shows the POM photos of PPC/PLA/PPA sample films, which have been melted for 6 min at 185 °C and then crystallized at 110 °C for 60 min. It clearly illustrated that the PLA spherulites had obvious Maltese cross patterns and relatively big size in Fig. 7(e). From Figs. 7(a)–7(c), it could be observed that blending PLA with the amorphous PPC led to a decrease of the spherulite size of PLA. In Fig. 7(d), the PLA spherulites formed a continuous phase filling the whole view field when the PLA content was 73 wt%. In this case, the PPC was dispersed in the amorphous PLA phase, or in other words, between the lamellae of PLA. However, further increase of the PPC content up to 36 wt% led to an evident phase separation with birefringent PLA crystals not filling the whole field anymore. The discrete PLA domains with strong birefringence were dispersed in a nonbirefringent amorphous matrix. It was acceptable when the low crystallinity of PLA was considered. In this situation, the amorphous PPC together with the noncrystalline PLA, which could be increased under the

influence of PPC, led to a high content of amorphous material and therefore formed a continuous amorphous matrix with the crystalline PLA domains dispersed in it. From these observations, a conclusion might be drawn that, when the PPC content in PPC/PLA/PPA films increased up to 36 wt%, the PLA crystals formed isolated phase randomly dispersed among the continuous amorphous PPC component, the amorphous PLA portion, and PPA.

The above results clearly demonstrated the influence of blend ratio on the phase structure of PPC/PLA/PPA films. For the PLA-rich films, the PLA crystals filled the whole film sample with the PPC dispersed among them. However, predominate PLA crystals with strong birefringence formed isolated domains inserted in the amorphous PPC matrix in the PPC-rich films. This kind of phase structure could be produced either by crystallization of PLA in the phase-separated domains or by crystallization-induced phase separation due to the exclusion of noncrystallizable materials into the crystal growth front, which limited the propagation of the crystal and created isolated crystal domains^[38].

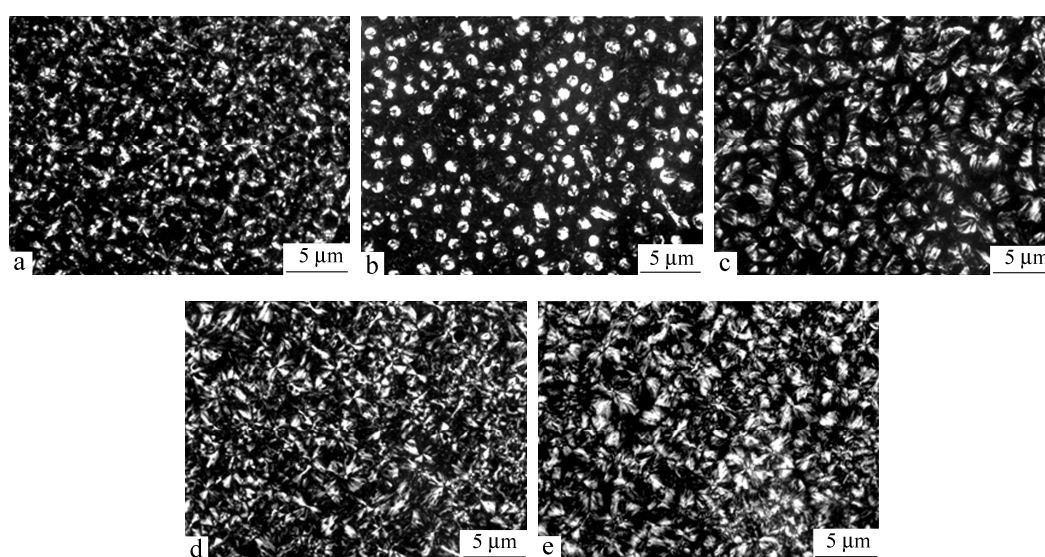


Fig. 7 Micrographs of spherulitic morphologies for PPC/PLA/PPA films: (a) 73/18/9, (b) 55/36/9, (c) 36/55/9, (d) 18/73/9 and (e) 0/91/9

Mechanical Properties

The aim of adding PPA to PPC/PLA film is to enhance plastic elongation and reduce brittleness. The tensile properties and tear strength of PPC/PLA/PPA films are given in Table 3. It could be seen that PLA-rich films had low elongation at break and PPC-rich films had high elongation at break. For instance, the elongation at break decreased from 535% and 462% of 73/18/9 PPC/PLA/PPA film to 12.2% and 36.2% of 18/73/9 PPC/PLA/PPA film in the machine direction (MD) and transverse direction (TD), respectively. It could also be seen that PLA-rich films had high tensile strength and Young's modulus. PPC had significantly changed the tensile behavior of the PPC/PLA/PPA films. While the PLA content was beyond 36 wt%, the PPC/PLA/PPA films showed ductile fracture upon the tensile load. It was very interesting to find that the 55/36/9 PPC/PLA/PPA film had higher elongation at break of 285% and 308%, while the tensile strength remained as high as 29.2 and 33.8 MPa in the machine direction and the transverse direction, respectively. The tensile strength of polyethylene film was 17.12 and 18.18 MPa in the machine direction (MD) and transverse direction (TD), respectively^[39]. It indicated that the tensile strength of the PPC/PLA/PPA films was higher than that of polyethylene film. Moreover, the Young's modulus decreased from 2651 and 2466 MPa of 0/91/9 PPC/PLA/PPA film to 1073 and 934 MPa of 83/18/9 PPC/PLA/PPA film in the machine direction (MD) and transverse direction (TD), respectively. This result suggested that PPC and PPA were conducive to improve the flexibility of PPC/PLA/PPA films.

Table 3. Mechanical and optical properties of PPC/PLA/PPA films

PPC/PLA/PPA (W/W/W)	Tensile strength MD/TD (MPa)	Elongation at break MD/TD (%)	Young's modulus MD/TD (MPa)	Tear strength MD/TD (kN/m)	Transmittancy (%)	Haze (%)
73/18/9	32.8/29.5	535/462	1073/934	100.6/112.8	63.8	28.4
55/36/9	29.2/33.8	285/308	1440/1302	119.2/126.7	74.9	17.4
36/55/9	39.5/40.7	185/188	1796/1353	119.5/127.4	84.1	8.8
18/73/9	48.8/43.0	12.2/36.2	1985/1224	131.8/143.4	86.7	5.3
0/91/9	49.0/52.3	2.2/6.3	2651/2446	122.0/123.6	89.3	3.8

It was worth noted that the tear strength of the PPC/PLA/PPA films was slightly strengthened with an increase of PLA content, as shown in Table 3. The 73/18/9 PPC/PLA/PPA film exhibited relatively low tear strength values at 100.6 and 112.8 kN/m in the machine direction (MD) and transverse direction (TD), respectively. In contrast, the PPC/PLA/PPA films revealed an increase in tear strength values as their PLA contents increased. The tear strength values in machine and transverse directions increased from 100.6 and 112.8 kN/m in the 73/18/9 PPC/PLA/PPA film to 131.8 and 143.4 kN/m in the 18/73/9 PPC/PLA/PPA film, respectively. For the PPC/PLA/PPA blown films, the tear resistance was always higher along the machine direction relative to the transverse direction. This difference could be ascribed to the varying degrees of orientation of the lamellae within the plane of the film. The tear strength of polyethylene film was 73.26 and 83.33 KN/m in the machine direction (MD) and transverse direction (TD)^[39]. It indicated that the tear strength of the PPC/PLA/PPA films was higher than that of polyethylene films.

These results suggested that the tear strengths of the PPC-rich films could be improved after melt-blending the appropriate amounts of PLA. The chemical structures of PLA and PPC are similar, they are consequently expected to be miscible and compatible to some extent^[28]. It could be explained by that the entanglement increased by incorporation about 36 wt%–55 wt% PPC was conducive to enhance the intermolecular force between PPC and PLA.

Optical Properties

Transparency is an important property of plastic films. The refractive index of PLA chosen in this study was 1.45. The visible light transmittance and haze value of the PPC/PLA/PPA films are given in Table 3. The PPC-rich films, the 73/18/9 and the 55/36/9, exhibited poor optical properties and the transmittance values were 63.8% and 74.9%, respectively. However, the optical properties of the PPC/PLA/PPA films were improved significantly with increasing PLA content. For example, the transmittance value increased from 63.8% in the 73/18/9 PPC/PLA/PPA film to 86.7% in the 18/73/9 PPC/PLA/PPA film and the haze value decreased from 28.4% in the 73/18/9 PPC/PLA/PPA film to 5.3% in the 18/73/9 PPC/PLA/PPA film. It could be concluded that PLA improved the optical properties of PPC/PLA/PPA blown films and PLA-rich films had excellent optical properties.

Morphology of Films

In order to clarify the fracture mechanisms responsible for the high tear strength, the tearing fracture surface along the machine direction of PPC/PLA/PPA blown films was observed by SEM. The micrographs are shown in Fig. 8. For the PPC-rich films, the fracture surface of 73/18/9 and 55/36/9 PPC/PLA/PPA films was relatively rough and had no cavitations, indicating that little plastic deformation had taken place during the tearing test, as shown in Figs. 8(a) and 8(b). The result was in a good agreement with their lower tear strength values. However, some voids and plastic deformation could be observed for the PLA-rich films, as shown in Figs. 8(c), 8(d) and 8(e), which exhibited the ductile fracture and massive voids formation with plastic deformation. These cavities were formed when the volumetric strain energy released by forming a void was greater than the surface energy needed to form new surface plus the energy needed to make a space for the void. In particular, extensive plastic deformation of the PLA matrix could be observed clearly, which implied that shear yielding of the PLA matrix had taken place. It was a typical feature of a ductile fracture.

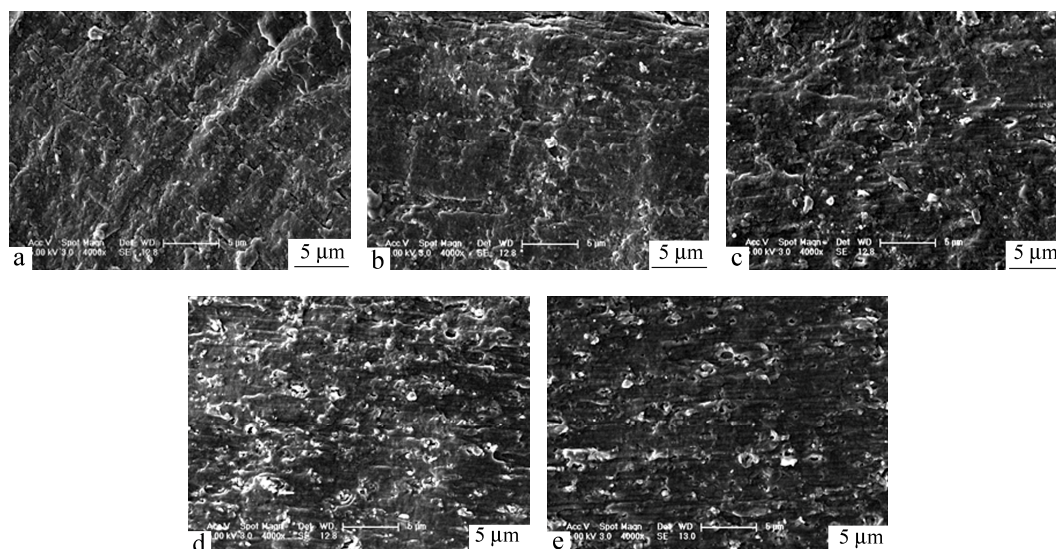


Fig. 8 SEM micrographs of the tearing fracture surfaces of torn PPC/PLA/PPA blown films: (a) 73/18/9; (b) 55/36/9; (c) 36/55/9; (d) 18/73/9 and (e) 0/91/9

CONCLUSIONS

In this study, the rheology, miscibility, phase morphology, crystallization behavior and mechanical properties of the PPC/PLA/PPA blends were investigated by rheological measurements, DMA, DSC, POM, SEM, tensile and tear tests in detail. DMA results indicated that PLA was partially miscible with PPC under the plasticizing effect of PPA. However, the T_g of PLA component shifted toward lower temperatures compared to that of neat PLA, which might be attributed to the presence of the PPA as a plasticizer. The addition of PPC and PPA enhanced the cold crystallization of PLA in the blends and its final degree of crystallinity increased significantly. The increased cold crystallization ability of PLA in the blends probably resulted from the spherulite growth enhancement of PLA due to the enhanced chain mobility caused by the PPC and PPA. With increasing PLA content, the films showed increased tensile strength and modulus; however, the elongation at break decreased significantly. In addition, the tear strength improved with increasing of PLA content. SEM images of the tear fracture surfaces of the films after tear tests indicated that the fracture behavior changed from brittle fracture behavior for PPC-rich films to ductile fracture behavior for the PLA-rich films. The plastic deformation in the form of matrix drawing or shear yielding due to the cavitations was involved in the toughening of the blends. Thus, the melt strength, the crystallization ability and mechanical properties of PPC/PLA/PPA films could be improved significantly by simple blending PPC, PLA and PPA while good optical properties are expected for the PLA-rich films. These results may extend the practical application of PLA in future.

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