

Studies on Rheological, Thermal, and Mechanical Properties of Polylactide/Methyl Methacrylate-Butadiene-Styrene Copolymer/Poly(propylene carbonate) Polyurethane Ternary Blends

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Studies on Rheological, Thermal, and Mechanical Properties of Polylactide/Methyl Methacrylate-Butadiene-Styrene Copolymer/Poly(propylene carbonate) Polyurethane Ternary Blends

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Abstract Polylactide (PLA), methyl methacrylate-butadiene-styrene copolymer (MBS), and poly(propylene carbonate) polyurethane (PPCU) were blended and subjected to blown film process. The rheological, mechanical, morphological, thermal, and crystalline properties of the PLA/MBS/PPCU ternary blends and the mechanical properties of the resulting films were studied. Results of mechanical test showed that PPCU and MBS could synergistically toughen PLA. The impact strength of 50/10/40 PLA/MBS/PPCU blend (74.7 kJ/m²) was about 7.5 times higher than that of the neat PLA (10.8 kJ/m²), and the elongation at break of 50/10/40 PLA/MBS/PPCU blend (276.5%) was higher by about 45 times that of PLA (6.2%). The tear strength of PLA/MBS/PPCU films was 20 kN/m higher than that of PLA, and the elongation at break (MD/TD) of 50/10/40 PLA/MBS/PPCU films was 271.1%/222.3%, whereas that of PLA was only 2.7%/3.0%. POM observations displayed that the density of spherulite nucleation increased and the size of crystalline particles decreased with the addition of MBS. With increasing PPCU content from 5% to 20%, the density of spherulite nucleation increased and the size of crystalline particles decreased continuously, but the nucleation density of spherulites was slightly lowered with increasing PPCU content from 30% to 40%. The PLA/MBS/PPCU films exhibited excellent mechanical properties, which expanded the application range of these biodegradable films.

Keywords Biodegradable; Polylactide; Poly(propylene carbonate) polyurethane; Methyl methacrylate-butadiene-styrene copolymer; Films

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INTRODUCTION

Polylactide (PLA), one of the most promising biodegradable, biocompatible, and bioresorbable materials, has attracted the interest of many researchers.^[1,2] PLA has outstanding properties which include high strength and modulus, non-toxicity and biodegradability, easy processability *etc.* However, its structural and property drawbacks such as brittleness, slow crystallization rate, low crystallinity, and low thermal resistance^[3,4] have limited widespread applications, especially as blown films. The alternative methods for improving the ductility and flexibility of PLA are to graft or to blend with other flexible polymers, as well as employing plasticizers or nucleator.^[5–19] For example, PLA could be blended with poly(ethylene-glycidyl methacrylate) (PEG-MA),^[7] poly(ethylene octene) grafted with glycidyl meth-

acrylate (GPOE),^[8] ethylene/*n*-butyl acrylate/glycidyl methacrylate (EBA-GMA),^[9] glycidyl methacrylate functionalized acrylonitrile-butadiene-styrene (ABS-g-GMA),^[10] poly(butyl acrylate) (PBA),^[11] poly(butylene-succinate-co-adipate) (PBSA),^[12] poly(propylene carbonate) polyurethane (PPCU),^[13] poly(diethylene glycol adipate) (PDEGA),^[14] diethylene glycol monobutyl ether adipate (DGBEA),^[15] core-shell structural acrylate copolymer (ACR),^[16,17] and methyl methacrylate-butadiene-styrene copolymer (MBS).^[18,19]

Poly(propylene carbonate) polyurethane (PPCU) is a biodegradable and linear aliphatic thermoplastic. PPCU can be prepared by using PPC and polyols as the raw materials and hexamethylene-diisocyanate (HDI) as the extender chain.^[20] Poly(propylene carbonate) (PPC) is of low cost and also a biodegradable aliphatic polycarbonate.^[21] The addition of PPCU could remarkably toughen PLA.^[13]

Methyl methacrylate-butadiene-styrene copolymer (MBS) is one of the important types of toughening agent of PLA.^[19] MBSs as the impact modifiers are used regularly to improve the toughness of PLA depending on its major attractive features, namely the rubbery core of a random styrene-

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butadiene copolymer provides resistance to impact, and the grafted glassy shell of poly (methyl methacrylate) (PMMA) provides “good adhesion” with PLA.

Our team has successfully toughened PLA with MBS and PPCU, separately. Zhang *et al.*^[19] reported that PLA was remarkably toughened by adding MBS. PLA was compatible with the shell of MBS. The impact strength of the 75/25 PLA/MBS blend was about 21 times that of the neat PLA. Recently, Yang *et al.*^[13] reported that PPCU could prominently toughen PLA as well. The impact strength and elongation at break of PLA were enhanced and the ability of crystallization for PLA was improved by adding PPCU. On the basis of our previous work, PLA was blended with MBS and PPCU to afford a PLA/MBS/PPCU ternary blend. To the best of our knowledge, this kind of blend film has not been reported so far. The cost of MBS is about 30000 yuan per ton and that of PPCU is about 20000 yuan per ton. PPCU is cheaper than MBS by about 10000 yuan per ton. Therefore, PPCU could reduce the cost and improve the biodegradable properties of the PLA/MBS/PPCU blends at the same time. The purpose of the present study is to improve the mechanical properties of biodegradable blends and to check whether MBS and PPCU have synergistic effect on toughening PLA. The rheological, miscibility, thermal, mechanical, and crystallization properties of the PLA/MBS/PPCU blends were investigated.

EXPERIMENTAL

Materials

Poly lactide (PLA, Grade 4032D, 2% D-lactide, 98% L-lactide content, a weight-average molecular weight of 2.07×10^5 g/mol and dispersity of 1.73) was obtained from NatureworksTM in pellet form. MBS (trademark: B-625) was purchased from Kaneka Corporation, Japan. Thermoplastic poly(propylene carbonate) polyurethane blend (PPCU) was purchased from Jiangsu Zhongke Jinlong Chemical Co., Ltd. The sketches of PLA, MBS, and PPCU are shown in Fig. 1.

Preparation of PLA/MBS/PPCU Blends and Films

PLA, MBS, and PPCU were dried at 70 °C for 8 h in a vacuum oven before each processing step (melt-compoun-

ding and blown film extrusion) and rheological characterizations, in order to avoid hydrolytic degradation. The PLA/MBS/PPCU blends were melt-blended using a co-rotating twin-screw extruder (SHJ-20, length/diameter ratio was 32:1, screw diameter was 20 mm, rotating speed was 100 r/min) and there were nine heating zones, which can be controlled independently. The processing temperatures at different zones were 160, 180, 195, 195, 200, 200, 200, 200, and 180 °C. The mixed components of the PLA/MBS/PPCU blends were 100/0/0, 90/10/0, 85/10/5, 80/10/10, 70/10/20, 60/10/30, and 50/10/40 (W/W/W). The PLA/MBS/PPCU blends were prepared by melt mixing at 185 °C with a twin-screw extruder at a rotating speed of 200 r/min. The PLA/MBS/PPCU blends were dried at 70 °C for 8 h in a vacuum oven. Then, all the samples were compression molded into sheets with a thickness of 1.0 mm at 190 °C for rheological measurements and differential scanning calorimetry tests. All the PLA/MBS/PPCU blends were blown using a 30.0 mm smooth-bore single-screw extruder having an aspect ratio of 30:1 and fitted with a 65 mm diameter blown film die using external cooling air of 15 °C. The processing temperatures at different zones were 160, 168, 170, 160, and 162 °C. The screw speed was kept at 38 r/min. Moreover, the extruder output was 7 kg/h, the blow up ratio (BUR) was 3, the frost line height (distance from die exit) was 15 cm, and the winding speed was 7.0 m/min.

Characterization

Rheological behavior

Rheological measurements of the PLA/MBS/PPCU blends were conducted on a rheometer (TA Instruments AR 2000ex, USA). Frequency sweep for the PLA/MBS/PPCU samples was performed under nitrogen atmosphere using 25 mm plate-plate geometry. The gap distance between the parallel plates was 0.9 mm for all tests. The sheet samples were about 1.0 mm in thickness. A strain sweep test was initially performed 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 maintained at 190 °C.

Mechanical property tests

The tensile properties of the blends were tested by using an

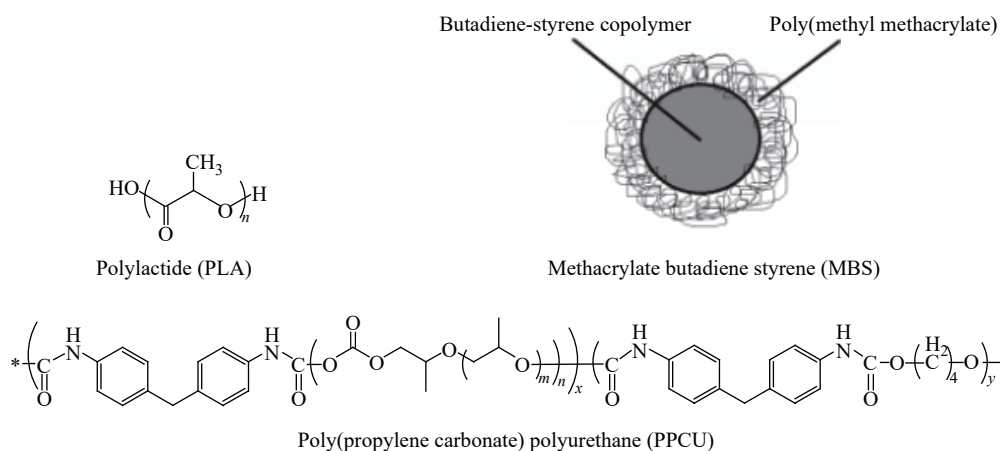


Fig. 1 Sketch of PLA, MBS, and PPCU

Instron 1211 testing machine (Canton MA, USA) at a cross-head speed of 20 mm/min according to ASTM D638-2008 standard. The samples were melted for 5 min at 190 °C, hot pressed at 1 MPa for 3 min, then quickly removed out, and cold pressed at 1 MPa at room temperature for 5 min. The dumbbell-shaped specimens (4 mm × 1 mm × 20 mm) for tensile testing were punched out from the compression-molded sheets. Samples were conditioned for at least 24 h prior to testing at room temperature and 50% relative humidity controlled environment. At least five runs were carried out for each sample, and the results were averaged. Tensile strength, Young's modulus, and elongation at break were obtained.

Notched Izod impact tests were performed at (23 ± 2) °C according to ASTM D256-2010 on an impact testing machine (Changchun City Intelligent Instrument Equipment Co., Ltd. China). The samples were melted for 5 min at 190 °C, hot pressed at 1 MPa for 3 min, then quickly removed out, and cold pressed at 1 MPa at room temperature for 5 min. The specimens with dimension 80.0 mm × 10.0 mm × 4.0 mm were obtained from compression-molded samples. The notch was milled in having a depth of 2.54 mm, an angle of 45°, and a notch radius of 0.25 mm.

The tensile properties of the PLA/MBS/PPCU films were assessed at (23 ± 2) °C on an XLW(pc) testing machine (Labthink, China). Specimens (100 mm × 15 mm) were cut from the previously blown films in both machine direction (MD) and transverse direction (TD). The measurements were conducted at a cross head speed of 50 mm/min at room temperature according to GB/T 1040.1-2006 standard. At least five runs were carried out for each sample, and the results were averaged.

The right angle tearing strength was tested at (23 ± 2) °C on XLW(pc) testing machine (Labthink, China). The measurements were separately conducted in MD and TD at a crosshead speed of 50 mm/min at room temperature according to QB/T 1130 specification in the machine direction and transverse direction. The size of the sample is shown in Fig. 2. At least five runs were carried out for each sample, and the results were averaged.

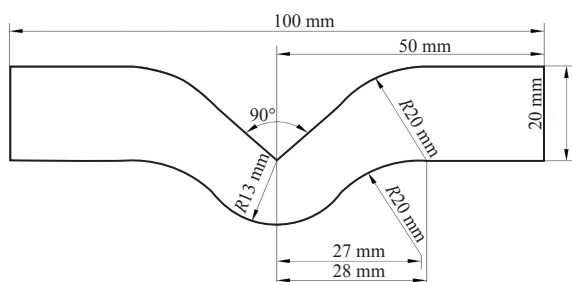


Fig. 2 Size of tear specimen

Scanning electron microscopy (SEM)

SEM (Carl Zeiss Microscopy GmbH, 73447 Oberkochen, Germany) was used to characterize the phase morphology of PLA/MBS/PPCU blends after impact fracture and tensile tests. A layer of platinum was sputter-coated uniformly over all the fractured surfaces before SEM observation.

Differential scanning calorimetry (DSC)

The crystallization behavior of PLA/MBS/PPCU blends was studied by differential scanning calorimetry (TA Instruments DSC Q20, USA) with a universal analysis 2000 under nitrogen atmosphere. The weights of the samples varied between 5.0 and 8.0 mg. The samples were heated first from −60 °C up to 190 °C at 10 °C/min (the first heat scan), held at 190 °C for 5 min to eliminate previous thermal history, then cooled at the same rate, and heated again finally.

Crystallization morphology

The crystallization morphology of PLA/MBS/PPCU blends was observed with a Leica DMLP polarized microscope (POM) (Wetzlar, Germany) equipped with a Linkam TM600 hot stage and a computer-controlled charged-coupled-device (CCD) camera. A small amount of sample with a 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 190 °C at a rate of 30 °C/min, held there for 3 min to eliminate any thermal and mechanical history, and then quenched to 110 °C at the rate of 30 °C/min for isothermal crystallization and held for 60 min. The morphological changes were recorded during the crystallization process.

Wide angle X-ray diffraction (WAXD)

Wide angle X-ray diffraction experiments were performed on a D8 advance X-ray diffractometer (Bruker, Germany) at room temperature in the range of 5°–55° at a scanning rate of 3 (°)/min. The Cu K α radiation ($\lambda = 0.1542$ nm) source was operated at 40 kV and 200 mA.

RESULTS AND DISCUSSION

Rheological Behavior

Rheological behavior plays an important role in polymer processing. Dynamic rheological experiments were carried out for the PLA/MBS/PPCU blends over the whole composition range. Fig. 3 presents the variations of dynamic viscosity properties of storage modulus (G') versus angular frequency. From Fig. 3, with angular frequency at 0.1 rad/s, G' of PLA was about 0.1 Pa while the value of PLA/MBS 90/10 blends was around 10^3 Pa; the modulus increased about four orders of magnitude. However, G' showed little change after addition of PPCU. Over the whole range of angular frequency, it can be noted that G' of PLA increased by about six orders of magnitude with angular frequency while it increased about two orders of magnitude after the addition of MBS and PPCU in PLA. The higher absolute values of dynamic modulus indicated the formation of entanglement structures among PLA chains, PPCU chains, and the grafted shell polymer chains of MBS. This explains that the entanglement structure was formed at lower frequencies.^[19]

Fig. 4 shows the relationship between loss modulus (G'') and angular frequency of the PLA/MBS/PPCU blends. It is indicated that G'' of PLA increased with angular frequency. At low frequencies, the loss modulus of 90/10 PLA/MBS was much higher than that of PLA. The much higher loss modulus indicated higher viscosity. At high frequencies, the loss modulus of PLA/MBS was lower than that of the neat PLA. This further explains that the entanglement structure

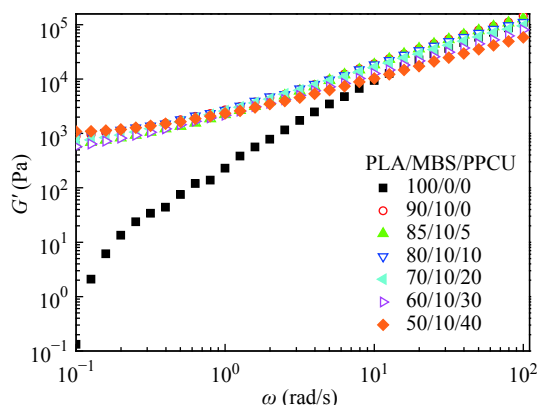


Fig. 3 Plots of storage modulus versus angular frequency for PLA/MBS/PPCU blends compared with that of PLA

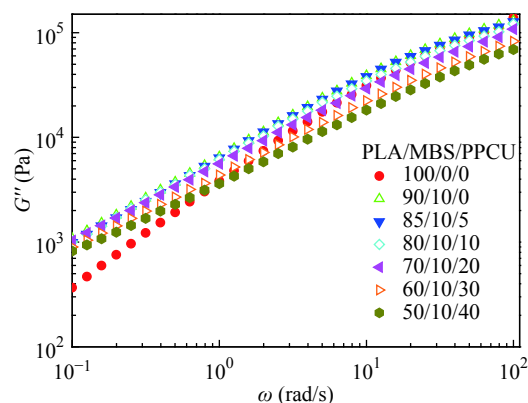


Fig. 4 Plots of loss modulus versus angular frequency for PLA/MBS/PPCU blends compared with that of PLA

was formed at low frequencies.^[19] In the entire frequency range, G'' of the PLA/MBS/PPCU blends gradually decreased with increasing PPCU content in the blends. Neat PLA is a stiff, relatively brittle polymer. After adding PPCU, the ductility increased significantly. As expected, the flexible ether bond in the molecular chain of PPCU was beneficial to improving the mobility of the molecular chain and increasing the toughness of the blends, so as to improve the mechanical properties of the film.

Fig. 5 illustrates the relationship between complex viscosity (η^*) and angular frequency of PLA/MBS/PPCU blends. Neat PLA displayed a Newtonian behavior at the low frequency region, with a zero-shear rate viscosity value (around 2000 Pa·s). The addition of MBS had a significant effect on the complex viscosity of PLA, and the viscosity curve indicated a non-Newtonian behavior. The complex viscosity values of PLA/MBS blends were much higher than that of neat PLA. Compared with PLA, the increase in viscosity and elasticity of 90/10 PLA/MBS blends could be attributed to the increase of interfacial adhesion between PLA chains and the grafted shell chains of MBS. The toughening effect derived from the energy dissipation given that these tiny core-shell structure MBS particles had strong interfacial adhesion between the MBS shell and the PLA matrix.^[19] With increasing PPCU content from 5% to 40%, the complex viscosity of PLA/MBS/PPCU blends decreased gradually. When the con-

tent of PPCU was 30%–40%, the complex viscosity of the blends decreased significantly. Such decrease could be related to an increased free volume caused by the flexible ether bond in the molecular chains of PPCU.

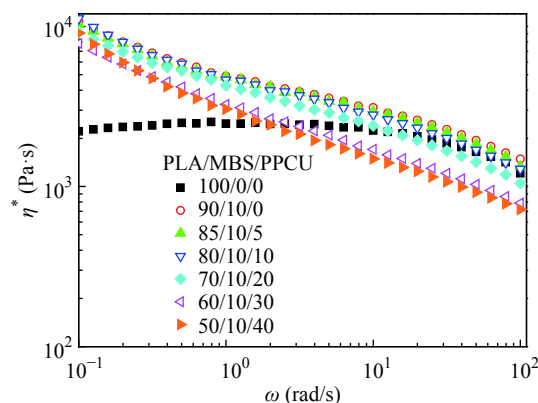


Fig. 5 Plots of complex viscosity versus angular frequency for PLA/MBS/PPCU blends compared with that of PLA

Fig. 6 shows the plots of phase angle (δ) versus absolute value of the complex modulus ($|G^*|$) for PLA/MBS/PPCU blends. In the literature, the plots were shown as the van Gurp-Palmen, which was used to detect the rheological percolation of filled polymeric composites.^[22,23] The low-frequency δ of neat PLA was close to 90°, which indicated that the viscoelastic fluid presented a flow behavior. With the addition of MBS, the value getting closer to 45° suggested a rheological fluid-solid transition in the binary system. With the addition of PPCU, the low-frequency δ decreased to 55° and 35° in 85/10/5 and 50/10/40 PLA/MBS/PPCU blends, respectively, which indicated an enhanced elastic behavior. The enhancement would be beneficial to blowing film during the actual production process.

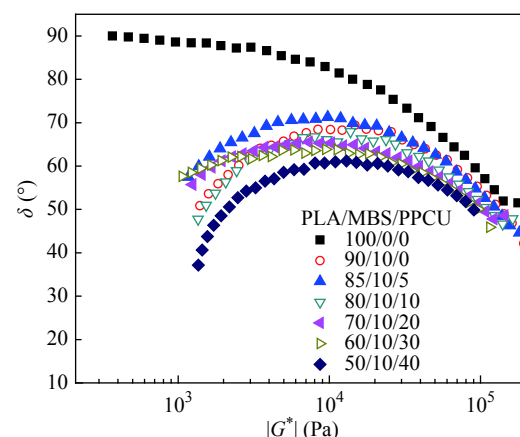


Fig. 6 Phase angle (δ) of the PLA/MBS/PPCU blends compared with that of PLA

Mechanical Properties

The tensile strength and elongation at break of PLA, PLA/MBS, and PLA/MBS/PPCU blends are depicted in Fig. 7, with relevant data summarized in Table 1. Neat PLA is very rigid and brittle which showed a tensile strength of 65.9 MPa

and a elongation at break about 6.2%. The tensile strength of PLA/MBS (90/10) was 46.0 MPa and the elongation at break was 62.7%. The tensile strength of PLA/PPCU (90/10) was 48.8 MPa and the elongation at break was 244.1%. PPCU would have a significant effect on the elongation at break of PLA/MBS/PPCU blends. After the addition of PPCU, the tensile behavior and elongation at break of the blends changed significantly. With increasing PPCU content from 5% to 40%, the tensile strength of PLA/MBS/PPCU blends decreased from 45.9 MPa to 35.4 MPa; however, the elongation at break was increased from 79.0% to 276.5%. The common method for determining the stiffness is to measure the Young's modulus.^[24] As shown in Table 1, Young's modulus of the neat PLA was 1553 MPa, and after the addition of MBS and PPCU, Young's modulus of the PLA/MBS/PPCU blends decreased from 1460 MPa to 1044 MPa with increasing PPCU content from 5% to 40%. The decrease of tensile strength and Young's modulus and the increase in elongation at break of PLA indicated that the ductility and flexibility had been improved with the addition of MBS and PPCU.

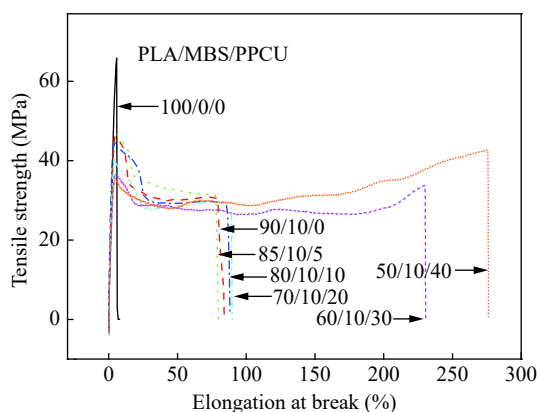


Fig. 7 Tensile behavior of the PLA/MBS/PPCU blends compared with that of PLA

The impact strength of PLA/MBS/PPCU blends is shown in Table 1. In the part, the notched Izod impact behavior of the PLA/MBS/PPCU blends was investigated as a function of PPCU content. The notched impact strength of neat PLA was about 10.8 kJ/m². It increased to 44.3 kJ/m² for the PLA/MBS 90/10 blend, which showed that a brittle-ductile transition of the blends was realized when MBS was added. The notched impact strength of PLA/PPCU (90/10) was about 5.3 kJ/m². MBS induced a significant enhancement on the impact strength of PLA/MBS/PPCU blends. The impact strength was increased from 63.3 kJ/m² to 74.7 kJ/m² with increasing PPCU content from 5% to 40%. PPCU and MBS had a certain promoting effect on toughening the PLA matrix synergistically.

PLA is a very commonly used material as films but its use as a biodegradable packaging material is limited by its brittleness and low strength. The tensile properties and tear strength of PLA/MBS/PPCU films are presented in Table 2. The tensile strength of neat PLA film was 44.9 MPa in the machine direction (MD) and 36.0 MPa in the transverse direction (TD), and the elongation at break was only about 2.7% (MD) and 3.0% (TD). The film showed brittle fracture upon tensile load. With increasing PPCU content from 5% to 40%, the tensile strength of the PLA/MBS/PPCU films was decreased from 33.5 MPa (MD) and 28.2 MPa (TD) to 27.4 MPa (MD) and 24.2 MPa (TD) respectively. The elongation at break of the PLA/MBS/PPCU films was significantly increased from 139.3% (MD) and 65.7% (TD) to 271.1% (MD) and 222.2% (TD), respectively.

From Table 2, the tear strength of neat PLA was 81.8 kN/m (MD) and 79.7 kN/m (TD); however, the values of all PLA/MBS/PPCU films were more than 100 kN/m. It indicated that the tear strength of the PLA films was improved with the addition of PPCU. For the blown films, the tear resistance was always higher along the transverse direction than that along the machine direction. It could be explained as the parallel orientation of molecular chains in the ma-

Table 1 Mechanical properties of the PLA/MBS/PPCU blends compared with those of PLA

PLA/MBS/PPCU (W/W/W)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Impact strength (kJ/m ²)
100/0/0	65.9 ± 3.7	6.2 ± 1.6	1553 ± 83	10.8 ± 0.7
90/10/0	46.0 ± 0.9	82.7 ± 3.4	1405 ± 175	44.3 ± 1.6
90/0/10	48.8 ± 1.8	244.1 ± 8.5	1249.2 ± 80	5.3 ± 0.1
85/10/5	45.9 ± 2.0	79.0 ± 2.0	1460 ± 60	63.3 ± 1.4
80/10/10	44.3 ± 1.0	88.5 ± 11.5	1385 ± 105	66.8 ± 1.7
70/10/20	40.0 ± 0.7	90.5 ± 5.5	1385 ± 45	71.9 ± 0.7
60/10/30	36.8 ± 1.8	233.3 ± 6.7	1257 ± 57	73.1 ± 2.2
50/10/40	35.4 ± 2.0	276.5 ± 10.5	1044 ± 81	74.7 ± 1.2

Table 2 Mechanical properties of the PLA/MBS/PPCU films compared with those of the PLA film

PLA/MBS/PPCU (W/W/W)	Tensile strength MD/TD (MPa)	Elongation at break MD/TD (%)	Tear strength MD/TD (kN/m)
100/0/0	(44.9 ± 1.6)/(36.0 ± 4.5)	(2.7 ± 0.1)/(3.0 ± 0.5)	(81.8 ± 8.2)/(79.7 ± 6.6)
90/10/0	(34.2 ± 4.0)/(28.6 ± 3.1)	(113.8 ± 11.8)/(57.4 ± 2.4)	(115.1 ± 8.8)/(111.7 ± 1.2)
90/0/10	(25.5 ± 5.4)/(23.8 ± 4.3)	(42.8 ± 7.8)/(38.6 ± 6.3)	(78.8 ± 9.4)/(79.9 ± 8.2)
85/10/5	(33.5 ± 2.1)/(28.2 ± 3.2)	(139.3 ± 8.0)/(65.7 ± 5.4)	(123.7 ± 8.2)/(131.6 ± 5.4)
80/10/10	(31.6 ± 6.2)/(27.1 ± 6.2)	(159.7 ± 5.5)/(73.1 ± 2.7)	(108.9 ± 7.6)/(110.8 ± 4.1)
70/10/20	(30.5 ± 6.0)/(26.1 ± 3.4)	(189.7 ± 5.2)/(82.1 ± 3.0)	(105.0 ± 6.3)/(113.1 ± 7.6)
60/10/30	(29.7 ± 2.8)/(25.4 ± 3.5)	(234.3 ± 11.2)/(106.8 ± 10.2)	(109.1 ± 8.0)/(106.2 ± 7.3)
50/10/40	(27.4 ± 4.1)/(24.2 ± 1.9)	(271.1 ± 13.3)/(222.3 ± 59.4)	(106.6 ± 9.8)/(104.3 ± 6.6)

chine direction. Tearing rupture was easier along the parallel orientation than the direction perpendicular to the molecular chains.

Toughening Mechanism

The factors affecting the process variables are temperature, deformation type, and rate. The property parameters of the blend components include viscosity ratio, interfacial tension, continuous phase viscosity, and elasticity.^[25,26] The final morphology of immiscible polymer blends is a combination

of all these factors.

The dispersion of MBS and PPCU in PLA matrix is a key factor influencing mechanical properties of the blends. The surface of neat PLA appeared to be relatively smooth as shown in Fig. 8(b1). With the addition of 10% MBS shown in Fig. 8(b2), the surface of PLA/MBS was much rougher than that of neat PLA. The MBS particles (cavities) were evenly distributed in the PLA matrix, agglomeration of MBS occurred locally, and there was obvious boundary at the phase interface. From Fig. 8(b3), with the addition of PPCU,

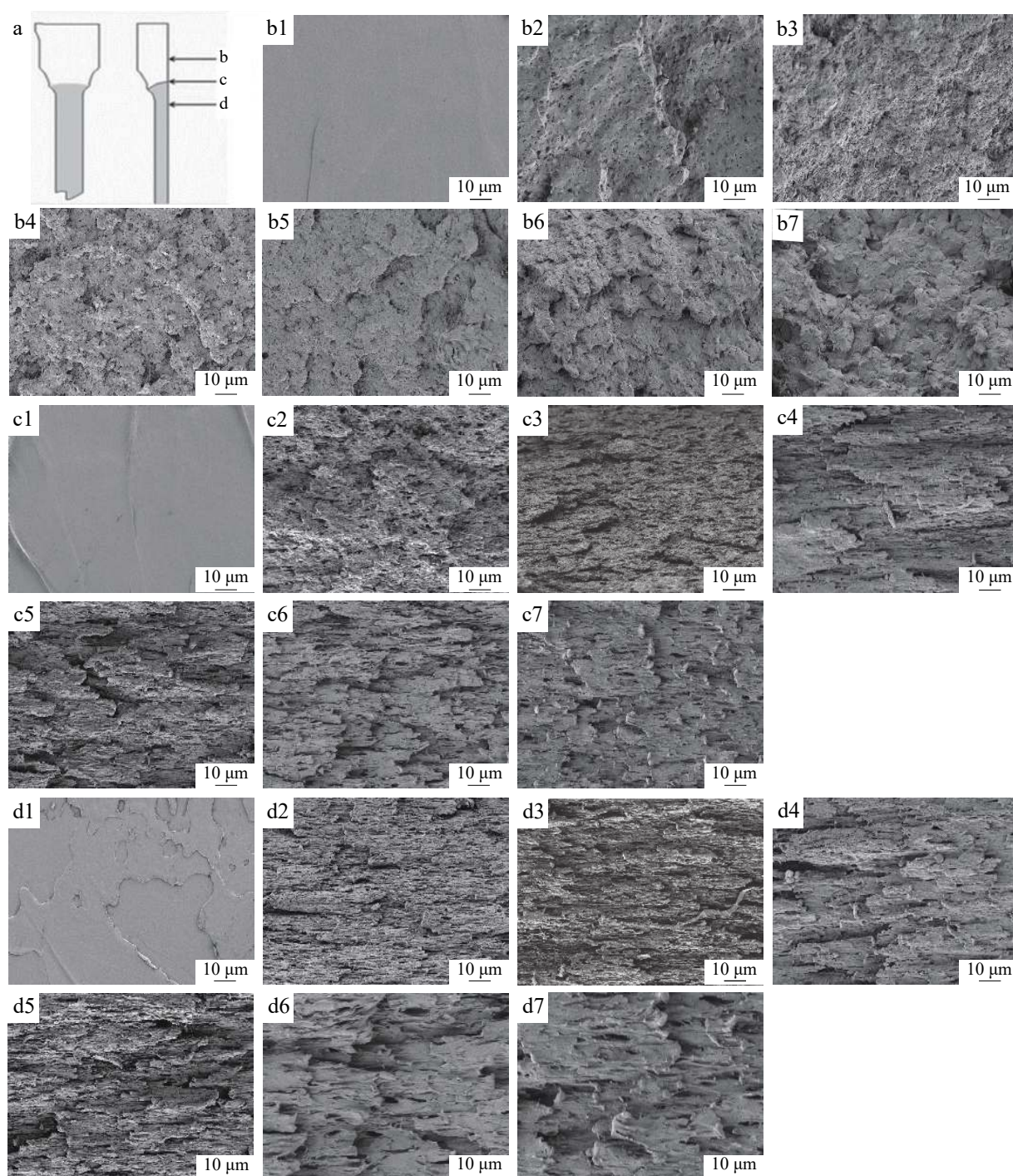


Fig. 8 (a) Schematic diagram of the locations for SEM observations of PLA/MBS/PPCU blends during tensile testing; (b–d) SEM images at respective locations of samples 100/0/0 (1), 90/10/0 (2), 85/10/5 (3), 80/10/10 (4), 70/10/20 (5), 60/10/30 (6), and 50/10/40 (7)

MBS and PPCU were evenly distributed in the PLA matrix, and agglomeration of MBS disappeared with the addition of 5% PPCU. From Figs. 8(b4) and 8(b5), it can be found that PPCU was well-distributed in the PLA matrix without obvious phase separation. The dispersion phase size gradually increased with increasing PPCU content from 10% to 20%. From Figs. 8(b6) and 8(b7), with increasing PPCU content from 30% to 40%, PPCU evolved into a co-continuous phase within PLA. The fracture surface of 60/10/30 and 50/10/40 PLA/MBS/PPCU blends was rough and had many root-like whiskers and long stretches of the ligaments, which suggested that the impact specimen broke yieldingly.

To study the toughening mechanism of PLA/MBS/PPCU blends, the necking regions of the tensile samples were cryo-fractured longitudinally as shown in Fig. 8. The micrographs focus on different deformation regions of the blends during stretching as depicted in Fig. 8(a). As Bucknall *et al.*^[27–29] and Lazzeri and Bucknall^[30] reported, cavitation was so important for notched specimens that it could enable the blends to yield at appropriate stress under the plane strain conditions. From Figs. 8(b1)–8(d1), neat PLA which had no necking in the tensile test showed a quite smooth longitudinal fracture surface without visible plastic deformation. In Figs. 8(b2)–8(d2), oval cavities are visible near the necked down region of the PLA/MBS blends during tension where dilating stresses were created. These cavities were formed when the volumetric strain energy released by forming a void is greater than the sum of surface energy needed to form new surface and the energy needed to stretch the surrounding rubber to make space for the void.^[15,28] These cavities were enlarged in the stress direction along with the deformation of the matrix. Due to the cavitation induced by MBS particles, stress whitening caused by light scattering can be observed. Figs. 8(b3)–8(d5) display the same cavitation phenomena as those in Figs. 8(b2)–8(d2). With the increasing addition of PPCU from 5% to 20%, a certain plastic deformation occurred, but not obviously. With the plastic growth of voids, the deformation and shearing of the PLA matrix became easier. As shown in Figs. 8(b6)–8(d7), the continuous growth of cavities and extensive plastic deformation of the PLA

matrix could be observed clearly, which implied that shear yielding of the PLA matrix had taken place. The results are consistent with those of the mechanical properties. The toughening-mechanism investigation reveals that shear yielding occurred in the PLA matrix; the cavitation and plasticizing deformation were induced by MBS particles and PPCU, respectively. Therefore, MBS and PPCU can be used to toughen PLA simultaneously.

The impact fracture surfaces of PLA/MBS/PPCU blends were further observed. From Fig. 9(a), the impact fracture surface of neat PLA was relatively smooth and hence, indicating that brittle fracture had occurred during the impact test. This is in accordance with the low impact strength of neat PLA.^[10] From Fig. 9(b), due to the addition of MBS to the blend, rough surfaces and some cavities could be seen due to MBS debonding from the PLA matrix.^[19] From Figs. 9(c)–9(e), when the PPCU content of PLA/MBS/PPCU blends reached 20%, rough surface can be seen on the fracture surface of PLA/MBS/PPCU blends. This is consistent with the results of the impact testing of the blends. There are many root-like whiskers and long stretches of the ligament structure existing on the fracture surface of the 80/10/10 and 70/10/20 PLA/MBS/PPCU blends. From Figs. 9(f) and 9(g), more obvious filiform structures appear on the fracture surface of PLA/MBS/PPCU blends with the further increase of PPCU content from 30% to 40%.

Thermal Properties

DSC heating thermograms of PLA/MBS/PPCU blends are shown in Fig. 10, and the corresponding parameters are summarized in Table 3. The DSC curves exhibit three main transitions successively: a glass transition, a cold crystallization exotherm, and a melting endotherm.

The degree of crystallization of the samples was evaluated from the heat evolution 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 samples, ΔH_f is the heat of fusion for PLA in the blend, ΔH_f^0 is the heat of fusion

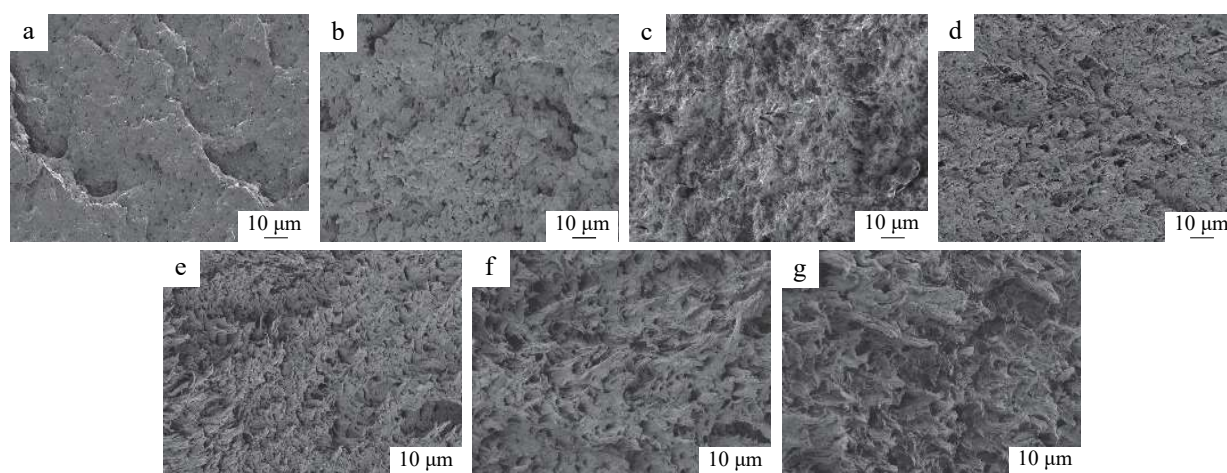


Fig. 9 SEM images of the impact fracture surface of PLA/MBS/PPCU blends: (a) 100/0/0; (b) 90/10/0; (c) 85/10/5; (d) 80/10/10; (e) 70/10/20; (f) 60/10/30; (g) 50/10/40

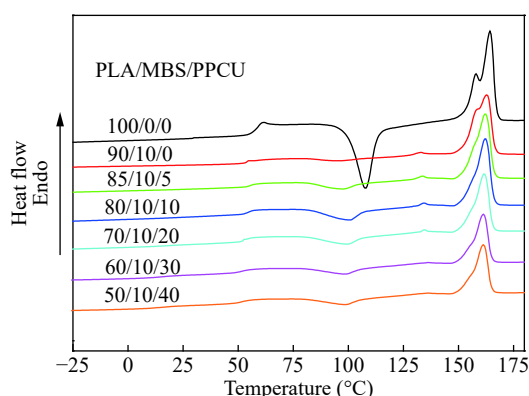


Fig. 10 DSC thermograms for the PLA/MBS/PPCU blends with compositions from 100/0/0 to 50/10/40 in the second heating run

for 100% crystalline PLA (93 J/g),^[31] and w_{PLA} is the weight fraction of PLA in the blend.

Table 3 indicates that the glass transition temperature (T_g) of PLA was 61.0 °C; with the addition of 10 wt% MBS, it decreased to 55.3 °C. When increasing the PPCU content from 5 wt% to 40 wt%, T_g decreased from 56.8 °C to 53.2 °C in the second heating run, which indicated that PPCU promoted the PLA molecular movement. The cold crystallization temperature (T_{cc}) decreased from 111.1 °C for neat PLA to 97.5 °C for the 90/10 PLA/MBS blend. As Zhang *et al.*^[19] reported, the addition of MBS enhanced the crystallization ability of PLA, indicating that the dispersive particles of MBS acted as heterogeneous nucleation agents and increa-

sed the degree of crystallinity of 90/10 PLA/MBS blends. While T_{cc} increased from 100.3 °C to 103.7 °C with increasing PPCU content, it was still below that of PLA (111.1 °C). It could be explained as that the addition of PPCU made PLA easier to crystallize.

From Fig. 10, neat PLA showed a bimodal melting peak, and with the incorporation of MBS, the bimodal melting peak disappeared. This clearly indicates that MBS acted as a nucleating agent and promoted the crystallization of PLA; hence, the less perfect crystals decreased and even disappeared, and the bimodal melting peak changed into single melting peak. With the addition of MBS, the degree of crystallinity greatly increased by about 7%, indicating that MBS as the nucleating agent could improve the crystallization ability of PLA. The beneficial effect of PPCU on the crystallization ability of PLA could be further confirmed from the low heat of fusion (ΔH_f) of the PLA/MBS/PPCU blends in comparison to that of neat PLA (Table 3). However, with increasing PPCU content in the blends, the value of $w_{\text{PLA}} \times \Delta H_f^0$ decreased faster than that of ΔH_f , which suggested that PPCU enhanced the crystallinity of PLA. The reduced ΔH_f indicated that the crystallinity of blends was decreased with increasing PPCU content in the blends. The lower crystallinity is beneficial to improving the impact strength of the PLA/MBS/PPCU blends.

Crystal Morphology

Fig. 11 shows the POM images of PLA/MBS/PPCU blends, which were melted for 3 min at 190 °C and then crystallized at 120 °C for 60 min. From Fig. 11(a), neat PLA spherulites

Table 3 Crystallization properties of PLA/MBS/PPCU blends from the second heating run

PLA/MBS/PPCU (W/W/W)	T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_f (J/g)	X_c (%)
100/0/0	61.0	111.1	32.5	169.6 *	31.6	33.9
90/10/0	55.3	97.5	1.5	167.8	33.9	40.5
85/10/5	56.8	100.3	4.0	167.3	31.1	39.4
80/10/10	56.0	101.6	4.4	169.1	29.9	40.4
70/10/20	54.1	102.5	5.7	166.7	26.5	40.7
60/10/30	54.2	102.3	3.7	166.4	21.7	38.9
50/10/40	53.2	103.7	5.0	166.0	19.0	40.8

ΔH_f of PLA is 93 J/g; * $T_{m1} = 162.7$ °C, $T_{m2} = 169.6$ °C

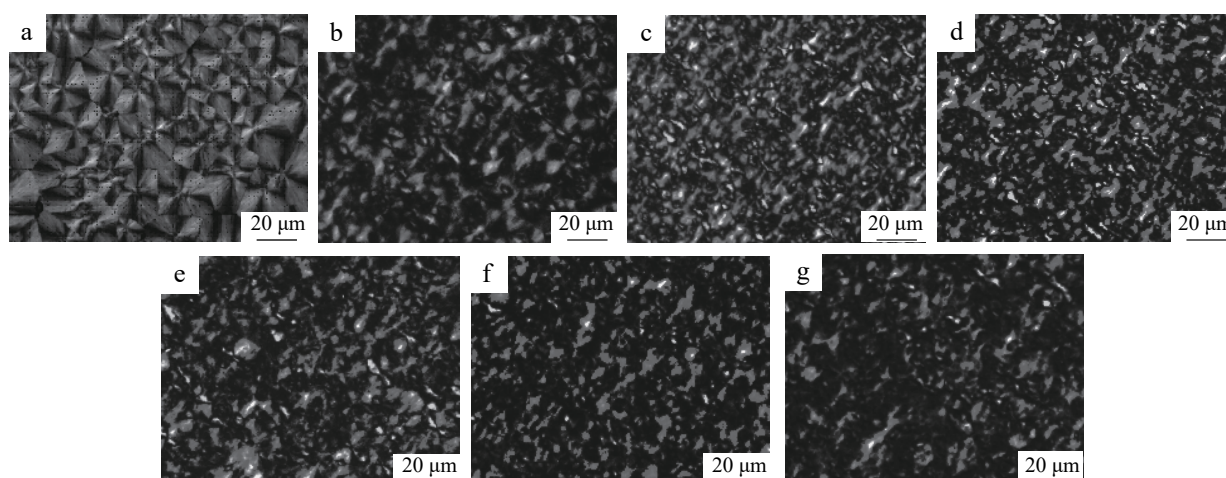


Fig. 11 Polarizing optical micrographs of spherulitic morphologies for PLA/MBS/PPCU blends at crystallization temperature of 120 °C for 15 min: (a) 100/0/0; (b) 90/10/0; (c) 85/10/5; (d) 80/10/10; (e) 70/10/20; (f) 60/10/30; (g) 50/10/40

appeared as an obvious Maltese cross pattern. As shown in Fig. 11(b), the density of spherulite nucleation increased, the size of the crystalline particles decreased, and the spherulite boundary became clear. It indicates that MBS could act as a heterogeneous nucleation agent, leading to the perfect crystal structure. From Fig. 11(c) to Fig. 11(e), the density of spherulite nucleation increased and the size of crystalline particles decreased continuously with the increasing PPCU content from 5% to 20%. However, the spherulite boundary was a little obscure. As for Figs. 11(f) and 11(g), the nucleation density of spherulites was slightly lower with increasing PPCU content from 30% to 40%. It can be seen that PPCU particles gradually weakened with the formation of bicontinuous phase, resulting in the weakening of nucleation effect. At 120 °C, PPCU began to melt and the molten PPCU could act as a solvent to improve the movement of PLA molecular chains. The PLA spherulites were easier to grow.

Wide Angle X-ray Diffraction (WAXD)

In order to further understand the crystal morphology of neat PLA and PLA/MBS/PPCU blends, wide-angle X-ray diffraction (WAXD) experiments were carried out. Fig. 12 displays the WAXD patterns of neat PLA and PLA/MBS/PPCU blends. The samples were isothermally crystallized at 120 °C for 60 min. The most representative peaks of PLA crystallization could be observed at diffraction angles 2θ of 14.8° (010), 16.7° (200), 19.0° (203), and 22.3° (213),^[10,28,31–34] indicating that PLA is the typical orthorhombic crystal. It can be further seen that the incorporation of MBS and PPCU did not alter the crystal structure of the PLA matrix. The peaks of PLA/MBS/PPCU blends could be observed at diffraction angles 2θ of 14.8° (010), 16.7° (200), 19.0° (203), and 22.3° (213) when the sample was crystallized at 120 °C for 1 h. The most common explanation for this phenomenon is that isothermal crystallization at appropriate temperatures could contribute to the formation of thin slices and hence, crystals might be more perfect in size or thickness of thin slices, resulting in better tissues spherulites and increase in crystallinity. These results indicated that the formation of complete crystals could be related to the composition of additives, crystallization temperature, and crystallization time.

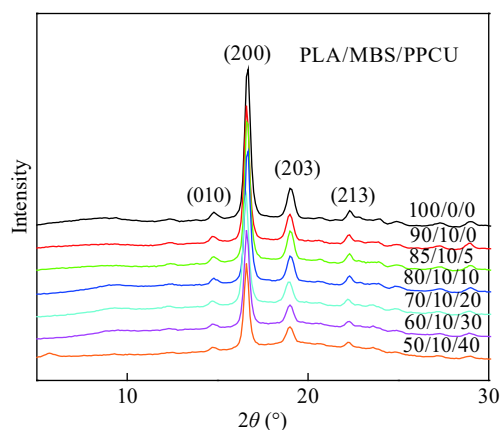


Fig. 12 X-ray diffraction patterns of PLA/MBS/PPCU blends with compositions from 100/0/0 to 50/10/40 at 120 °C for 1 h

CONCLUSIONS

In this study, the rheology, mechanical properties, phase morphology, and crystallization behavior of the PLA/MBS/PPCU blends/films were investigated by rheological measurements, tensile and tear tests, SEM, DSC, WAXD, and POM in detail. The mechanical test results showed that PLA could be obviously toughened by the addition of MBS and PPCU. The elongation at break of PLA had been improved from 6.2% for neat PLA to 276.5% after addition of 40 wt% PPCU. The impact strength was increased from 10.8 kJ/m² for neat PLA to 74.7 kJ/m² for PLA/MBS/PPCU 50/10/40, which showed that the brittle-ductile transition of the blends was obtained when MBS and PPCU were added. The toughening-mechanism investigation revealed that shear yielding of PLA matrix was triggered by the cavitation of MBS and the plasticizing deformation of PPCU. DSC analysis revealed that MBS and PPCU enhanced the ability of crystallization for PLA; MBS made it by promoting nucleation whilst PPCU through plastic deformation. POM observations displayed that the density of spherulite nucleation increased and the size of crystalline particles decreased with the addition of MBS. With increasing PPCU content from 5% to 40%, the density of spherulite nucleation increased and the size of the crystalline particles decreased. The molten PPCU has similar effect of melt, making the movement of PLA chains easier. In conclusion, this research suggested that PLA could be toughened synergistically by MBS and PPCU; the PLA/MBS/PPCU (50/10/40) blends and films had excellent properties, which would be widely used in the biodegradable packaging application.

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