

Modification of poly(lactic acid)/poly(propylene carbonate) blends through melt compounding with maleic anhydride

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Abstract. Maleic anhydride (MA) is incorporated into poly(lactic acid) (PLA)/poly(propylene carbonate) (PPC) blends to modify its properties through melt compounding. It is interesting to note that the toughness of PLA/PPC blends can be improved by 1355% while the strength is almost kept constant by adding very low content (as low as 0.9%) of MA into the blends. However, higher MA content in the blends leads to decrease in strength and further increase in toughness indicating an obvious plasticizing effect, while MA is shown to have no effect on the toughness of neat PLA. Rheological, scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA) studies have been carried out to understand the above results. It is believed that the improvement in mechanical performance originated from the largely retained molecular weight of PPC and improved interfacial interaction after processing. And relative large amount of MA in the blends is shown to mainly plasticize the PPC phase rather than the PLA phase. Such an effective method could provide PLA based biodegradable polymer blends with novel properties for industrial applications.

Keywords: biodegradable polymers, melt compounding, mechanical properties, poly(lactic acid), poly(propylene carbonate)

1. Introduction

Poly(lactic acid) (PLA) is an example of a promising biopolymer prepared through a combination of biotechnology and chemistry. It is prepared from 100% renewable resources such as corn, sugar beets or rice [1, 2]. PLA degrades biologically into lactic acid, a product of the carbohydrate metabolism. Thanks to its biocompatibility, PLA is suitable for sutures [3, 4], drug delivery systems [5, 6], scaffold material [7], and implants for bone fixation [8, 9]. It offers a potential alternative to petrochemical plastics for many applications, partially because of its high strength and stiffness. However, its toughness is not satisfactory. Blending PLA with other polymers presents a practical and economic measure to obtain toughened products [10]. To retain the integrity of biodegradability, blending PLA with other biodegradable polymers is particularly interesting. PLA/poly(*\varepsilon*-caprolactone) (PCL) blends have been extensively studied and have shown greatly improved mechanical properties compared to neat PLA [11-13]. Previous researchers also have shown that the addition of plasticizers such as polyethylene glycol (PEG), glucosemonoesters, poly(vinyl acetate) and partial fatty acid esters successfully overcame the brittleness and widened the application of PLA [14-16]. Jacobsen and Fritz [14] revealed that plasticization played an important role in improving the elongation at break and impact strength of PLA. Poly(propylene carbonate) (PPC) is a new thermoplastic polymer derived from carbon dioxide and propylene oxide [17]. It is also a biodegradable polymer, many studies concentrated on the biodegradability, we know the molecular weight would

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decrease in specific solutions [18]. It has interesting physical and chemical properties, being an attractive green environmental material for many applications [19-22]. It can be used in adhesives, solid electrolytes, polyols, photoresists, propellants, barrier materials, flexibilizers and plasticizers. The ester units provide PPC with chain flexibility and good melt flow characteristics. Although PPC can be melt processed, its poor thermal stability has limited its application. Many efforts have been devoted to improve the thermal stability of the PPC [23–25]. Tao et al. [25] prepared UV-crosslinkable PPC through terpolymerization of CO₂, propylene oxide (PO), and allyl glycidyl ether (AGE). The crosslinked PPC showed obvious improvement in thermal and mechanical properties in comparison with pure PPC. However, its preparation process is very complicated.

Furthermore, PPC is an amorphous polymer, with about 40–50% of units in the PPC copolymer chain being carbonate. Recently, some efforts have been invested to apply PPC as plasticizer for rubber or thermoplastics, and surfactant [26-29]. PPC is an amorphous polymer with a chemical structure similar with PLA. In the study reported by Ma et al. [30], the compatibility of melt-mixed blends of PLA/PPC in different ratios was characterized. They illustrated that PLA and PPC are partially miscible and compatible to some extent due to their similarity in chemical structure. However, they reported that more than 40 wt% of PPC are needed in the PLA to modify its brittle fracture behavior. As a result, the strength of the blends is largely affected by the large content of PPC. Inevitably, the process-ability of the blends containing large content of PPC is quite poor due to the poor thermal stability of PPC. The blend of PLA and PPC is a biodegradable polymer system, and it has potential as medical and packing materials. In our previous work, it was demonstrated that the mechanical and thermal properties of PPC can be improved dramatically through end-capping PPC with MA [31]. In this article, MA will be added to the binary blend of PLA and PPC to further improve the properties.

To the best of our knowledge, no systematic study has been reported so far to investigate the properties of MA end-capped PPC toughened PLA composites. Therefore, it is the aim of this study to investigate the effect of MA content on the mechanical, thermal and rheological properties of PLA/MA/ PPC blends. The weight ratio between PLA and PPC ranges from 90:10 to 10:90, and the weight percentage of the MA was varied from 0 to 1.5 wt% of the total weight of the PLA/PPC blends. Scanning electron microscopy (SEM), Differential Scanning Calorimetry (DSC), Dynamic mechanical analysis (DMA), Gel permeation chromatography (GPC), tensile test and rheological study are carried out on these blends to perform systematic investigation. It is proposed that part of the MA is end-caped onto PPC, and the rest is present as a blend. Furthermore, possible homopolymerization of MA is also suggested.

2. Experimental 2.1. Materials

1. PLA is provided by Zhejiang Haizheng Biomaterial Co (Zhejiang, China). It is levorotatory, represents a semi-crystalline and biodegradability. Its GPC measured weight-average molecular weight is $1.59 \cdot 10^5$ g/mol, and $M_w/M_n = 2.75$. PPC is obtained from State Key Polymer Physics and Chemistry Laboratory, Changchun Institute of Applied Chemistry, China. Its weight-average molecular weight is $2.48 \cdot 10^5$ g/mol, and $M_w/M_n = 3.2$. MA (purity> 99.5 wt%) was purchased from Tianjin Bodi Chemical Co (Tianjin, China).

2.2. Preparation of PLA/PPC and PLA/MA/PPC blend

Blends containing PLA and PPC in the ratio of 90/10, 70/30, 50/50, 30/70, and blends containing PLA, MA and PPC with the ratio of 70/0/30, 70/0.15/30, 70/0.3/30, 70/0.6/30, 70/0.9/30, 70/1.5/30, 10/0.3/90, 30/0.3/70, 50/0.3/50, 70/0.3/30 and 90/0.3/10 were melt compounded using a Haake Rheomix internal mixer (Thermo Fisher Scientific, Waltham, MA, USA) at a barrel temperature of 150°C and a rotation speed of 50 rpm for 5 mins, respectively. PLA, PPC and MA were dried at 50°C overnight before the melt blending to prevent PLA and PPC from hydrolysis during blending. Then, PLA/MA/ PPC blends were ground into fine particles for further sample preparation. All specimens used were manufactured with a hot compression molding method. It was conducted at 160°C for 6 mins, with a holding pressure of 10 MPa.

2.3. Characterizations

2.3.1. Mechanical testing

Tensile properties were characterized with Universal Testing Machine (SANS company, Shenzhen, China) in tension mode. Specimens used for tensile test were cut from hot pressed films of PLA/MA/ PPC. And the sample dimension was 4 mm in width, 0.4–0.5 mm in thickness and 75 mm in length. They are slabs with dog bone shapes. Five samples were used for each measurement and averaged results are reported. The cross-head speed used was 10 mm/min.

2.3.2. Gel permeation chromatography (GPC)

The molecular weight (M_w) and molecular weight distribution (MWD) of the blends were measured with gel permeation chromatography system (GPC, agilent1100, Agilent Technologies, Santal Clara, CA, USA) with tetrahydrofuran (THF) as solvent. Calibration was performed with polystyrene standards.

2.3.3. Scanning electron microscopy (SEM)

The morphologies of etched specimens and tensile fractured surfaces were examined under an acceleration voltage of 20 kV with SEM (JEOL JSM-5900 LV, Jeol, Tokyo, Japan). Prior to examination, the specimens of blends were cryogenically fractured in liquid nitrogen, then the fracture surfaces were etched with the acetone/ethanol (1:1) mixed solution to remove PPC and MA. For the tensile fractured specimens, a thin layer of gold was coated on their fracture surfaces before examination.

2.3.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of the prepared composites (storage modulus and tan) were characterized with DMA (Q800, TA Instruments, New Castle, DE, USA) in tension mode. Temperature scan was conducted from -20 to 120°C at a heating rate of 3°C/min. A fixed frequency of 1 Hz was used. A static force of 0.01 N and the force track of 120.0% were employed. The film was cut into the plates for DMA test. And the sample dimension of the film was 4 mm in width, 0.4–0.5 mm in thickness and 14–18 mm in length.

2.3.5. Differential scanning calorimetry (DSC)

A DSC (Perkin-Elmer Pyris I, Perkin Elmer Corp. Waltham, MA, USA) with nitrogen as the purge gas was used to investigate the melting and crystallization behaviors of the blends. The mass of tested sample was around 5 mg. The sample was heated from room temperature to 200°C at a heating rate of 10°C/min. This first heating process was regarded as melting scan for the analysis. The crystallization and melting temperatures were determined as the temperatures at the maximum values of crystallization and melting peaks.

2.3.6. Rheological measurement

Oscillatory shear measurements in the linear viscoelastic region were performed on a Gemini 200 dynamic rheometer (Malvern Instruments Ltd, Malvern, UK) using 2.5 cm diameter and 1.2 mm distance parallel plates at 160°C. Dynamic frequency sweep was performed in the region of linear viscoelastic response (LVR), with 1% strain for the blends, starting from high frequency, 100 down to 0.01 rad/s. Dynamic frequency sweep tests were subsequently performed to determine the dynamic properties of the materials. Test sample disks with a thickness of 1.5 mm and a diameter of 2.5 mm were prepared by compression molding at 160°C.

3. Results and discussion 3.1. Mechanical properties

Mechanical test was performed to investigate the mechanical performance of PLA and blends. Neat PLA exhibits yielding with a short quasi constant stress regime, and fails at a strain around 3.6% (see Figure 1a). It is noted that all the neat PLA specimens fractures without necking. In the binary PLA/PPC blends, the strain at break is increased from 10.1 to 82% with PPC content increasing from 10 to 70%. However, the tensile strength is decreasing with increasing PPC loading, and the blends fracture in an almost brittle manner without yielding, except the one containing 70% PPC. This is slightly different from the work reported by Ma et al. [30], as the strain at break is much smaller in the current work. It might be caused by the difference in the neat PLA used. For PLA/MA/PPC blends containing the same amount of MA (see Figure 1b), the elongation at break is obviously improved comparing with their original binary blends, respectively. Nevertheless, their strength is almost the same with the previous values (see Figure 2a).



Figure 1. Stress–strain curves for (a) PLA, PLA/PPC blends in the ratio of 90/10, 70/30, 50/50 and 30/70, (b) PLA/MA/PPC blends in the ratio of 90/0.3/10, 70/0.3/30, 50/0.3/50, 30/0.3/70 and 10/0.3/90, (c) PLA/MA/PPC blends in the ratio of 70/0.15/30, 70/0.3/30, 70/0.6/30, 70/0.9/30 and 70/1.5/30

To investigate the effect of MA content on the properties of ternary blends, PLA/MA/PPC blends with PLA/PPC in the ratio of 70/30 containing different amount of MA is characterized (see Figure 2b). The addition of 0.15 wt% MA results in a slight increase in tensile strength compared with the PLA/PPC binary blend. Interestingly, the specimens show intense stress whitening followed by necking, resulting in a large yielding regime and hence slight increase in strain at break (20.4%). With the addition of 0.3, 0.6 and 0.9 wt% MA, the strain at break is dramatically increased to 59.3, 164.3 and 142.5%, respectively. Consequently, the toughness which are calculated from the definite integrals of the strain -stress curves is 1.5, 3.1, 5.8, 13.4, 44.7, 42.0 and 60.6 MJ/m^3 for neat PLA, PLA/PPC (70/30), PLA/MA/PPC (70/0.15/30), PLA/MA/PPC (70/0.3/30), PLA/MA/PPC (70/0.6/30), PLA/MA/PPC (70/0.9/30), PLA/MA/PPC (70/1.5/30), respectively. It is interesting to notice that the mechanical properties including toughness and strength is improved (8.2% increase in strength, 188.7% increase in toughness) by adding very low content (as low as 0.15%) of MA into the blends. While a maximum of 1961.2% increase in toughness is obtained for the blends containing 1.5% of MA. And the toughness can be improved by 1355% while the strength was almost kept constant by adding very low content (as low as 0.9%) of MA into the blends. All the PLA/ MA/PPC blends yields with noted stress whitening across the whole gauge length accompanied with necking. However, there is little improvement in tensile strength compared with the binary blend. Above results are summarized in Table 1, it can be concluded that the PLA/MA/PPC ternary blends experience significant necking. This indicates the presence of shear yielding. The improvement in toughness with additional MA shows the interface between PLA and PPC polymer chains may be effectively enhanced by end-capping MA onto PPC, MA can be grafted onto PPC molecules by reactive

blending. The scheme is shown in Figure 3 [31].

Furthermore, the increased molecular weight of the

PPC component (as discussed in our previous work

[31]) could also be partially responsible for this sig-

nificant increase in toughness, as more entangle-

ments between polymer chains might be formed at

higher molecular weight. Nevertheless, the tensile

strength shows an obvious decrease with increasing

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Figure 2. (a) Tensile strength and elongation at break of PLA/PPC, PLA/MA/PPC (0.3 phr MA is loaded) blends as a function of PPC content. (b) tensile strength and elongation at break of PLA/MA/PPC(PLA/PPC wt. ratio is 70/30) blends as a function of MA content.



Figure 3. Melt end-capping PPC with MA

Table 1. Summary of mechanical properties of the specimens shown in Figure 1.

	Tensile strength [MPa]	Elongation at break [%]	Toughness [MJ/m ³]	
PLA	67.3±1.33	3.6±0.31	1.5	
PLA/PPC (90/10)	58.6±0.74	11.2±0.37	4.9	
PLA/ PPC (70/30)	42.7±1.21	10.1±2.43	3.1	
PLA/ PPC (50/50)	39.5±2.03	3 ±0.65	0.9	
PLA/ PPC (30/70)	28.9±1.00	82±5.76	15.0	
PLA/MA/PPC (90/0.3/10)	56.7±1.58	7.5±1.51	2.2	
PLA/MA /PPC (70/0.3/30)	41.7±1.25	59.3±3.79	13.4	
PLA/MA /PPC (50/0.3/50)	36.6±1.54	27.4±4.55	8.6	
PLA/MA /PPC (30/0.3/70)	27.4±1.40	127.4±6.08	21.4	
PLA/MA /PPC (10/0.3/90)	31.7±0.40	88.5±5.21	12.6	
PLA/MA/PPC(70/0.15/30)	46.2±0.94	20.4±9.95	5.8	
PLA/MA/PPC(70/0.3/30)	41.7±0.88	59.3±16.35	13.4	
PLA/MA/PPC(70/0.6/30)	39.7±1.36	164.3±20.07	44.7	
PLA/MA/PPC(70/0.9/30)	40.5±1.26	142.5±18.35	42.0	
PLA/MA/PPC(70/1.5/30)	34.5±1.10	243.1±4.55	60.6	

MA content. For the PLA/MA/PPC blends containing 1.5 wt% MA, the tensile yield strength is decreased dramatically, meanwhile the strain at break is significantly increased to 243.1%. The excess MA may act as plasticizer, which might be responsible for the decrease in strength and the increase in strain at break. In order to further investigate the effect of MA on the blends, PLA is compounded with different contents of MA. The mechanical properties of these compounds are summarized in Table 2. It is obvious to note that MA is not acting as plasticizer for neat PLA. The excess MA may only act as plasticizer to PPC component. As inter-

 Table 2. mechanical properties of the PLA/MA blends with different content of MA

	Tensile strength	Elongation at break
	[MPa]	[%]
PLA	67.3±1.33	3.6±0.31
PLA/MA (100/0.15)	65.39±2.69	3.8±0.39
PLA/MA (100/0.3)	61.72±4.58	3.6±0.70
PLA/MA (100/0.6)	54.22±3.82	3.5±0.33
PLA/MA (100/0.9)	62.65±1.45	3.7±0.29
PLA/MA (100/1.5)	61.88±1.49	3.7±0.45

esting behavior has been demonstrated by blends containing different amounts of MA, following characterization is mainly carried out to investigate the effect of MA content on different properties.

3.2. GPC measurement

To understand the effect of processing and the addition of MA on the molecular weight of PPC and PLA, blends were studied by GPC measurements. The weight average molecular weight (M_w) and the molecular weight distribution (MWD) of PLA/PPC (70/30) and PLA/MA/PPC blends are summarized in Table 3. It is well known that the thermal degradation of PPC molecular chain is likely to occur during melt compounding [31]. However, $M_{\rm w}$ for PLA/MA/PPC (70/0.15/30, 70/0.3/30) is obviously higher than that of processed neat blends. This indicates that the addition of MA prevents the thermal degradation of PPC. As MA serves as end capping agent, which inhibits initial chain unzipping and prevents the thermal decomposition of PPC [32]. It is noted that the $M_{\rm w}$ is obviously decreasing with increasing more MA content (see the M_w for the blend PLA/MA/PPC (70/0.6/30, 70/0.9/30, 70/1.5/30)). It might be due to the fact that the end capping reaction is better performed at lower MA contents. Since the chance for homo-polymerization of MA increases with increasing MA content, which competes with end-capping reaction. This results in improvement in the molecular weight (especially for PLA/MA/PPC (70/1.5/30)), where the excessive MA could even promotes the degradation of the polymer during processing (in our previous work have proved it [31]).

3.3. Morphology analysis

To explore the mechanism for toughening observed in the blends, the morphology of tensile specimens and etched specimens were investigated with SEM. PLA/MA/PPC ternary blends with different content of MA and PLA/PPC (70/30) binary blend were selected to be investigated as shown in Figure 4 and 5.

It can be observed from the fractured surfaces of specimens taken from tensile test that a smooth surface without obvious plastic deformation is obtained in PLA/PPC (70/30) (Figure 4a). It clearly reveals that some PPC spheres remains at the fracture surface. This indicates that the weak interfacial adhesion associated with the incompatibility in PLA/ PPC blend. The applied stress could not be efficiently transferred through the interface between polymers, which in turn result in a limited improvement in mechanical properties. The morphology of the tensile fractured surface from PLA/MA/PPC (70/0.9/30) ternary blend is distinctly different from binary blend, exhibiting considerable ductile behavior. In Figure 1c, PLA/MA/PPC (70/0.9/30) demonstrates necking behavior and a large strain at break

Table 3.	The weight a	verage molecular	weight (M_{m})	distributing	index (D)) of PL/	A/PPC an	d PLA/MA	PPC blends
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	PLA/PPC (70/30)	PLA/MA/PPC (70/0.15/30)	PLA/MA/PPC (70/0.3/30)	PLA/MA/PPC (70/0.6/30)	PLA/MA/PPC (70/0.9/30)	PLA/MA/PPC (70/1.5/30)
M _w	$4.67 \cdot 10^4$	5.45·10 ⁴	6.17·10 ⁴	5.20·10 ⁴	4.61·10 ⁴	3.88.104
D	2.35	2.35	2.18	2.19	2.33	2.56



Figure 4. Tensile-fractured surface morphology of the blends: (a) PLA/PPC (70/30), 5000×; (b) PLA/MA/PPC (70/0.9/30), 5000×



Figure 5. SEM micrographs of the surfaces of PLA/PPC (70/30 w/w) blends with varying MA contents. The surfaces were prepared by etched with the acetone/ethanol (1:1) mixed solution to remove PPC and MA. (a) PLA/PPC (70/30), (b) PLA/MA/PPC (70/0.15/30), (c) PLA/MA/PPC (70/0.3/30), (d) PLA/MA/PPC (70/0.6/30), (e) PLA/MA/PPC (70/0.9/30), (f) PLA/MA/PPC (70/1.5/30).

value. Correspondingly, its SEM micrograph exhibits intensive plastic deformation (Figure 4b), indicating the presence of large deformation in the blend. The rough fracture surface suggesting that the cracking propagation absorbs considerable amount of strain energy before failure [33]. And the addition of MA increases the interfacial adhesion between PLA and PPC components, leading to a significant improvement in toughness.

PPC component is etched out to investigate the phase morphology in the blends as shown in Figure 5. The size of PPC component is quite large for the binary blend (see Figure 5a). It decreases with the addition of MA, indicating the compatibility between PPC and PLA is improved. With further increase in MA content, the size of the PPC component is almost kept constant (see Figure 5b–f), indicating only a small amount of MA is needed to achieve compatibilization.

3.4. Dynamic mechanical analysis

DMA study was carried out to study the thermal mechanical properties and glass transition temperature of these blends. Figure 6a shows the dynamic storage modulus (E') of neat PLA matrix, PLA/PPC and PLA/MA/PPC blends over a temperature range of -20–80°C. The storage modulus (E') is plotted against temperature. For most samples, a decrease in E' can be observed for the investigated temperature range comparing with that of neat PLA, indicating elastic properties is reduced by additional PPC. All samples lost most of their stiffness at temperatures above their $T_{\rm g}$. The stiffness of blends and pure polymers below T_g is governed by the glassy phase, where polymer chain movement is restricted. Above 60°C, the E' curves for the blends display a short plateau comparing with pure PLA. This indicates a decrease in thermal-mechanical stability with additional PPC in PLA. The addition of impact modifier and plasticizer in PLA is often reported to decrease the stiffness, where a dramatic decrease in E' of PLA is noted with the addition of polyethylene glycol (PEG) as plasticizer [34]. Comparing PLA/ PPC with PLA/MA/PPC, the storage modulus gradually decreases with further increasing MA content. Accordingly, the temperatures corresponding to a relative modulus (the ratio of storage modulus to initial modulus) of 0.8 are 34.7, 34.7, 34.7, 31.7, 28.8 and 26.1°C (Figure 6b) for PLA/PPC, PLA/MA/



Figure 6. DMA curves including (a) storage modulus, (b) ralative modulus (the ratio of storage modulus to initial modulus) and (c) tanδ as a function of temperature for PPC, PLA, PLA/PPC (70/30) and PLA/MA/PPC blends with different MA content

PPC (30/0.15/70, 30/0.3/70, 30/0.6/70, 30/0.9/70, 30/1.5/70), respectively. This indicates that the

stiffness of PLA/MA/PPC blends is decreasing with the addition of large amount of MA. This result agrees well with the above results from mechanical test.

Figure 6c shows $tan\delta$ as a function of temperature for the pure polymer, PLA/PPC and PLA/MA/PPC blends. Two relaxation peaks, a and a' corresponding to T_{g1} of the PPC-rich phase and T_{g2} of the PLArich, respectively, are observed in each tand curve. T_{g1} and T_{g2} are summarized in Table 4. For PLA/PPC (70/30) and PLA/MA/PPC (70/0.15/30, 70/0.3/30), the tand peak is shifted to slightly higher temperatures comparing with pure polymers. T_{g} is shifted to lower temperatures with further increasing MA content. This may be due to the fact that excessive MA serve as plasticizer. However, T_{g1} decreases from 41 to 33.6°C, showing a much larger drop than T_{g2} (which decreases only 3°C). It indicates that most of the excessive MA mainly plasticize PPC phase. In the blends, the plasticized PPC plasticize PLA phase. This agrees well with the mechanical behavior observed in Figure 1 and Table 2. Furthermore, no improvement in toughness is observed while MA is added into neat PLA (see Table 2). Therefore, it is concluded that most of the excessive MA mainly plasticize PPC phase as the toughness

40.7±0.2

 $T_{g1} [°C]$

of the blends is significantly improved with the addition of MA.

We know that, if the blends is completely compatible, the $T_{\rm g}$ calculated from the compositions by applying Fox's equation is 55.96°C, when the T_{g1} and T_{g2} close to it, indicate the compatibility is improved [17]. As shown in Table 4, only for the PLA/MA/PPC (70/0.15/30) blend have the trend that T_{g} close to each other comparing with neat binary blend, and the T_{g1} corresponding to the PPCrich phase increase suggesting that the blend is partially miscible. This result agrees well with the above mechanical property result, where the tensile strength and elongation at break for PLA/MA/PPC (70/0.15/30) is increased. In addition, the $T_{\rm g}$ for other blends move farther indicating the poorer compatibility is obtained while more MA is added. As a result, decreasing tensile strength is obtained with increasing MA content.

3.5. Differential scanning calorimetry

(70/0.6/30)

38.9±0.2

To further understand the mechanical behavior observed, DSC was carried out to investigate the melting and crystallization behavior of these blends. Figure 7 shows the DSC results of PLA binary and ternary blends from the first heat scan at a rate of

(70/0.9/30)

37.0±0.2

(70/1.5/30)

33.6±0.2

Table 4. The T_{g1} for PPC, T_{g2} for PLA obtained from the tano curve of PPC, PLA, PLA/PPC (70/30) and PLA/MA/PPC blends with different MA contentPLAPPCPLA/PPCPLA/MA/PPCPLA/MA/PPCPLA/MA/PPCPLA/MA/PPCPLA/MA/PPC(T0/0.12)(T0/0.12)(T0/0.12)(T0/0.12)(T0/0.20)(T0/0.20)(T0/0.20)(T0/0.20)

(70/0.3/30)

41.4±0.2

(70/0.15/30)

41.9±0.2

(70/30)

41.0±0.2



Figure 7. DSC traces of the PLA, PLA/PPC (70/30) and PLA/MA/PPC (70/0.15/30, 70/0.3/30, 70/0.6/30, 70/0.9/30, 70/1.5/30) blends at a heating rate of 10°C/min

10°C/min. The exothermic peaks can be correlated to the crystallization of PLA due to the amorphous nature of PPC and semi-crystalline nature of PLA. As the processed PLA is 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. In Figure 7a the cold crystallization temperature (106.7°C) of the neat PLA is clearly decreased with the incorporation of PPC, the reason may be the presence of PPC increase the mobility of PLA chains. The presence of PPC result in a lower cold crystallization temperature (T_c) without additional MA. This could be caused by the increased number of low molecular polymer arising from the decomposition of PPC [35]. For the blends, the decomposition of PPC is largely avoided during processing thanks to the addition of MA. Therefore, the T_c observed for the blends is higher than that of neat binary blend.

In Figure 7b, neat PLA shows a melting peak at 150.1°C (T_{m1}) and 158.3°C (T_{m2}). The increase in additional MA content gradually decreases the melting temperature. This bimodal melting peak is induced during slow DSC scan while the less perfect crystals have enough time to be melted and reorganized into crystals with higher structural perfection, and re-melted at higher temperature [36, 37]. Low-melting-temperature crystals have similar structure with high-melting-temperature ones, but with smaller lamellar thickness. For PLA/PPC binary blend, the decrease in the first peak temperatures (T_{m1}) suggesting larger number of less perfect crystals are nucleated at the particle surface. They are reorganized into a more stable form at higher temperature (T_{m2}) and melted again at around the same temperature. By comparing PLA/PPC (70/30) with PLA, the melting enthalpy of these is almost the same. This suggests that the amorphous PPC has no apparent effect on the crystallinity. For PLA/MA/ PPC (70/0.15/30, 70/0.3/30, 70/0.6/30, 70/0.9/30), T_{m1} is kept almost constant, but T_{m2} is decreased due to the crystallization of perfect PLA crystalline is hindered by high molecule weight PPC component. With increasing MA content, a decrease in melting temperature is observed. This agrees with above results that excessive MA serves as plasticizer in the blends.

3.6. Rheological properties

The rheological properties of the blends are investigated in this study to understand the properties variations shown in Figure 1c. As shown in Figure 8, the shear storage moduli (G'), shear loss moduli (G''), and complex viscosities (η^*) are plotted versus the applied shear frequency, respectively. All



Figure 8. (a) storage modulus (G'); (b) loss modulus (G");
(c) complex viscosity (η*) versus frequency for the PLA/PPC (70/30) and PLA/MA/PPC (70/0.15/30, 70/0.3/30, 70/0.6/30, 70/0.9/30, 70/1.5/30) blends

the samples are featured by a typical increase in G'and G'' with increasing frequency (ω). At the frequency scanned area for all the samples the G' is smaller than G'', indicating a classical liquid-like behavior of polymer melt.

The complex viscosities of the PLA/MA/PPC (70/0.6/30, 70/0.9/30, 70/1.5/30) blends exhibit a Newtonian behavior (η^* is independent of frequency) with values around 250, 170 and 60 Pa·s, respectively. Then, a shear-thinning takes place at frequency above 30 rad/s. In Figure 8, the increase in moduli and viscosity obtained for PLA/MA/PPC (70/0.15/30, 70/0.3/30) demonstrates the reinforcing effect from additional MA on the polymer melt. It is thought that such an effect originates from the higher molecular weight of PPC and better interfacial adhesion in these specimens. Furthermore, the lowest moduli and viscosity is obtained for PLA/ MA/PPC (70/1.5/30). This agrees well with the results observed above as excessive MA serve as plasticizer in the system. It is also interesting to note that neat binary blend is demonstrating stronger shear thinning effect comparing with other blends, especially the ones containing higher MA content. It is reported in literature that low molecular weight polymer shows Newtonian-like behavior at shear rates similar with film extrusion [38]. Therefore, such an effect is likely caused by the presence of low molecular PPC chains which come from the decomposition of PPC.

4. Conclusions

In order to improve the mechanical performance of PLA, PPC and MA is melt compounded with PLA. The PLA/MA/PPC blends yield with noted stress whitening across the whole gauge length accompanied with necking with the addition of MA. The strain-at-break is dramatically increased comparing with PLA/PPC binary blend. It is interesting to note that the toughness can be improved by 1355% while the strength is almost kept constant by adding very low content (as low as 0.9%) of MA into the blends. DMA study shows that the $T_{\rm g}$ of PPC and PLA decrease with the addition of relative large amount of MA, indicating the plasticizing effect of MA in the blends. However, the magnitude of such a decrease is more pronounced in PPC. By considering the results from both mechanical test and DMA, it is

believed that MA mainly plasticize PPC component in the blends. SEM results indicate that the addition of MA increases the interfacial adhesion between PLA and PPC phases, leading to ductile fracture behavior and decrease in the size of PPC domain. Rheological analysis demonstrates that the viscosity is increased by adding small amount of MA into the polymer melt. Such an increase is thought to be caused by the largely retained molecular weight of PPC during processing and improved interfacial adhesion between PLA and PPC phases. As a result, enhanced mechanical properties for PLA/PPC blends are observed.

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