Synergistic effect of PLA–PBAT–PLA tri-block copolymers with two molecular weights as compatibilizers on the mechanical and rheological properties of PLA/PBAT blends†

Zhiqiang Sun, Bao Zhang, Xinchao Bian, Lidong Feng, Han Zhang, Ranlong Duan, Jingru Sun, Xuan Pang,* Wenqi Chen and Xuesi Chen

Two types of polylactide–poly(butylene adipate-co-terephthalate)–polylactide (PLA–PBAT–PLA) tri-block copolymers with different molecular weights (CP1 and CP2) were synthesized as compatibilizers for PLA/PBAT blends. Synergistic effects of CP1 and CP2 on the mechanical and rheological properties of the blends have been studied in detail. The addition of small amounts of CP1 and CP2 remarkably increased the elongation at the break point. 0.5 and 0.5 wt% of CP1 and CP2 led to an increase of elongation by over eightfold. Thermal, morphological and rheological analyses showed that addition of CP1 and CP2 increased the miscibility and interfacial bonding strength between PLA and PBAT, in addition to decreasing the melt viscosity. It was thought that the low-molecular-weight compatibilizer CP1 with high mobility would have a positive effect during the transportation of the high-molecular-weight CP2 from the matrix to the interface. In addition, CP2 played a key role in improving the interaction at the interface.

Introduction

As one of the most important bio-based and biodegradable aliphatic polyesters, polylactide (PLA) has been attracting increasing attention during the past few decades.1–3 PLA, particularly poly(l-lactide), shows several favorable properties such as high modulus and strength comparable to that of many petroleum-based plastics. This makes it promising as a substitute for conventional polymers, e.g., in the fields of food packaging, tableware, nonwoven fibers, biomedical use, agricultural films and single-use disposable items.4 However, the inherent brittleness or stiffness, slow crystallization, low elongation at the break point and physical aging of PLA resins have imposed constraints for their further applications.5,6

Therefore, intensive studies on improving the toughness of PLA have been carried out by means of copolymerization, plastification and blending methods.7,8 Among these approaches, blending is one of the most practical and economically feasible methods for industrial applications.9 Extensive efforts have been devoted to the study of blending PLA with other flexible and biodegradable polymers.10 In view of its high toughness and biodegradability, poly(butylene adipate-co-terephthalate) (PBAT) was considered to be a good candidate for PLA toughening.11–13

The oil-based aliphatic–aromatic copolyester of PBAT is fully biodegradable, and it was demonstrated that no indication of an environmental risk was found when PBAT was introduced into the composting processes.14 Although dynamic mechanical analysis suggests that the presence of carbonyl groups in PBAT makes it potentially miscible with PLA, experimental results show that after blending equal to or more than 5 wt% of PBAT in the PLA resin, the PBAT molecules are phase-separated with the PLA molecules.15–17 Because the macrophase separation and low adhesion between the two components would lead to poor mechanical properties of the blending materials, compatibilization is essential for the application of PLA/PBAT blends.

It has been demonstrated that addition of bi-, tri- and multiblock copolymers into the blends could enhance the compatibility of most miscible and partially miscible blending systems.18–21 The segments of these copolymers could be chemically identical with those in the respective phases or miscible with or adhered to one of the phases. A sharp decrease in interfacial tension might be observed with the addition of small amounts of block copolymer.22–25 Once the concentration reached the critical micelle concentration (CMC), the continued addition of more copolymer became unnecessary. The redundant copolymer did not affect the interfacial situation; instead, it produced the micelles of the copolymer, which...
would disperse in the homopolymer phases. It has been proved that the CMC fell rapidly with the increasing molecular weight of the block copolymer, as a micellar structure was preferred in the bulk homopolymer for long copolymer chains.

Recently, a number of studies have focused on the mechanical and rheological properties, as well as the morphology and miscibility of PLA/PBAT blends. Dil et al. carried out a detailed examination of the miscibility, interfacial tension and morphology of PLA/PBAT blends by a variety of microscopy and rheological techniques. Arruda and coworkers investigated the effects of chain extender and blend composition on the morphology and mechanical properties of the PLA/PBAT blown films. In the present study, two types of PLA–PBAT–PLA tri-block copolymers with different molecular weights were synthesized by the ring-opening polymerization (ROP) of L-lactide (L-LA) using dihydroxy PBAT (HO–PBAT–OH) as the macro-initiator. Different amounts of each triblock copolymer as well as their mixture were intentionally added into the melt-blending system of PLA/PBAT (80/20, w/w) as compatibilizers. It was thought that the tri-block copolymers with a low molecular weight (CP1) and high mobility could act as carriers for delivering their coworkers with high molecular weight (CP2) to the interface (as illustrated by Scheme 1). The synergistic effects of the two copolymers on the mechanical and rheological properties of the blends were discussed. The two-component copolymer compatibilizers increased the elongation at the break points of the blends more efficiently than each of the single copolymers, simultaneously maintaining other mechanical properties, including Young’s modulus and tensile strength. The improved mechanical properties should be attributed to the synergistic effects: low viscosity of the melts caused by a low molecular weight compatibilizer CP1, as well as the strong interaction between PLA and PBAT phases owing to the high molecular weight CP2.

Scheme 1 Schematic of the synergistic compatibilization effect of two-component tri-block copolymer compatibilizers.

### Experimental section

#### Materials

PLA ($M_w = 152,000$ with a polydispersity of 1.3, $T_g = 59.7 \, ^\circ C$, $T_m = 153.4 \, ^\circ C$) used in this study was obtained from Zhejiang Hisun Biomaterials Co., Ltd (China). PBAT ($M_w = 70,000$ with a polydispersity of 2.3, $T_g = -31.2 \, ^\circ C$, and $T_m = 119.9 \, ^\circ C$) was purchased from BASF Corporation. HO–PBAT–OH macro-initiators and PLA–PBAT–PLA tri-block copolymers were prepared in our laboratory. The characterization data of the macro-initiators and copolymers are listed in Table 1. SnOct2 and l-lactide (l-LA) were purchased from Aldrich, and l-LA was repeatedly recrystallized from dry ethyl acetate three times before use. Adipic acid (A.R.), 1,4-butanediol (A.R.), dimethyl terephthalate (A.R.) and tetrabutyldistannate (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd (China) and used directly without further purification.

#### Representative synthesis of HO–PBAT–OH macro-initiator

HO–PBAT–OH macro-initiators were prepared by a polycondensation reaction using tetrabutyl titanate as a catalyst (Fig. S1,† step 1). Dimethyl terephthalate (19.4 g, 0.10 mol), adipic acid (14.6 g, 0.10 mol), 1,4-butanediol (19.8 g, 0.22 mol), overdosed to ensure that the resulting polymers are terminated by –OH on both ends) and 0.1 wt% catalyst were charged into a 500 mL three-necked flask equipped with a stir bar, a nitrogen inlet and a condensation column. First, the monomer mixture was melted for 0.5 h at 160 °C. The temperature was then increased to 180 °C and maintained for 2 h in an N2 gas atmosphere. Furthermore, the pressure of the reaction system was gradually decreased, and the polycondensation reaction was continued under a final reduced pressure lower than 200 Pa for 6 h. Moreover, the temperature was increased from 180 °C to 225 °C during this period. Finally, the flask was cooled to room temperature, and the atmospheric pressure was restored under the protection of a nitrogen flow. After the reaction was completed, the mixture was dissolved in chloroform and precipitated in tenfold ice-cold ethanol. The product was subsequently separated by centrifuging and dried under a vacuum to obtain HO–PBAT–OH macro-initiators in the form of

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_{PBA}^a$</th>
<th>$N_{PBT}^a$</th>
<th>$N_{PLA}^a$</th>
<th>$M_n^b$</th>
<th>$T_g^c$ (°C)</th>
<th>$T_m^c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiator-1</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td>4300</td>
<td>-40.6</td>
<td>127.5</td>
</tr>
<tr>
<td>Initiator-2</td>
<td>25</td>
<td>18</td>
<td>0</td>
<td>9000</td>
<td>-41.3</td>
<td>107.7</td>
</tr>
<tr>
<td>CP1</td>
<td>10</td>
<td>10</td>
<td>21</td>
<td>7300</td>
<td>3.8</td>
<td>118.8</td>
</tr>
<tr>
<td>CP2</td>
<td>25</td>
<td>18</td>
<td>38</td>
<td>-18.8</td>
<td>135.6</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Average number of the PBA, PBT and PLA units ($N_{PBA}$, $N_{PBT}$ and $N_{PLA}$) in the initiators and tri-block copolymers, estimated by $^1$H NMR. $^b$ $M_n$ evaluated from $^1$H NMR spectra. $^c$ Glass-transition ($T_g$) and melting temperatures ($T_m$) are calculated from reversing heat-flow traces of DSC in the second heating run.
a white powder. Two types of HO–PBAT–OH with different components and molecular weights were prepared and used as macro-initiators (initiator-1 and 2 in Table 1). Initiator-1: \(^1\)H NMR (CDCl\(_3\) with 0.05% v/v TMS, 300 MHz): \(\delta 1.26\) (s, 2H), 1.72–1.61 (m, 64H), 1.93–1.78 (m, 40H), 2.04–1.94 (s, 20H), 2.35 (s, 40H), 3.75 (d of t, \(4\text{H}_{\text{J}_{\text{H},\text{H}}}=12\) Hz, \(4\text{H}_{\text{J}_{\text{H},\text{H}}}=12\) Hz), 4.21–4.06 (m, 40H), 4.48–4.35 (m, 40H), 8.16–8.08 (s, 40H). Initiator-2: 1H NMR (CDCl\(_3\) with 0.05% v/v TMS, 300 MHz): \(\delta 1.73–1.62\) (m, 154H), 1.92–1.78 (m, 86H), 2.08–1.92 (s, 36H), 2.34 (s, 100H), 3.76 (d of t, \(4\text{H}_{\text{J}_{\text{H},\text{H}}}=12\) Hz, \(4\text{H}_{\text{J}_{\text{H},\text{H}}}=12\) Hz), 4.22–4.40 (m, 72H), 4.50–4.35 (m, 72H), 8.16–8.07 (s, 72H).

**Representative synthesis of PLA–PBAT–PLA tri-block copolymers**

The PLA–PBAT–PLA tri-block copolymers were synthesized by ROP of \(\lambda\)-LA using HO–PBAT–OH as a macro-initiator and Sn(Oct)\(_2\) as the catalyst (Fig. S1† step 2). The typical procedure is described in the following manner. HO–PBAT–OH (initiator-2, 10.3 g, 1.14 \(\times\) 10\(^{-3}\) mol) and \(\lambda\)-LA (12.9 g, 0.0896 mol) were charged into a 250 mL round-bottom flask. After adding a stir bar and sealing with a rubber septum, the reaction system was deoxygenated by evacuation and backfilled three times with \(N_2\). The reaction mixture was then sealed followed by the immersion of the flask into an oil bath preheated at 130 °C. When the monomer and initiator melted, Sn(Oct)\(_2\) (4 mg, 9.88 \(\times\) 10\(^{-6}\) mol) was introduced into the flask to begin the polymerization under \(N_2\) gas protection. After reacting for 24 h, the mixture was cooled to room temperature and exposed to air, after which it was dissolved in chloroform and precipitated in tenfold ice-cold ethanol. The product was separated by centrifuging, and dried under a vacuum for 24 h at 40 °C to obtain PLA–PBAT–PLA tri-block copolymers (CP1 & CP2 in Table 1).

**Blends preparation**

Before melt-blending, PLA and PBAT were dried in a vacuum oven for 24 h at 60 °C and 40 °C, respectively, to prevent the polymer materials from hydrolyzing during the melt blending process. The blending process was performed by a Torque Rheometer (XSS-300) with a rotor speed of 32 rpm for 5 min at 180 °C. PLA/PBAT blends at a fixed ratio (80/20, w/w) were prepared by melt blending in the presence of various amounts (i.e. from 0 to 2 wt%) of tri-blockcopolymer CP1 or/and CP2. Sample codes (MBx–y) and compositions of blends are provided in Table S1,† wherein x and y are the approximate percentages of CP1 and CP2 in the blends, respectively. The obtained blends were compressed into flat sheets of about 1.0 mm in thickness by a compression molding machine under 10 MPa pressure for 5 min at 180 °C. The samples were then cooled to room temperature in another compression-molding machine for further characterizations.

**Characterizations**

\(^1\)H NMR spectra were obtained on a Bruker AV 300 M in CDCl\(_3\) (\(\delta 7.27\)) at 25 °C. Chemical shifts are given in parts per million from tetramethylsilane. Gel permeation chromatography (GPC, Waters 410) was used with chloroform as the eluent (flow rate: 1 mL min\(^{-1}\), at 25 °C). Conventional calibrations were performed using polystyrene standards. Elongation at the break point, tensile strength, and Young’s modulus of the samples were measured on a universal testing machine (Instron 1211) at 25 ± 2 °C. The crosshead speed was 10.0 mm min\(^{-1}\), and the Young’s modulus was measured between 0.05% and 0.25% strain. The hot-molded specimens were shaped with a dumbbell-shaped cutter, and their effective length, width, and thickness were 20, 4, and 1 mm, respectively. An averaged value of five replicated measurements was carried out for each sample. Differential scanning calorimetry (DSC) analysis was conducted on a TA Instrument DSC-Q100 under an \(N_2\) atmosphere. Samples were heated to 200 °C at 10 °C min\(^{-1}\) and kept isothermal for 3 min to erase the thermal history. The samples were then cooled to −60 °C at 10 °C min\(^{-1}\), and finally reheated to 200 °C at the same rate. 4–5 mg of each specimen was sealed in a 40 μL aluminum crucible. The rheological properties of molten-state blends were assessed using a parallel-plate (\(d = 25\) mm) rheometer (Anton-Paar, Physica MCR301). The specimens were loaded between the parallel plates and melted for 3 min at 190 °C. The parallel plates subsequently compressed the molten specimens to 1.0 mm in thickness prior to each test. The viscoelastic properties of the blends were determined by a dynamic frequency sweep test. The strain (5%) and frequency range (500–0.05 rad s\(^{-1}\)) were used during the testing. Complex viscosity (\(\eta^*\)), storage modulus (\(G'\)) and loss modulus (\(G''\)) in the molten state were obtained. The microstructure morphology of blends was observed by scanning electron microscopy (ESEM, XL30). All samples were immersed into liquid nitrogen for 10 min and then picked out and fractured immediately. The cryo-fracture surface was sputter coated with gold prior to examination. The acceleration voltage at the cathode was 5.0 kV.

**Results and discussion**

**Synthesis of PLA–PBAT–PLA tri-block copolymer compatibilizers**

The tri-block copolymer compatibilizers (CP1 and CP2) were synthesized by a two-step process (as illustrated in Fig. S1†). In the first step, two types of HO–PBAT–OH macro-initiators with two molecular weights were prepared by a polycondensation reaction. During this step, excess 1,4-butenediol was added to ensure that both ends of the macro-initiators were terminated by –OH groups; second, the ROP of \(\lambda\)-LA was initiated by these dihydroxy macro-initiators. The molecular structure and thermal properties of the macro-initiators and their offspring tri-block copolymers are listed in Table 1. The molecular components and the absolute molecular weights were determined by \(^1\)H NMR spectral analysis. For example, the doublet of triplets (Fig. S2A†) at around 3.75 ppm was assigned to the methylene protons adjacent to –OH at the end of initiator-1. After the ROP of \(\lambda\)-LA (Fig. S2B†), the aforementioned doublet of triplets disappeared. In addition, a multiplet appeared at about 5.18 ppm, which was assigned to the methane protons in the repeat units of PLA. Moreover, the doublet of triplets was used as an internal standard to determine the molecular structure of macro-initiators and tri-block copolymers. The
singlet at 8.11 ppm was assigned to the aromatic protons of polybutylene terephthalate (PBT) repeat units, and the singlet at 2.32 ppm was assigned to the methylene protons of -CH₂-COO- group in polybutylene adipate (PBA) repeat units. Thus, the average number of the PBA, PBT and PLA units (N\textsubscript{PBA}, N\textsubscript{PBT} and N\textsubscript{PLA}) in the macro-initiators and tri-block copolymer could be achieved. In addition, the absolute molecular weight could be calculated inherently by the \textsuperscript{1}H NMR results. The relative molecular weights and PDI were evaluated by GPC (Table S2†).

The higher percentage of PBT units in initiator-1 showed that T\textsubscript{g} and T\textsubscript{m} were higher than initiator-2 (Table 1). CP\textsubscript{2} showed T\textsubscript{m} (135.6 °C) obviously higher than that of CP\textsubscript{1} (118.8 °C) due to its longer block chains of PLA units. In addition, T\textsubscript{m} value of CP\textsubscript{2} was between T\textsubscript{m} value of PBAT (119.9 °C) and PLA (153.4 °C).

**Mechanical properties of blends**

To study the influence of copolymer compatibilizers on the properties of melting blends, the melt-blended specimens with various amounts of CP\textsubscript{1} or/and CP\textsubscript{2} (listed in Table S1†) were prepared, and the PLA/PBAT ratio was fixed to 80/20 (w/w). The typical tensile stress-extension curves of the melt-blended specimens with different compositions (Fig. 1A and S3†) showed that the tensile property of the PLLA/PBAT melt-blending system could be altered by adding a small amount of tri-block copolymer compatibilizers (less than 2.0 wt%). As shown in Fig. S3A and B† the addition of 0.5% or 1.0% CP\textsubscript{1} or CP\textsubscript{2} led to moderate improvements in elongation at the break point. However, when the amounts of the block copolymer compatibilizers were more than 2%, no visible improvements were found. This phenomenon is similar with the theoretical and experimental results reported for other melt-blending systems in the presence of block copolymers.\textsuperscript{21,27} It can be noted that adding 0.5% or 1.0% of CP\textsubscript{1} and CP\textsubscript{2} simultaneously led to significant improvement of elongation at break values (Fig. 1A). The bar chart of Fig. 1B visually demonstrated that MB0.5–0.5 showed elongation at the break point (≈226%) more than eight times of MB0–0 (≈27%). This improvement in elongation was also distinctive compared with MB0.5–0 (≈38%), MB0–0.5 (≈66%), MB1.0–0 (≈34%) and MB0–1.0 (≈77%). Moreover, MB1.0–1.0 showed elongation at the break value (204%) higher than that of MB1.0–0 (≈34%), MB0–1.0 (≈77%), MB2.0–0 (≈13%) and MB0–2.0 (≈29%). The noticeable improvements drop a hint that these two types of copolymers with different molecular weights might have synergistic effects on influencing the toughening properties of PLA/PBAT blends. Fig. S4A and B† showed that the tensile modulus and strength of different melt-blending samples changed for blends with different amounts of compatibilizers. However, the change values were statistically negligible, which indicated that the addition of tri-block compatibilizers at this level (less than 2 wt%) could increase the elongation at the break point, whereas retaining the tensile modulus and strength of the blends.

**Thermal analysis of blends**

Typical DSC thermograms of PLA/PBAT specimens with various amounts of copolymer compatibilizers are shown in Fig. 2. It is well known that T\textsubscript{g} is an important indicator for the miscibility of blend components.\textsuperscript{14} If two components are partially miscible, their T\textsubscript{g} would shift towards each other.\textsuperscript{34,35} The T\textsubscript{g} of PLA and PBAT in the blends shifted towards each other after the addition of compatibilizers, suggesting miscibility improvement between PLA and PBAT components. Sample MB0.5–0.5 with the highest value of elongation at the break point, showed the smallest ΔT\textsubscript{g} (gap between T\textsubscript{g} of PLA and PBAT in the blends) among the blends listed in Table S3,† which indicated improved miscibility.

On the other hand, the melt-blending samples of MB\textsubscript{x–y} shown in Fig. 2 displayed cold crystallization exotherms with onset temperatures (T\textsubscript{onset}) near 106 °C and cold crystallization temperatures (T\textsubscript{c}) near 115 °C. As seen from Table S3,† MB0.5–0, MB0–0.5 and MB0.5–0.5 showed that T\textsubscript{onset}, T\textsubscript{g} and T\textsubscript{m} were

![Fig. 1](image1.png)

**Fig. 1** (A) Typical stress–strain curves of MB0–0, MB0.5–0.5, MB1.0–1.0 and MB2.0–2.0. (B) Average values of elongation at the break points of various melt-blended specimens, and each sample was tested with a sample size (n) = 5.0.

![Fig. 2](image2.png)

**Fig. 2** DSC curves of PLA/PBAT (80/20) blends with various amounts of copolymer compatibilizers. Heating rate 10 °C min\textsuperscript{−1} and data from the second heat.
lower than that of MB0–0. Moreover, the enthalpies of crystallization ($\Delta H_\text{c}$) and fusion ($\Delta H_\text{f}$) of these three samples were higher than that of MB0–0. In contrast, MB1.0–0 and MB0–1.0 showed $T_{\text{onset}}, T_\text{c}, T_\text{m}$ and $\Delta H_\text{m}$ higher than that of MB0–0. Sample M1.0–0 showed $\Delta H_\text{c}$ lower than that of MB0–0, and sample MB0–1.0 showed $\Delta H_\text{f}$ higher than that of MB0–0. All these results showed that adding 0.5 wt% CP1 or/and CP2 compatibilizers into the PLA/PBAT (80/20, w/w) blends could lower the crystallization temperatures and increase the degree of crystallinity in the blends. This suggested that small amounts of copolymer compatibilizers could act as nucleating agents for PLA in the blends. According to our experiments, when the amounts of compatibilizers increased to more than ~1 wt%, this regularity became ambiguous. In addition, sample MB0.5–0.5 showed most obvious improvement in crystallinity, which also implied the synergistic effect of the two compatibilizers.

It can be noted that the DSC thermogram of MB0–0 showed a melting peak at 153.3 °C with a shoulder near 158 °C. The addition of 0.5 wt% CP1 or/and CP2 compatibilizers clearly separated the melting peak and shoulder of MB0–0 into two individual peaks, as shown in curves of MB0.5–0, MB0–0.5 and MB0.5–0.5. The peaks at higher temperatures corresponded to the shoulder of MB0–0. It has been reported that these bimodal melting peaks were induced during the DSC scans, in which the less perfect crystals had sufficient time to melt and re-organized into crystals with higher structural perfection, and then remelted at a higher temperature.17,36 As for MB0–0 and MB0–1.0, the melting shoulder that appeared on MB0–0 disappeared. This phenomenon also proved that small amounts of compatibilizers could increase the PLA crystallization rate in the blends. In addition, this improvement might be attributed to the increase of PLA-chain-segment mobility caused by adding low molecular weight compatibilizers.

**Morphology analysis of blends**

Typical SEM images of the cryo-fracture surfaces of MBx–y specimens are shown in Fig. 3. All these blending samples had many demarcated phase-separated PBAT particles dispersing on their fracture surfaces. Fig. 3A and B showed that sample MB0–0 without a copolymer compatibilizer had an obvious interface between PBAT particles and the PLA matrix. In addition, only a few of the fibril structures could be observed in Fig. 3A. For sample MB0.5–0 with 0.5 wt% of CP1, a lot of short fibril structures appeared on the fractured surface (Fig. 3C). The enlarged image of Fig. 3D showed that these fibril structures mainly dispersed at the interface between PBAT particles and the PLA matrix, which indicated that the CP1 molecules were mainly located at the interface. However, an obvious interface still could be seen in Fig. 3D, which should be attributed to the low interfacial bonding strength between the two phases. When 0.5 wt% CP2 was added into the blends (Fig. 3E), more fibril structures could be observed compared with that in Fig. 3A, and the fibril structures were obviously longer than those in Fig. 3C. It can be noted that these fibril structures appeared at the interface and also could be found rooting in the PLA matrix. This implied that it was more difficult for CP2 to move from the matrix to the interface than CP1. Moreover, the interfacial debonding phenomenon showed in Fig. 3F was more obvious than that in Fig. 3B and D, which suggested even lower interfacial bonding strength in MB0–0.5. From Fig. 3C–F, no obvious compatibilization effect could be observed at the interface by the addition of CP1 or CP2.

In contrast, sample MB0.5–0.5 using 0.5 and 0.5 wt% CP1 and CP2 as two-component compatibilizers showed notable differences in microscopic morphologies from other specimens. As shown in Fig. 3G, more PBAT particles were adhered on the surface compared with other samples, which implied stronger bonding strength at the interface. There are three PBAT particles marked in the enlarged image of Fig. 3H. Particle no. 1 was mostly buried in the PLA matrix, showing no obvious interface between the two phases. A small cap-like structure could be observed on the surface of particle no. 2, which was assumed to be a small piece of PLA torn from the matrix. A few octopus-tentacle-like structures could be observed attached on the particle being dragged off from the PLA matrix (particle no. 3). These three cases proved that the addition of 0.5 and 0.5 wt% CP1 and CP2 significantly improved the miscibility and obviously increased the interfacial bonding strength at the interface. Furthermore, the addition of 1.0 wt% CP1 or CP2 (sample MB1.0–0 and MB0–1.0) could slightly improve the miscibility of the blends (seen from Fig. S5A–D†), which showed distinctive
Rheological properties

\( \eta^* \), \( G' \) and \( G'' \) with different amounts of \( CP1 \) or/and \( CP2 \) are compared in Fig. 4. In Fig. 4A, \( M0.5 \)–0 showed that \( \eta^* \) was lower than \( M0.5 \)–0, and \( MB1.0 \)–0 showed that \( \eta^* \) was lower than \( MB0.5 \)–1.0. This indicated that the addition of \( CP1 \) resulted in lower viscosity than its high-molecular-weight counterpart of \( CP2 \). Among all these melt blending specimens, \( MB0.5 \)–0.5 showed the lowest \( \eta^* \), \( G' \) and \( G'' \) at low frequencies, and only a slightly higher than that of \( MB0.5 \)–0 at the high frequencies. The rotor speed (32 rpm) for melt blending was about 3.35 rad s\(^{-1}\) in angular frequency, which was just within the low frequency area. This means that during the blending process, \( MB0.5 \)–0.5 showed melt viscosity similar to \( MB0.5 \)–0 and lower than all of the other blends. Moreover, \( MB1.0 \)–1.0 showed that \( \eta^* \), \( G' \) and \( G'' \) was lower than \( MB1.0 \)–0 and \( MB0 \)–1.0. Thus, these rheological curves proved that \( CP1 \) and \( CP2 \) had synergistic effects on decreasing the blend viscosity. In melting state, the Cole–Coles plot is an important characterization of the viscoelastic properties of polymer materials.\(^{37-39} \) The straight line \( (G' = G'') \) divides the coordinate into two parts. Below the straight line \( (G' < G'') \), the polymer materials present major viscosity properties; conversely, it exhibits elasticity. As shown in Fig. 4D, Cole–Coles plots of the PLLA/PBAT (80/20, w/w) blends were almost located below the straight line of \( G' = G'' \), which proved that these blends with different amounts of compatibilizers were more viscous than elastic components at the melting state.

Conclusions

Two types of PLA–PBAT–PLA triblock copolymers with different molecular weights were synthesized by ROP of \( \varepsilon \)-lactide (\( \varepsilon \)-LA) using HO–PBAT–OH as macro-initiators. Different amounts of the triblock copolymers were added into the melt-blending system of PLLA/PBAT as compatibilizers. Interestingly, these two types of copolymers demonstrated synergistic effects on the mechanical and rheological properties of the blends. The addition of 0.5 and 0.5 wt% of \( CP1 \) and \( CP2 \) led to an increase of elongation at the break value by more than eightfold. It was thought that the compatibilizer with a low molecular weight and high mobility had reduced the viscosity of the blends and acted as carriers for their coworkers with a high molecular weight. In contrast, the compatibilizer with a high molecular weight could increase the interaction between the PLA matrix and PBAT particles. It was expected that this study could provide a new strategy for improving the mechanical and rheological properties of melt-blending materials, which might be able to decrease the usage amount of copolymer compatibilizers as well as the total costs of the blends.

Acknowledgements

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Notes and references