Original article

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Effect of blending procedures and reactive compatibilizers on the properties of biodegradable poly(butylene adipate-co-terephthalate)/poly(lactic acid) blends

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Abstract: The effect of Joncryl ADR[®]-4368 (abbreviated ADR) and dicumyl peroxide (DCP) on poly(butylene adipate-co-terephthalate) (PBAT)/poly(lactic acid) (PLA) blend was investigated. Two different blending procedures were adopted: (1) one-step blending of all components for 8 min; (2) premixing of PBAT and ADR (or DCP) for 4 min followed by addition of PLA blending for 4 min. ADR and DCP were effective compatibilizers for the PBAT/PLA blend by one-step blending which were confirmed by improving the phase interface between PBAT and PLA, decreasing the dispersed phase size, increasing the elasticity, viscosity and tensile strength. Moreover, the addition of ADR into PBAT/PLA blend by two-step blending was more efficient than the one-step blending based on refined morphology and further increased tensile properties. The two-step blending was beneficial to produce a larger amount of PBAT-graft-PLA (PBAT-g-PLA) copolymers at the phase interface. However, DCP was added to the PBAT/PLA blend by the two-step blending which showed lower properties than one-step blending. DCP triggered free branching reactions in a fast way. Based on the character of compatibilizers, choosing properly blending procedures can enlarge the tensile properties. These results would be

interesting for industrial polymer materials, and may be importance to the wider practical application of PBAT/PLA blends.

Keywords: biodegradable polymers; compatibilization; mechanical properties.

1 Introduction

Polymers have been developed and used in many fields in the past century and have become an integral part of human life [1]. However, these polymers are most derived from nonrenewable fossil resources and can't be degraded in nature. With the development of society, biocompostable and bio-based polymers have received considerable attention in the past two decades due to the environmental concerns and sustainability issues associated with petroleum-based polymers [2].

Recently, significant attention has been paid to the poly(butylene adipate-co-terephthalate) (PBAT). PBAT is one of synthetic biodegradable resins based on aliphatic-aromatic copolyesters. Its flexibility was derived from aliphatic hydrocarbons and rigidity was supported by aromatic. It has been commercialized [3] and is designed for film production [4] with a high elongation at break. However, the low yield strength and modulus restricted the large-scale industrial applications. Compared with the copolymerization method, the blending modification of PBAT is more economical and effective for industrial production.

Poly(lactic acid) (PLA) is an aliphatic thermoplastic polyester with rigidity and clarity similar to polystyrene (PS) and poly(ethylene terephthalate) (PET) [1]. PLA is compostable and renewable. It has relatively high tensile strength but is brittle. In order to improve mechanical properties and processability of PLA and retain its advantage of biodegradability, blending PLA with flexible biodegradable

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polymers was used, such as polycaprolactone (PCL) [5, 6], poly(butylene succinate) (PBS) [7–9], poly(butylene adipate-co-terephthalate) (PBAT) [10–14], poly(ethylene oxide-*b*-amide-12) [15], poly(propylene carbonate) (PPC) [16], poly(butylene-succinate-co-adipate) (PBSA) [17], poly(hydroxyalkanoate)s (PHAs) [18]. In term of the unique character of PLA which is widely used for blending with PBAT to extend the range of applications and improve their properties.

However, the poor compatibility of PBAT and PLA usually lead to inferior mechanical properties [19]. Li et al. [20] studied the rheological behavior and morphology of PLA/PBAT blends with a wide range of compositions. In spite of their incompatibility, the authors proved the interaction existing between the two polymers at certain blend ratio based on the rheological result. However, the mechanical properties of the blends remained low.

Compatibilization is essential in optimizing mechanical properties of polymer blends because the mechanical properties of a multiphase blend are usually driven by the ability of interface to transmit stress from one phase to the other [21]. According to the previous documents, the incorporation of a compatibilizer agent to the blend or producing the agent by an *in situ* reaction was effective to improve the compatibilization between PBAT and PLA. Dong et al. [22] studied the properties of PLA/PBAT blends in the presence of 4,4'-methylenediphenyl diisocyanate (MDI) which acted as a reactive chain extender. SEM micrographs showed not only a reduction in the PBAT phase size but also a significant increase in interfacial adhesion between the PLA and PBAT phases with increasing of MDI. However, the interest in using such molecules was limited due to its toxicity and its high volatility of MDI. Coltell et al. [23] reported on the addition of (2,5-dimethyl-2,5-di(ter-butylperoxy)hexane) (Trigonox 101) to the PLA/PBAT blend. The mechanical properties were improved and the corresponding dispersed phase diameter decreased as a consequence of PLA-*g*-PBAT copolymers formation through a radical coupling mechanism. Lu et al. [24] also prepared various PBAT materials with different melt viscosity by the addition of dicumyl peroxide (DCP), and then PLA/PBAT blends with different viscosity ratio were prepared. The experimental results showed that the morphology and properties of PLA/PBAT blends also strongly depended on the viscosity ratio.

Many multifunctional chain extenders containing epoxy groups have been used to improve the properties of PLA/PBAT blends. Wang et al. [9] prepared PLA/PBAT blends in the presence of compatibilizer with multifunctional epoxy groups. Adding the compatibilizer improved the tensile and impact toughness for all ratios of PLA/PBAT

blends. Al-Itry et al. [18] studied the incorporation of multi-functional oligomer into PLA/PBAT blends. Their thermal stability was enhanced. The mechanisms of degradation and chain extending with GMA functions were shown [3]. Moreover, they also investigated the blowing properties with the addition of reactive multifunctional epoxide into PLA/PBAT blends. A reduction of the instability defects had been detected and the thermo-mechanical properties of blown film were shown to be improved [25].

This paper presented the effects of incorporating ADR and DCP according to different blending procedures on the properties of binary PBAT/PLA blends. Despite the interesting nature of the research discussed above, there was no report which attempted to comprehend both the morphological evolution and other properties with the incorporation of ADR and DCP in PBAT/PLA blends with different blending strategies. Through this work, we presented a promising route to overcome the lower tensile strength and enhance the compatibilization. Two blending procedures were used: the first one consisted of introducing all components simultaneously in the internal mixer and the second one consisted of modifying PBAT by melt blending PBAT with ADR or DCP and then subsequent adding the PLA. This study focused to use ADR and DCP to compatibilize PBAT/PLA blends. ADR was selected because it contained reactive epoxide functions which can react with both hydroxyl and carboxyl reactive functional end chains of PLA and PBAT. DCP could provide a simple way to develop in the interfacial region of PLA-*g*-PBAT necessary for modifying the state of interface by the inter-macromolecular radical coupling mechanism. A comparison study of two different mixing methods on the phase morphology, mechanical properties, thermal properties, and rheological properties of the PBAT/PLA blends with and without ADR or DCP were studied in detail. The improved compatibility between PBAT and PLA can obtain not only by the addition of compatibilizers, but also the process methods. The morphology was developed to understand the induced mechanical properties. This study provided significant guidance for the preparation of high-performance polymer blends.

2 Materials and methods

2.1 Materials

The poly(lactic acid) (PLA grade 2003D) used in this study was in the form of pellets and purchased from NatureWorks (USA), $M_w = 230000 \text{ g}\cdot\text{mol}^{-1}$. The poly(butylene adipate-co-terephthalate)

(PBAT) was produced by Xinjiang Blue Ridge Tunhe Polyester Co, Ltd. (China), $M_w = 139000 \text{ g}\cdot\text{mol}^{-1}$. A commercially modified acrylic copolymer with epoxy functions (Joncryl ADR®-4368, abbreviated ADR) was obtained from BASF (Germany). Its average functionality on epoxide is 9 with an epoxy equivalent weight of $285 \text{ g}\cdot\text{mol}^{-1}$ and a molecular weight of $6800 \text{ g}\cdot\text{mol}^{-1}$. Commercial dicumyl peroxide (bis(1-methyl-1-phenylethyl) (DCP) was used without further purification.

2.2 Sample preparation

Before compounding, the PBAT and PLA were dried at 70°C for 24 h. Then the blends were prepared with a Haake Rheomix 40 (Germany) at a rotating speed 50rpm at 170°C . Two different mixing series were used: (I) one step mixing of all components PLA, PBAT and ADR or DCP; (II) melt blending of PBAT and ADR or DCP for 4 min followed by mixing of PLA for another 4 min. The content of ADR and DCP in the blends was set as 0.3 phr, respectively. After blending, all of the components were cut into small pieces. Then, all of samples were compression-molded into sheets with thickness of 1.0 mm at 170°C , a hold pressure of 10 MPa and a hold time of 3 min, followed by quenching to room temperature between two thick-metal blocks. The specimens were then sealed in plastic bags awaiting the analysis. The compositions of the studied blends were given in Table 1.

2.3 Experimental methods

2.3.1 Fourier transform infrared spectroscopy (FTIR): FTIR spectra of pure PBAT, pure PLA, PBAT/PLA blend and modified PBAT/PLA blends were obtained using a Nicolet NEXUS670 FTIR spectrometer (ThermoNicolet, USA) for per sample.

2.3.2 Scanning electron microscopy (SEM): SEM was used to describe the morphology of the PBAT/PLA blend. The morphological properties were examined using a field emission SEM (Zeiss UltraPlus, Germany) at an accelerating voltage of 5 kV. Samples were cryogenically fractured in liquid nitrogen and coated with gold for the duration of the analysis.

2.3.3 Rheological properties: Dynamic rheological measurements of the samples were carried out on a rheometer (Haake Mars III, Germany). Frequency sweep for all samples was adopted using 25 mm plate-plate geometry. The sheet samples were about 1.0 mm in thickness and the strain value was fixed at 1.25% in the linear viscoelastic range. The oscillatory frequency sweep was carried out at angular frequency range of 0.1–100 rad/s. All measurements were performed at 170°C .

Table 1: The composition and the designation of the studied blends.

Methods	Blend designation	PBAT	PLA	ADR	DCP
Route 1	PBAT/PLA	80	20	0	0
	PBAT/PLA/ADR	80	20	0.3	–
	PBAT/PLA/DCP	80	20	–	0.3
Route 2	(PBAT/ADR)/PLA	80	20	0.3	–
	(PBAT/DCP)/PLA	80	20	–	0.3

2.3.4 Tensile tests: Mechanical properties were determined using an Instron machine 5566 (USA) under ambient temperature (25°C) with a cross-head speed of 50 mm/min after storing for over 24 h under the test conditions. The dimensions of the dumbbell specimen were 20 mm in length, 4 mm in width and a thickness of 1 mm. At least five tests were undertaken for each specimen to calculate average values.

2.3.5 Differential scanning calorimetry (DSC): Thermal behavior of the blends was studied by DSC (NETZSCH Instruments DSC 214 Polyma Germany) under N_2 atmosphere. The sample weights varied between 5 and 8 mg. All the samples were heated from room temperature to 180°C at a heating rate of $10^\circ\text{C}/\text{min}$, holding for 3 min to erase previous thermal history. Then they were cooled to -50°C at a cooling rate of $10^\circ\text{C}/\text{min}$ (first cooling) and subsequently, the second heating scan was performed between -50 and 180°C at a heating rate of $10^\circ\text{C}/\text{min}$ to present the subsequent melting behavior (second heating). The basic data of glass transition temperature (T_g), the melting temperature (T_m), the cold crystallization temperature (T_{cc}) and the melt enthalpy (ΔH_m), crystallization enthalpy (ΔH_{cc}) of the samples were obtained from the second heating run. The melt crystallization temperature (T_c) and corresponding crystallization enthalpy (ΔH_c) of the samples were obtained from the cooling run.

3 Results and discussion

3.1 FTIR analysis

In order to investigate the effect of ADR and DCP on the interaction between PBAT and PLA, structure of PBAT/PLA blend and modified PBAT/PLA blends was characterized by FTIR spectra. Pure PBAT and pure PLA were also included in the FTIR investigations. Figure 1 shows the FTIR spectra of the PBAT, PLA, PBAT/PLA blend and modified PLA/PBAT blends. PBAT and PLA showed sharp

Figure 1: FTIR spectra of pure PBAT, pure PLA, ADR, PBAT/PLA blend and the modified PBAT/PLA blend.

absorption peak at 1714 and 1752 cm^{-1} corresponding to the C=O stretching vibration in PBAT and PLA. The peak at 849, 908 and 1252 cm^{-1} assigned to the C-O stretching peak of the ADR epoxy group [26]. For the PBAT/PLA spectra, it was only showed a strong peak at 1714 cm^{-1} corresponding to C=O stretching vibrations of the ester groups suggesting the interactions between PBAT and PLA. In addition, there were no similar epoxy group characteristic peaks in the PBAT/PLA/ADR and (PBAT/ADR)/PLA spectra which indicated the terminal carboxyl and hydroxyl groups of PLA and PBAT could react with the epoxy groups [4]. FTIR spectra confirmed that the epoxy group of ADR can react with the hydroxyl or carboxyl group of PLA and PBAT in reactive blending. As far as PBAT/PLA/DCP and (PBAT/DCP)/PLA spectra, the similar spectra were observed compared with the PBAT/PLA spectra. DCP generated free radicals by the thermal decomposition, which initiated the formation of branching structure via hydrogen abstraction. It didn't change the FTIR spectra significantly.

3.2 Mechanical properties

Figure 2 exhibits the typical stress-strain curves of PBAT/PLA, PBAT/PLA/ADR, (PBAT/ADR)/PLA, PBAT/PLA/DCP and (PBAT/DCP)/PLA blends. The mechanical properties were summarized in Table 2. PLA was a hard and brittle polyester material at room temperature with tensile strength close to 59.0 MPa and elongation at break of only 2.4%, while, PBAT was ductile and elongation at break was 948.8% and tensile strength was 34.2 MPa. The incorporation of PLA into PBAT, the yield strength of PBAT/PLA blend increased slightly from 6.3 MPa for neat PBAT to 7.7 MPa, while, the elongation at break and tensile strength significantly decreased to 578.9% and 21.9 MPa, respectively. The tensile curve of PBAT/PLA blend was just over the corresponding curve of PBAT and broke beforehand. PBAT/PLA blend didn't show excellent complementary properties because PBAT and PLA were immiscible. In

Table 2: Mechanical properties of neat PBAT, neat PLA, PBAT/PLA blend and modified PBAT/PLA blends.

Samples	σ_y (MPa)	σ (MPa)	ϵ_b (%)
PBAT	6.3 ± 0.1	34.2 ± 2.1	948.8 ± 25.0
PLA	—	59.0 ± 1.5	2.4 ± 0.2
PBAT/PLA	7.7 ± 0.1	21.9 ± 1.6	578.9 ± 32.4
PBAT/PLA/ADR	8.9 ± 0.3	31.3 ± 1.5	572.7 ± 39.4
(PBAT/ADR)/PLA	12.1 ± 0.2	37.6 ± 1.0	546.1 ± 5.9
PBAT/PLA/DCP	9.4 ± 0.3	32.5 ± 0.5	567.9 ± 7.6
(PBAT/DCP)/PLA	10.3 ± 0.2	27.4 ± 0.3	496.7 ± 47.5

order to improve the compatibilization between PBAT and PLA, ADR or DCP as the reactive compatibilizer were added into PBAT/PLA blend. The tensile strength and yield strength of PBAT/PLA/ADR blend increased from to 21.9 and 7.7 MPa of PBAT/PLA blend to 31.3 and 8.9 MPa, increasing by 42.9 and 13.5%, and the elongation at break remained stable. Moreover, the tensile strength and yield strength of (PBAT/ADR)/PLA blend produced by two-step blending were further increased from to 21.9 and 7.7 MPa of PBAT/PLA blend to 37.6 and 12.1 MPa, increasing by 71.7 and 57.1%, but the elongation at break decreased slightly. With the addition of ADR, the tensile strength and yield strength of all PBAT/PLA/ADR and (PBAT/ADR)/PLA blends were improved. The fundamental improvement of tensile properties mainly depended on the increasing compatibilization of PBAT and PLA with the PBAT-g-PLA copolymer generated by the reaction between PLA and PBAT with ADR [3, 4, 10]. The epoxy groups of ADR were reactive with -COOH and -OH groups of the PBAT and PLA chains during melt processing. The PLA and PBAT molecule chain were combined together by one molecular of ADR, forming the effective double comb PBAT-g-PLA copolymers. PBAT-g-PLA copolymer can exist in the phase interface layer and enhance the interfacial adhesion force which was conducive to transfer the interface stress and improve tensile strength when subjected to stress.

What caused the difference in the degree of increase in tensile properties? We considered that the dispersion of

Figure 2: Tensile properties of pure PBAT, pure PLA, the PBAT/PLA blend and modified PBAT/PLA blends.

ADR in the incompatible PBAT/PLA blend was the main cause. ADR was dispersed at the interface to make it easier to form a PBAT-g-PLA copolymer through the reactive blend, which should exhibit good compatibilization effect. The difference in tensile properties may show the amount difference of ADR at the interface. More ADR at the interface, more tensile properties were enhanced. The further explanation in detail was given in the last section.

The tensile strength and yield strength of PBAT/PLA/DCP blend increased to 32.5 and 9.4 MPa, increasing by 48.4 and 22.1%. The improvement in mechanical properties of the blend was attributed to the formation of PBAT-g-PLA copolymers by the free radical branching reaction. The PLA-g-PBAT copolymer chains act as a bridge between PLA and PBAT interfaces to improve the compatibilization of PLA and PBAT. The enhancement of interfacial adhesion and molecular chain entanglement allows the blend to consume more energy when damaged. However, a different result occurred. The tensile strength of (PBAT/DCP)/PLA blend produced by two-step blending was remarkable lower than that of PBAT/PLA/DCP blend, but it was also higher than PBAT/PLA blend. For the PBAT/PLA/DCP blend, DCP play the role of in suit compatibilization by formation of the PBAT-g-PLA copolymers. The enhancement of interfacial adhesion and molecular chain entanglement allowed the blends to consume more energy when damaged. For the (PBAT/DCP)/PLA blend, the produced free radicals mainly initiated the branching reaction of PBAT due to high efficiency of DCP. The branching PBAT molecular chains were the main factors that improved the mechanical properties. However, the improvement effect on the tensile properties of branching PBAT was limited compared with more amounts of PBAT-g-PLA copolymers.

3.3 Phase morphology

SEM micrograph of PBAT/PLA blend is presented in Figure 3a. The PBAT/PLA blend illustrated a classic matrix-dispersed phase morphology with a spherical PLA minor phase were dispersed in the major one. The dispersion phase particles were quite uneven. Most of the droplets in this SEM micrograph remained in the quenched-section being displayed, while others were pulled out during fracture leaving empty cavities. The obtained morphology proved the incompatible polymer pairs between PBAT and PLA as well as the present of strong interfacial tension in the PBAT/PLA blend.

The change in mechanical properties caused by the introduction of ADR or DCP should undoubtedly be highly

consistent with the SEM results. Figure 3b illustrates a notable reduction of the dispersion phase average size from 1.02 μm of PBAT/PLA blend to 0.59 μm . In addition, the interface became fuzzy compared with the SEM photo of unmodified PBAT/PLA blend. Hence, compatibility caused by ADR decreased the size of dispersed phase and improved the interfacial adhesion.

Figure 3c depicts the SEM micrograph of (PBAT/ADR)/PLA blend. A significant decrease of the average size of dispersed particles to 0.37 μm was showed. Moreover, it was highlighted by a better dispersion of the minor phase was observed. Consequently, we can conclude that by the two-step mixing, the studied blend became much more compatible. This might be because the epoxy groups firstly concentrated in the PBAT phase, the chain extension and branching reaction occurred. In the second stage, when adding the PLA, the remained epoxy groups can react with end groups of PLA, which increased the possibility of the PBAT-g-PLA copolymers at the two-phase interface. The PLA-g-PBAT copolymer chains act as a bridge between PLA and PBAT interfaces to improve the compatibility of PBAT and PLA.

As far as PBAT/PLA/DCP blend, as shown in Figure 3d, the average diameter of PLA droplets decreased from 1.02 μm of PBAT/PLA blend to 0.55 μm . Moreover, we also noticed that the nearly disappearance of interfacial gaps indicating the remarkable increase of interfacial adhesion. Also, the particles seemed to be better dispersed in the matrix phase and their diameters decreased remarkably. The in suit compatibility effect of PBAT/PLA/DCP blend was better than PBAT/PLA/ADR blend by the one-step mixing according to SEM observation. The same content of DCP formed more PBAT-g-PLA copolymers than ADR because of the synergistic effect of radical coupling mechanism and the low molecular weight of DCP corresponding to the high molar mass.

With regard to the (PBAT/DCP)/PLA blend, the average diameter of PLA droplets decreased from 1.02 μm of the PBAT/PLA blend to 0.7 μm . It was bigger than that of PBAT/PLA/DCP blend. Furthermore, the interface between PBAT and PLA was clear. In the (PBAT/DCP)/PLA blend, almost no the branched PBAT-g-PLA copolymers were produced due to the high reaction efficiency of DCP. Why did the dispersed phase sizes get smaller? Studies had shown that blend composition was the major factor governing the morphology of incompatible blends. Secondly, viscosity ratio and interfacial surface free energy may strongly influence morphology. For the (PBAT/DCP)/PLA blend, the half-life period of DCP was relative short, and the radical reaction mainly triggered branching reaction of PBAT. The melt blending of PBAT with DCP

Figure 3: SEM images of the cryogenic fractured surfaces and the size distribution of the dispersed phase of the (a) PBAT/PLA blend, (b) PBAT/PLA/ADR blend, (c) (PBAT/ADR)/PLA blend, (d) PBAT/PLA/DCP blend and (e) (PBAT/DCP)/PLA blend.

resulted in substantially increasing matrix melt strength. The high melt strength of the DCP modified PBAT resulted in high shear forces capable of deforming and comminuting the dispersed particles. The morphology of (PBAT/DCP)/PLA blend changed due to the high melt strength of modified PBAT, which decreased the PLA dispersion phase size. This cause was also thought-provoking for (PBAT/ADR)/PLA blend. A fraction of epoxy groups played the role of compatibilizer, which decreased the dispersion phase diameter and a portion of epoxy groups happened the chain extension and branching reaction of

PBAT which increased the melt strength of PBAT. They had the synergistic effect on the decrease in dispersion phase diameter.

3.4 Rheological properties

To verify effect of formed PBAT-g-PLA copolymer in PBAT/PLA blends, the rheological behavior was studied. The angular frequency-dependent storage modulus and complex viscosity for the PBAT/PLA blend and the

modified PBAT/PLA blends are showed in Figure 4. After the addition of ADR, the storage modulus and complex viscosity of PBAT/PLA blends produced by one-step blending and two-step blending were higher than the PBAT/PLA blend. This can be explained by the branching reaction. However, the increase showed different levels. For the PBAT/PLA/ADR blend, the complex viscosity was lower than that of PLA, it was suggested that ADR preferentially to locate in the PBAT phase in the PBAT/PLA/ADR blend due to PBAT having the lowest viscosity and highest content up to 80 wt%. The possible reaction between ADR and PBAT was higher than that between ADR and PLA. In other words, branched PBAT-ADR-PBAT copolymers were relatively large, while, the branched PBAT-g-PLA and PLA-ADR-PLA was insufficient. Nevertheless, the molecular weight of PBAT was much lower than that of PLA. That was to say, the branch length and entanglement were low. The storage modulus and complex viscosity of (PBAT/ADR)/PLA blend produced by two-step blending were significantly increased. This implied PBAT-g-PLA copolymers with a longer polymer chain formation, which affected the chain elasticity and mobility during measurement [27].

The elastic modulus and complex viscosity of PBAT/PLA/DCP blend and (PBAT/DCP)/PLA blend were higher than that of PBAT/PLA blend. The addition of DCP into PBAT/PLA blend by the one-step blending and two-step blending had similar rheological behavior. DCP can trigger the free branching reaction and the branching efficiency was high. In the one-step blending, DCP can induce chain branching reaction of PBAT, PLA or forming PBAT-g-PLA copolymers, while, for the two-step blending, the DCP mainly caused free branching of PBAT, which all resulted in the increase of the elasticity and viscosity of the PBAT/PLA blends. According to DSC curves (Figure 5), after addition of ADR or DCP, the crystallinity of PBAT matrix did not change much and the crystallinity of PLA was week. The crystallinity character of modified PBAT/PLA blends may account for the thermal properties had no marked influence on modulus and viscosity.

In comparison with the PBAT/PLA blend, the modified PBAT/PLA blends showed a significant shear-thinning behavior at the whole frequencies, especially for the (PBAT/ADR)/PLA blend, PBAT/PLA/DCP blend and (PBAT/DCP)/PLA blend. There were more chain entanglements in

Figure 4: The rheological properties depended angular frequencies at 170 °C of (a) the storage modulus versus angular frequencies, (b) the complex viscosity versus angular frequencies, (c) Cole-Cole plots and (d) Han plot.

Figure 5: (a) The second heating curves and (b) the first cooling curves of pure PBAT, pure PLA, PBAT/PLA blend and the modified PBAT/PLA blends.

the modified PBAT/PLA blends than in PLA, PBAT and PBAT/PLA blend. Moreover, the chain disentanglement or chain alignment in the modified PBAT/PLA blends was much more difficult (much longer relaxation time) than that in neat polymers and unmodified PBAT/PLA blend due to the chain branching effect.

The chain branching effect can restricted the chain mobility of the blends [28]. This restriction was further confirmed by the Cole–Cole plots shown in Figure 4c.

Usually, the single arc of the neat polymer represented relaxation process with a relaxation time distribution. Li et al. [20] studied the viscoelastic properties of the incompatible PLA/PBAT blends, the obtained Cole–Cole plots yielded a tail or second circular arc, which corresponded to the simultaneous occurrence of the two material phases with very different relaxation times. In other words, such Cole–Cole plots clearly displayed two different relaxation mechanisms corresponding to two different phases. In this work, the shape of PBAT/PLA blend curve still showed an arc, which showed no sign of the coexisting phases in the PLA/PBAT blend due to the low PLA content.

With addition of the ADR, the Cole–Cole plots of PBAT/PLA/ADR blend was divided into two parts: a half-baked arc at low viscosities corresponding to the local dynamic of molecular chains and a rigid tail at high-viscosity region, which was indicative of the long-term relaxation of those restrained molecular chains. In particular, as far as the (PBAT/ADR)/PLA blend, it showed the rigid tail, indicating that the long-term relaxation of the restrained molecular chains became the dominant one in the whole relaxation behaviors of the blend. For the PBAT/PLA/DCP blend and (PBAT/DCP)/PLA blend, the Cole–Cole plots also exhibited the rigid tail meaning the changed relaxation characterization of restrained molecular chains. These results confirmed that the molecular chain structure of modified PBAT/PLA blends changed. The compatibility effect of different compatibilizers and blending methods was verified by the following Han plots.

Han et al. [29] established a rheological criterion to determine the homogeneity of copolymers and polymer blends in the melt state as well as the compatibilization of polymer blends [30]. Moreover, Han-plot can provide information about elastic and viscous properties of polymers in low-frequency region, where the linear viscoelastic data are most sensitive to differences in structure. Figure 4d displays such Han plots for the PBAT/PLA blend and the unmodified PBAT/PLA blend. The curves of PBAT/PLA blend exhibited a nonlinear correlation, indicating incompatibility. However, for the modified PBAT/PLA blends, it can be clearly observed that the curves of all the modified blends showed the good linear correlation at the whole frequency range, which confirmed that the improved compatibilization of PBAT/PLA blends with different compatibilizers and blending methods. The intersection ($G' = G''$) determined the transition from more elastic behavior ($G' > G''$) to more viscous behavior ($G' < G''$). The slope of $\log G'$ versus $\log G''$ was also informative. $\log G'$ for mono dispersive flexible polymers should be proportional to $\log G''$ with a slope of 2 [31]. We can calculate from Figure 4d that the slopes were 1.36, 1.13, 1.22 and 1.27 for PBAT/PLA/ADR blend, (PBAT/ADR)/PLA blend, PBAT/PLA/DCP blend and (PBAT/DCP)/PLA blend, respectively. PBAT/PLA blend was closer to a viscous polymer while (PBAT/ADR)/PLA blend, PBAT/PLA/DCP blend and (PBAT/DCP)/PLA blend behaved more elastic (closer to the straight line $\log G' = \log G''$) due to the contribution from the long-chain branching. The long-chain branches would increase the abundant entanglements and improve the melt elasticity.

3.5 Thermal properties

PLA and PBAT were semicrystalline polymers. The crystallization and melting behavior of PBAT/PLA blend and the modified PBAT/PLA blends were examined to investigate whether the crystallization behavior of PLA and PBAT

changed by the addition of compatilizers and the different blending procedures. Figure 5 shows the second heating and first cooling curves of pure PBAT, pure PLA, PBAT/PLA blend and various modified PBAT/PLA blends and Table 3 displays a summary of the DSC results. The T_g and T_m of pure PBAT were -30.2 and 120.0 °C, on the other hand, the T_g and T_m of pure PLA located at 60.9 and 150.4 °C, respectively. The melt crystallization rate of pure PLA was slow and PLA cannot produce significant melt crystallization, but it can exhibit cold crystallization process at the second heating process. The T_{cc} of pure PLA was observed at approximately 115.5 °C. For the pure PBAT, there was no cold crystallization signal presented in the second heating curve. However, an obvious melt crystallization peak occurred in the cooling cycle.

As shown in Figure 5a, all PBAT/PLA blends exhibited similar thermograms, including the glass transition of PBAT and PLA and subsequent melting of PBAT crystals. The values of ΔT_g of the modified PBAT/PLA blends were slight decreased, which may be attributed to the improved compatibilization between PBAT and PLA by the addition of ADR or DCP. It was worth noting that, the endothermic melting peak for PLA component in PBAT/PLA/ADR blend disappeared and the endothermic melting peak for PLA component in (PBAT/ADR)/PLA blend almost disappeared. This can be explained by the compatibilization by chain extension which restricted crystallization of PLA domains. However, the PLA endothermic melting peak in PBAT/PLA/DCP blend and (PBAT/DCP)/PLA blend increased compared with the one in PBAT/PLA blend. It may be due to the existence of branching points inducing

by DCP promoted crystallization of PLA phase. Figure 5b illustrates the main characterization of the melt crystallization behavior of PBAT in the cooling cycle. For the cooling curve, the melt crystallization peaks of the PBAT component were significant. Especially, the T_c of (PBAT/ADR)/PLA blend increased from 68.1 of PBAT/PLA blend to 78.1 °C, increased by 10 °C. Moreover, the T_c of PBAT/PLA/DCP and (PBAT/DCP)/PLA blends were also increased by 8 and 18 °C, respectively. Obviously, T_c increased markedly via the two-step mixing. It owed to the addition of the ADR or DCP into PBAT, the viscosity of the modified PBAT increased, the random thermal motion of molecular chain decreased, which was beneficial to the nucleation stability of PBAT. According to the document [32], the branching points can serve as nucleating points which contributed to increase the T_c . However, the ΔH_c of the modified PBAT/PLA blends decreased, indicating that the addition of ADR or DCP into PBAT/PLA blends inhibited the resultant crystallization of PBAT. The T_m values of PBAT component for the modified PBAT/PLA blends were about 0.2 – 3.5 °C higher than that of PBAT/PLA blend. It was reported that the crystals melted at different temperatures had similar structure but different lamellar thickness [33, 34]. Based on this, in this work, the increased T_c promoted chain segment movement, which may be lead to more perfect of the PBAT crystal and an increase in the lamellar thickness.

From the above discussion, it indicated that compatilizers and the different blending procedures affected crystallization kinetics markedly, but could not significantly change crystallinity.

Table 3: Thermal parameters of pure PBAT, pure PLA, PBAT/PLA blend and the modified PBAT/PLA blends.

Samples	T_g^b -PBAT (°C)	T_g^b -PLA (°C)	ΔT_g PBAT-PLA (°C)	T_m^b -PBAT (°C)	ΔH_m^b -PBAT (J/g)	X_c^b -PBAT (%)	T_m^b -PLA (°C)	ΔH_m^b -PLA (J/g)	X_c^b -PLA (%)	T_{cc} -PLA (°C)	ΔH_{cc} -PLA (J/g)	T_c^a -PBAT (°C)	ΔH_c^a -PBAT (J/g)
PBAT	-30.2	–	–	120.0	12.4	10.9	–	–	–	–	–	68.9	16.8
PLA	–	60.9	–	–	–	–	150.4	21.8	23.4	115.5	17.9	–	–
PBAT/PLA	-29.9	61.2	91.1	119.9	8.2	7.2	149.6	0.20	0.2	–	–	68.1	14.4
PBAT/PLA/ADR	-29.7	61.3	91.0	120.1	8.3	7.3	–	–	–	–	–	67.3	13.2
(PBAT/ADR)/PLA	-26.2	61.2	87.4	123.4	4.6	4.0	151.2	0.05	0.1	–	–	79.1	10.4
PBAT/PLA/DCP	-27.8	61.6	89.4	121.9	4.7	4.1	150.1	0.34	0.4	–	–	76.0	11.5
(PBAT/DCP)/PLA	-28.0	62.0	90.0	122.1	3.1	2.7	151.3	0.49	0.5	–	–	86.0	10.7

^aFirst cooling at a cooling rate of 10 °C min^{-1} . ^bSecond heating at a heating rate of 10 °C min^{-1} . ΔH_m , ΔH_{cc} , ΔH_c is corrected for the content of PLA in the blend. Degree of crystallinity was calculated from the ratio of ΔH_m and ΔH_m^0 (the melting enthalpy, ΔH_m^0 , of 100% crystalline PBAT and PLA being taken as 114 J·g⁻¹ [34] and 93 J·g⁻¹ [15], respectively).

3.6 Mechanism

In this paper, two different blending procedures combining with different compatibilizers were studied. The first approach was considered one-step blending, with all components being blended in the internal mixer. The second one (Second approach) consisted of modifying PBAT by pre-blending it with ADR or DCP in the internal mixer for 4 min, obtaining the modified PBAT, then adding PLA and mixing for another 4 min.

PLA and PBAT are thermodynamic immiscibility polymer pairs. This induced the macroscopic phase separation. For the PBAT/PLA blend without compatibilizers, the PLA segments formed droplet-like particles and aggregates embedded in the PBAT matrix.

The rheological behavior of modified PBAT/PLA blends as well as the Han plots coupled to the mechanical properties and SEM morphology confirmed that the addition of ADR by the two-step blending procedure was an effective method for improving the compatibility between the PBAT and PLA phases. For the PBAT/PLA/ADR blend, the valid compatibilization reaction diagram was shown in Figure 6a. The epoxy groups of ADR reacted with the terminal carboxyl groups and hydroxyl groups of PLA and PBAT to form a PLA-g-PBAT copolymers between the PLA and PBAT segments, thereby effectively reducing the interface tension between the two phases. When applying the force on the samples, the copolymers acted as a bridge to transfer the force received by the PBAT matrix effectively to the more dissipative energy PLA phases, thus causing a large increase of tensile strength. However, the one-step blending would lead to the random and average epoxy groups, especially ADR was easily embedded into PBAT phase with low melt viscosity which was not conducive to the generation of the PLA-g-PBAT macromolecules at the interface.

Figure 6b showed the possible reactions happened in the (PBAT/ADR)/PLA blend. Firstly, melt blending of PBAT with ADR led to enrichment of epoxy functional groups in PBAT segments, producing chain extension and branching reaction in PBAT phase, increasing the melt strength of PBAT, then blending of the ADR modified PBAT with PLA, the remained epoxy groups can react with PLA at the two-phase interface under the enhanced shear force due to the increased melt strength of PBAT, forming more amount of PBAT-g-PLA copolymers to increase the compatibilization.

Moreover, models of one-step and two-step blending around the PBAT and PLA interfaces are illustrated in Figure 6c, d.

Free radical reactivity of PBAT and PLA was different. PBAT had a higher radical reaction capacity that can be ascribed to the high ability of the DCP for developing reactive radical species at lower concentration of peroxide, due to the higher content of mobile H-atom of PBAT than in PLA. In particular, the $-\text{CH}_2-$ groups in the alpha position with respect to the carbonyl group of the adipic acid unit are the most reactive. In contrast, PLA has only methyl or methyne hydrogen; the former is not reactive and the methyne is sterically hindered and gives a rather stable free radical [23].

Firstly, the free radicals were generated by the thermal decomposition of DCP, which initiated the formation of macro-free radicals via a hydrogen abstraction. For the PBAT/PLA/DCP blend, both PBAT and PLA can form branched structures with peroxide. The PBAT-g-PLA copolymers can occur via a combination of PBAT and PLA free radicals. Figure 7 shows the formation of PBAT-g-PLA copolymers through the radical coupling mechanism. The *in situ* formed PBAT-g-PLA copolymers acted as compatibilizer between PBAT and PLA.

For the (PBAT/DCP)/PLA blend, in the premix period, the branching of PBAT happened according to recombination of macro-free radicals. The typical half-life time of DCP was about 1 min at 171 °C [35]. Based on Coltelli's report [36], different amount of DCP were added into the PBAT, PLA and PLA/PBAT (75/25) blend. Especially, the torque of PBAT reached maximum after about 1 min of blending with DCP and the torque remained stable after 3 min in the range 0.2–0.6 wt% of DCP. It completed the reaction at 3 min. Furthermore, based on the higher free radical activity of PBAT than PLA, almost all DCP triggered the branching reaction of molecular chains in PBAT, resulting in a substantial increase in the melt strength of PBAT polymers. In the second process, it was mainly a physical blending process and almost no PBAT-g-PLA copolymers formed. The corresponding morphology presented typical two-phase island-sea structure, but the diameter decrease to 0.7 μm compared with 1.02 μm of PBAT/PLA blend. The (PBAT/DCP)/PLA blend had a high melt strength of the polymer matrix, resulted in high shear forces capable of deforming and comminuting the dispersed particles, despite the high interfacial tension. According to the above result, we can believe that the formation of PBAT-g-PLA copolymers was the key factor to improve the tensile properties of PBAT/PLA blend.

From the above results and discussion, compatibilization effectiveness of the blends followed the order: (PBAT/ADR)/PLA blend > PBAT/PLA/DCP blend > PBAT/PLA/ADR blend > (PBAT/DCP)/PLA blend. Combined ADR with two-

Figure 6: Predicted reaction between polyesters and epoxy functions and models of graft copolymer formation: (a, c) one-step and (b, d) two-step blending.

step blending improved the compatibilization between PBAT and PLA markedly due to the effective formation of PBAT-g-PLA copolymers. For one-step blending process, DCP was

more effective than ADR to improve the compatibilization. The addition of DCP using two-step blending also refined the PLA dispersed phase, but the interface was distinct.

Figure 7: Scheme of branched reactions occurring in the PBAT/PLA blend (a, b) and models of graft copolymer formation: (c) one-step and (d) two-step blending.

4 Conclusions

Biodegradable PBAT/PLA blends with or without ADR or DCP were prepared. The effects of blending procedure were examined. The non-isothermal crystallization, rheological, morphology and mechanical properties of the blends were investigated. The results demonstrated that the compatibility and mechanical properties of PBAT/PLA blends were enhanced in the presence of ADR and DCP by one-step blending due to the formation of PBAT-g-PLA copolymers which increased the interface adhesion. The result showed that two-step blending was a successful method to enhance the tensile strength because more amount of ADR located at the interface between PBAT and PLA phases was confirmed by morphology and complex viscosity. A significant enhancement of the tensile strength to 37.6 MPa and a lower dispersion phase diameter to 0.37 μm of

(PBAT/ADR)/PLA blend were highlighted by the two-step blending. The smaller PLA particles lead to more efficient stress transfer, which resulted in the higher tensile strength. For the addition of DCP into PBAT/PLA blend, one-step blending was more efficient than the two-step blending in improving the tensile properties. In the two-step blending, the high viscosity of PBAT changed the morphology. The enhanced elastic modulus and complex viscosity confirmed the branching reaction occurrence. The formation of branching structure could accelerate the non-isothermal melt crystallization of PBAT as a nucleating agent.

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References

1. Sui G. P., Jing M. F., Zhao J., Wang K., Zhang Q., Fu Q. A comparison study of high shear force and compatibilizer on the phase morphologies and properties of polypropylene/poly(lactide) (PP/PLA) blends. *Polymer* 2018, 154, 119–127.
2. Han L. J., Han C. Y., Zhang H. L., Chen S., Dong L. S. Morphology and properties of biodegradable and biosourced polylactide blends with poly(3-hydroxybutyrate-co-4-hydroxybutyrate). *Polym. Compos.* 2012, 33, 850–867.
3. Al-Itry R., Lamnawar K., Maazouz A. Reactive extrusion of PLA, PBAT with a multi-functional epoxide: physico-chemical and rheological properties. *Eur. Polym. J.* 2014, 58, 90–102.
4. Al-Itry R., Lamnawar K., Maazouz A. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. *Polym. Degrad. Stabil.* 2012, 97, 1898–1914.
5. Wu D. F., Lin D. P., Zhang J., Zhou W. D., Zhang M., Zhang Y. S., Wang D. M., Lin B. L. Selective localization of nanofillers: effect on morphology and crystallization of PLA/PCL blends. *Macromol. Chem. Phys.* 2011, 15, 613–626.
6. Matta A. K., Umamaheswara R., Suman R., Rambabu K. N. S. Preparation and characterization of biodegradable PLA/PCL polymeric blends. *Procedia. Mater. Sci.* 2014, 6, 1266–1270.
7. Raksit S., Narin K., Suwabun C. Random poly(butylene succinate-co-lactic acid) as a multi-functional additive for miscibility, toughness, and clarity of PLA/PBS blends. *Polymer* 2016, 105, 1–9.
8. Wang R. Y., Wang S. F., Zhang Y., Wan C. Y., Ma P. M. Toughening modification of PLLA/PBS blends via *in situ* compatibilization. *Polym. Eng. Sci.* 2009, 49, 26–33.
9. Phasawat C., Thanawadee L., Pongkao K. D., Saowaroj C. Poly(lactic acid)/poly(butylene succinate) blends filled with epoxy functionalised polymeric chain extender. *Adv. Mater. Res.* 2013, 664, 644–648.
10. Wang X., Peng S. X., Chen H., Yu X. L., Zhao X. P. Mechanical properties, rheological behaviors, and phase morphologies of high-toughness PLA/PBAT blends by *in-situ* reactive compatibilization. *Compos. Part B* 2019, 173, 107–128.
11. DilEbrahim J., Carreau P. J., Favis B. D. Morphology, miscibility and continuity development in poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends. *Polymer* 2015, 68, 202–212.
12. Gu S. Y., Zhang K., Ren J., Zhan H. Melt rheology of polylactide/poly(butylene adipate-co-terephthalate) blends. *Carbohydr. Polym.* 2008, 74, 79–85.
13. Wang L. F., Rhim J. W., Hong S. I. Preparation of poly(lactide)/poly(butylene adipate-co-terephthalate) blend films using a solvent casting method and their food packaging application. *LWT – Food Sci. Techn.* 2016, 68, 454–461.
14. Dong W. F., Zou B. S., Yan Y. Y., Ma P. M., Chen M. Q. Effect of chain-extenders on the properties and hydrolytic degradation behavior of the poly(lactide)/poly(butylene adipate-co-terephthalate) blends. *Int. J. Mol. Sci.* 2013, 14, 20189–20203.
15. Han L. J., Han C. Y., Dong L. S. Morphology and properties of the biosourced poly(lactic acid)/poly(ethylene oxide-b-amide-12) blends. *Polym. Compos.* 2013, 34, 122–133.
16. Wang Z., Zhang M., Liu Z. Y., Zhang S. Y., Cao Z. Q., Yang W., Yang M. B. Compatibilization of the poly(lactic acid)/poly(propylene carbonate) blends through *in situ* formation of poly(lactic acid)-b-poly(propylene carbonate) copolymer. *J. Appl. Polym. Sci.* 2018, 135, 46009.
17. Ojijo V., Ray S. S., Sadiku R. Toughening of biodegradable polylactide/poly(butylene succinate-co-adipate) blends via *in situ* reactive compatibilization. *ACS Appl. Mater. Interfaces* 2013, 5, 4266–4276.
18. Ma P., Spoelstra A. B., Schmit P., Lemstra P. J. Toughening of poly(lactic acid) by poly(hydroxybutyrate-co-hydroxyvalerate) with high hydroxyvalerate content. *Eur. Polym. J.* 2013, 49, 1523–1531.
19. Deng Y. X., Yu C. Y., Wongwiwattana P., Thomas N. L. Optimising ductility of poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends through co-continuous phase morphology. *Polym. Environ.* 2018, 26, 3802–3816.
20. Li K., Peng J., Turng L. S., Huang H. X. Dynamic rheological behavior and morphology of polylactide/poly(butenes adipate-co-terephthalate) blends with various composition ratios. *Adv. Polym. Technol.* 2011, 30, 150–157.
21. Díaz M. F., Barbosa S. E., Capiati N. J. Reactive compatibilization of PE/PS blends: effect of copolymer chain length on interfacial adhesion and mechanical behavior. *Polymer* 2007, 48, 1058–1065.
22. Pan H. W., Li Z. L., Yang J., Li X., Ai X., Hao Y. P., Zhang H. L., Dong L. S. The effect of MDI on the structure and mechanical properties of poly(lactic acid) and poly(butylene adipate-co-butylene terephthalate) blends. *RSC Adv.* 2018, 8, 4610–4623.
23. Coltell M. B., Bronco S., Chinea C. The effect of free radical reactions on structure and properties of poly(lactic acid) (PLA) based blends. *Polym. Degrad. Stabil.* 2010, 95, 332–341.
24. Lu X., Zhao J. Q., Yang X. Y., Xiao P. Morphology and properties of biodegradable poly(lactic acid)/poly butylene adipate-co-terephthalate) blends with different viscosity ratio. *Polym. Test.* 2017, 60, 58–67.
25. Al-Itry R., Lamnawar K., Maazouz A. Biopolymer blends based on poly(lactic acid): shear and elongation rheology/structure/blowing process relationships. *Polymers* 2015, 7, 939–962.
26. Abdelwahaby M. A., Taylor S., Misra M., Mohanty A. K. Thermo-mechanical characterization of bioblends from polylactide and poly(butylene adipate-co-terephthalate) and lignin. *Macromol. Mater. Eng.* 2015, 300, 299–311.
27. Li X., Yan X. Y., Yang J., Pan H. W., Gao G. H., Zhang H. L., Dong L. S. Improvement of compatibility and mechanical properties of the poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends and films by reactive extrusion with chain extender. *Polym. Eng. Sci.* 2017, 58, 1868–1878.
28. Wu D. F., Wu L., Zhang M., Zhao Y. L. Viscoelasticity and thermal stability of polylactide composites with various functionalized carbon nanotubes. *Polym. Degrad. Stabil.* 2008, 93, 1577–1584.
29. Han C. D., Kim J. Rheological technique for determining the order–disorder transition of block copolymers. *J. Polym. Sci. B* 1987, 25, 1741–1764.

30. Lamnawar K., Vion-Loisel F., Maazouz A. Rheological, morphological, and heat seal properties of linear low density polyethylene and cyclo olefine copolymer (LLDPE/COC) blends. *J. Appl. Polym. Sci.* 2010, *116*, 2015–2022.
31. Wang L. Y., Jing X. B., Cheng H. B., Hu X. L., Yang L. X., Huang Y. B. Rheology and crystallization of long-chain branched poly(l-lactide)s with controlled branch length. *Ind. Eng. Chem. Res.* 2012, *51*, 10088–10099.
32. Bian Y. J., Han L. J., Han C. Y., Lin H. J., Zhang H. L., Bian J. J., Dong L. S. Intriguing crystallization behavior and rheological properties of radical-based crosslinked biodegradable poly(3-hydroxybutyrate-co-4-hydroxybutyrate). *Cryst. Eng. Comm.* 2014, *16*, 2702–2714.
33. Long J., Michael P. W., Zhang J. Study of biodegradable polylactide/poly(butylenes adipate-co-terephthalate) blends. *Biomacromolecules* 2006, *7*, 199–207.
34. Ravati S., Beaulieu C., Zolali A. M., Favis B. D. High performance materials based on a self-assembled multiple-percolated ternary blend. *AIChE J.* 2014, *60*, 3005–3012.
35. Ma P. M., Hristova-Bogaerds D. G., Lemstra P. J., Zhang Y., Wang S. F. Toughening of PHBV/PBS and PHB/PBS blends via in situ compatibilization using dicumyl peroxide as a free-radical grafting initiator. *Macromol. Mater. Eng.* 2012, *297*, 402–410.
36. Coltelli M. B., Bronco S., Chinea C. The effect of free radical reactions on structure and properties of poly(lactic acid) (PLA) based blends. *Polym. Degrad. Stabil.* 2010, *95*, 332–341.