

Properties of Ternary Blends of Compostable PLA/PBAT/PBS

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Abstract

Compostable plastics such as Poly (lactic acid) (PLA), Poly(butylene succinate) (PBS) and Poly(butylene adipate-co-terephthalate) (PBAT) have been extensively used in many applications, from commodity to engineering ones. These plastics offer the circularity of the carbon cycle. However, each of them has advantages and disadvantages. The ternary blend of these three are therefore very interesting in terms of phase morphology and their physical properties while offering compostable practices. In this work, the blends of PLA/PBAT/PBS were studied. PLA/PBAT was fixed at 50/50 whereas PBS was varied from 10 to 40 % wt. In order to ensure the compatibility, peroxide and carbodiimide compounds were used. The results show an immiscibility of PLA/PBAT/PBS blend, with continuous surface of PLA and PBAT while PBS is dispersed phase. However, it shows the better interfacial adhesion of PLA/PBAT/PBS when reactive compounds were added. The mechanical properties indicated the modulus of all blends higher than neat PBAT (~52 MPa) and PBS (~377 MPa). However, it insignificantly changed when increased PBS contents, similar to the tensile strength results.

Keywords: Circularity, Ternary blend, Compostable plastic

1. Introduction

There is a great concern on accumulative plastic waste. Many existing solutions include the new plastics economy pioneered by Ellen MacArthur (Ellen MacArthur Foundation, 2020). Plastics and circular economy have been put into the solutions in forms of the new design of products and processes as well as the materials substitution. In terms of materials regeneration and sustainability, biobased and biodegradable plastics are obvious choices. Depending on the applications, materials can be selected and designed for circularity. Thus, one of the options for plastics can be compostable plastic, which can provide the composting option and return carbon and nutrients for the plant growth. Among compostable plastics, poly(lactic acid) (PLA) is one of the most studied one because it has many advantages such as high strength, high modulus, biodegradable and low cost as well as commercialization on a large scale. However, PLA is highly brittle and has low toughness and heat

distortion temperature and barrier properties beside limited application (Chaiwutthinan, Chuayjuljit, Srasomsub, & Boonmahitthisud 2019; Hongdilokkul et al., 2015; Pitivut, Suttiruengwong, & Seadan, 2015; F. Wu, Misra, & Mohanty, 2020).

Many researchers have attempted to improve the properties of PLA to make it more widely applicable. One method that is widely used for improving the toughness of PLA is to blend PLA with a flexible polymer such as PBAT and PBS (Hongdilokkul et al., 2015; Pitivut et al., 2015; Prasong, Ishigami, Thumsorn, Kurose, & Ito, 2021; D. Wu et al., 2020). Poly(butylene adipate-co-terephthalate) (PBAT) is aliphatic aromatic polyester. Although PBAT has been commercialized with high toughness and flexibility, it still has low modulus (D. Wu et al., 2020). Therefore, blending PLA and PBAT can balance these properties. P. Chaiwutthinan et al. (2019) and Pitivut et al. (2015) studied the properties of PLA/PBAT blends in different ratios. The results showed that the addition of PBAT could improve

elongation at break of PLA while young's modulus and strength decreased with increased PBAT contents.

A few studies have involved in the blending of PLA and PBS, as PBS was a biodegradable polymer with good processability, high flexibility, high impact strength and better heat resistance compared to other biopolymer such as PLA and PBAT (Prasong et al., 2021; Ravati & Favis, 2013). Prasong et al. (2021) reported that PBS acted as a nucleating agent of PLA and induce crystallinity in PLA/PBS blend. Improving the crystallinity of the polymer resulted in an increase in the heat resistance of the blend. However, a study of ternary blends between PLA/PBAT/PBS has been limited up to our knowledge. Ravati, Beaulieu, Zolali, and Favis (2014) studied properties of the PBS/PLA/PBAT ternary blend in the equal ratio. SEM micrograph showed all phases were percolated and created a tri-continuous ternary PLA/PBS/ PBAT immiscible blend. The presence of this microstructure resulted in the ternary blend showing a very high level of properties including a high impact strength, high young's modulus, and high elongation at break. F. Wu, Misra, and Mohanty (2019) developed super toughened poly(lactic acid)-based ternary blends via enhancing interfacial compatibility. The results showed that the incorporation of PLA ensured that the blend with modulus above 1 GPa and strength above 30 MPa. In addition, the modulus increased with increased peroxide contents. On the other hand, the addition of peroxide into ternary blends resulted in the molecular chains with highly branched or cross-linked structures. It limited the chain movement, leading to the decreased elongation at break.

According to literature, the effect of PBS content on the properties of PLA/PBAT/PBS ternary blends has not been reported before. Therefore, the objective of this research was to study the effect of PBS content on the phase morphology and physical properties of PLA/PBAT/PBS ternary blends with and without reactive agent.

2. Materials and Methods

2.1 Materials

Poly(lactic acid) (PLA) 4043D grade was purchased from BC POLYMER MARKETING CO., LTD., Thailand. Poly(butylene adipate-co-terephthalate) (PBAT) Ecoflex F blend C1200 was purchased from POLYMATS CO., LTD., Thailand. Poly(butylene succinate) (PBS) FZ91PM grade was purchased from PTT MCC Biochem CO., LTD., Thailand. Di (tert-butylperoxyisopropyl) benzene (perkadox 14s) was purchased from AkzoNobel Co., Ltd. Bioadimide 100XT and 500XT were purchased from Optimal Tech CO., LTD., Thailand.

2.2 Preparation of PLA/PBAT/PBS blends

Prior to usage, PLA PBAT and PBS resin were dried in an oven at 60°C for 6 hours to remove moisture. Then PLA PBAT and PBS were blended via internal mixer (CHAREON TUT CO., LTD) at 190 °C with rotor speed 60 rpm for 10 min. The compositions of PLA/PBAT/PBS ternary blends both with and without reactive agents in this study were listed in table 1. PLA/PBAT ratio was fixed at 50/50 while PBS varied from 10 to 40 % wt. Perkadox (Per) and bioadimide (BioAd) 0.2 and 0.4 phr respectively were used for each of compositions to form reactive blended polymers.

Table 1. Compositions of PLA/PBAT/PBS blends.

Sample	PLA (%wt)	PBAT (%wt)	PBS (%wt)	Per (phr)	BioAd (phr)
Neat PLA	100	-	-	-	-
Neat PBAT	-	100	-	-	-
Neat PBS	-	-	100	-	-
PBS0	50	50	-	-	-
PBS10	45	45	10	-	-
PBS20	40	40	20	-	-
PBS30	35	35	30	-	-
PBS40	30	30	40	-	-
PBS0P0.2B0.4	50	50	-	0.2	0.4
PBS10P0.2B0.4	45	45	10	0.2	0.4
PBS20P0.2B0.4	40	40	20	0.2	0.4
PBS30P0.2B0.4	35	35	30	0.2	0.4
PBS40P0.4B0.4	30	30	40	0.2	0.4

2.3 Characterization

Melt flow index (MFI) of all samples was measured at 190°C/2.16 kg, according to ASTM D1238 using Plastomer: MFR1 (CHAREON TUT CO., LTD). The cryo-fracture surface morphology of neat polymers and their blends was examined by Field emission scanning electron microscope (FESEM) (MIRA3, TESCAN) operated at 5.0 KV and samples were sputtered with gold. Young's modulus, tensile strength, and elongation at break of all samples were determined according to ASTM D638-5 with a crosshead speed of 10 mm/min using universal testing machine (NRI-TS501-1508-5B, NARIN instrument CO., LTD).

3. Results and Discussions

3.1 Mixing torque

Mixing torque at 10 min of the sample with and without reactive agents is shown in figure 1. The mixing torque of neat PLA PBAT and PBS are 8.49, 10.18 and 5.46 Nm respectively. The mixing torques imply the melt viscosity of polymers. Therefore, PBAT has the highest melt viscosity whereas PBS has the lowest melt viscosity. Considering the mixing torques of the blends without reactive agent, the results showed that mixing torques decreased with increased PBS contents. On the other hand, the torque value of the blends with reactive agents increases with increasing PBS content due to Perkadox being highly reactive with PBS, resulting in molecular chain cross-linking (Cherykhunthod, Seadan, & Suttiruengwong, 2015; F. Wu et al., 2019). In addition, the presence of bioadimide as a chain extender can also increase the viscosity of the polymer. Thereby, increasing viscosity of the system led to higher torque value.

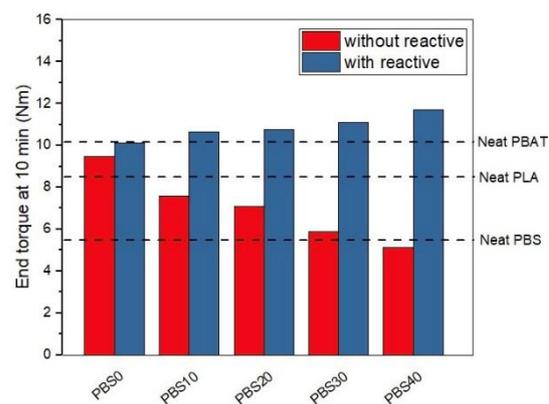


Figure 1. Mixing torque at 10 min of neat polymers and their blends with various PBS contents.

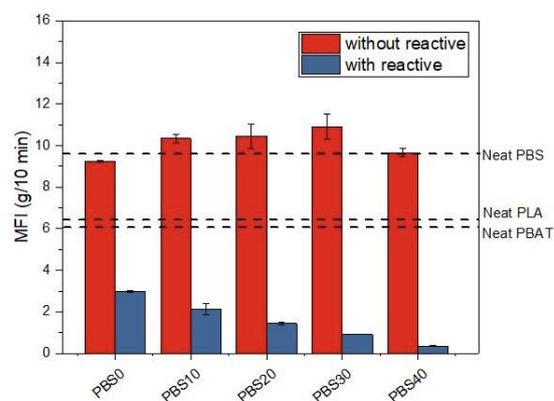


Figure 2. Melt flow index of neat polymers and their blends with various PBS contents.

3.2 Melt flow index

Figure 2 shows the melt flow index of neat polymers and their blends. The results showed MFI of neat PLA PBAT and PBS were 6.45, 6.08 and 9.58 g/10min respectively. In the case of the blends without reactive agent, MFI was increased with increasing PBS contents whereas MFI of the blends with reactive agent decreased with increasing PBS contents. This result is in a good agreement with the mixing torque. That is, polymers with high torque values would have low MFI or high viscosity.

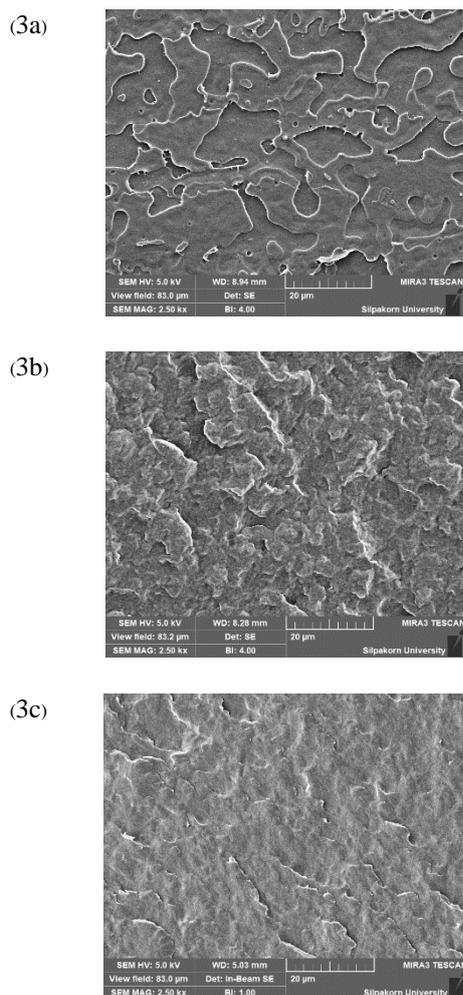


Figure 3. Cryo-fracture surface of (a) neat PLA, (b) neat PBS, (c) neat PBAT by SEM.

3.3 Morphology

SEM micrographs of neat polymers were shown in Figure 3. Neat PLA shows a smooth surface, indicating the brittle characteristic, while neat PBS and PBAT show a relatively rough fracture surface. Figure 4a and 4b show the morphology of the blends with PBS 10 and 20 %wt respectively and without reactive agent. The result indicated an immiscibility of PLA/PBAT/PBS blends, with smooth continuous surface, probably PLA phase while rough continuous surface, probably PBAT phase. In addition, PBS as minor content is dispersed. In case of the blends with reactive agent (Figure 4c and 4d), the morphology changed, indicating that adding perkadox was able to improve interfacial adhesion of the ternary blends. Therefore, the blends exhibited

a more uniform surface and dispersed phase was smaller.

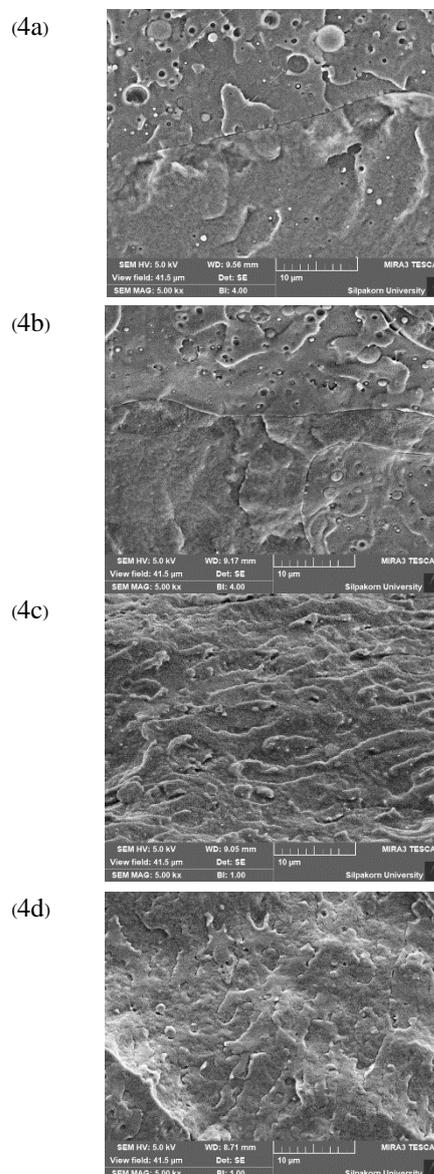


Figure 4. Cryo-fracture surface of (a) PBS10, (b) PBS20, (c) PBS10P0.2B0.4 and (d) PBS20P0.2B0.4 by SEM.

3.4 Mechanical properties

Young's modulus of all samples is shown in figure 5a. The results show that neat PLA had a high modulus (~1,574 MPa) while neat PBAT had a low modulus (~52 MPa). Blending PLA and PBAT in the ratio 50:50 resulted in modulus between both polymers. The blends combined with PBS had lower

modulus values. In addition, the modulus of all blends was higher than neat PBS (~377 MPa). However, it insignificantly changed when increased PBS content, similar to the tensile strength results (Figure 5b). Conversely, the elongation at break of all blends decreased with increased PBS content. Moreover, the addition of reactive agent resulted in lower elongation at break compared to the blends without reactive agent due to peroxadox causing crosslinked or branched molecular chains (F. Wu et al., 2019).

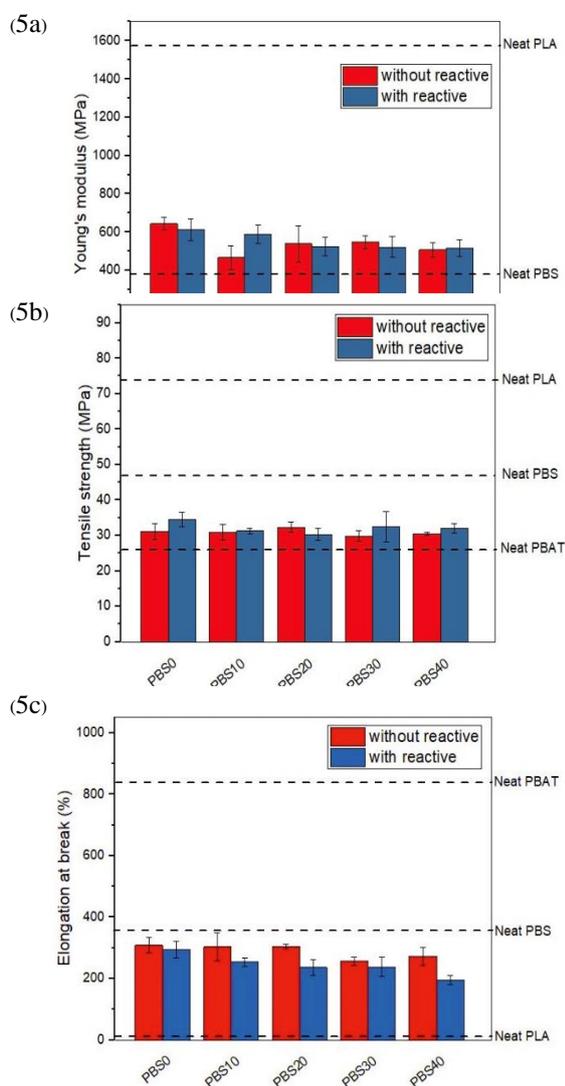


Figure 5. (a) Young's modulus, (b) tensile strength and (c) elongation at break of neat polymers and their blends with various PBS content.

4. Summary

In this work, ternary blends of compostable PLA/PBAT/PBS which fixed PLA/PBAT at 50/50 and varied PBS from 10 to 40%wt were prepared via internal mixer at 190°C for 10 min with rotor speed 60 rpm. Mixing torques of the blends increase after reactive agents were applied, indicating an increased melt viscosity. From morphology study, it represents the better interfacial adhesion of PLA/PBAT/PBS when reactive agents were added. In addition, the tensile modulus and strength differ insignificantly upon increasing PBS content. From all the experimental results mentioned above, it may not be clear what proportion of PLA/PBS/PBAT is the optimum. More studies on the phase behavior and crystal structure of the ternary blends are needed to explain the mechanical properties. In addition, this research can be further developed for various packaging applications.

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