

Effect of reactive agent and transesterification catalyst on properties of PLA/PBAT blends

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Abstract. This research aimed to study the properties of poly (lactic acid) (PLA)/poly (butylene adipate-co-terephthalate) (PBAT) blends with two different reactive systems: free radical reaction through peroxide (Perkadox) and transesterification catalyst (tetrabutyl titanate; TBT). Two blends composed of PLA as a matrix phase with the composition of 80 and 70 percent by weight. PLA/PBAT blends with Perkadox were prepared in twin screw extruder, whereas PLA/PBAT blends with TBT were prepared in an internal mixer. The morphology of the blends was investigated by scanning electron microscope (SEM). Tensile and impact testings of the blends were reported. In case of the blends with Perkadox, SEM micrographs revealed that the size of particles was substantially reduced when adding more Perkadox. Young's modulus and the tensile strength of all blend ratios were insignificantly changed, whereas the elongation at break was decreased when compared to non-reactive blends due to the possible crosslinking reaction as observed from melt flow index (MFI) values. When adding Perkadox, the impact strength of PLA/PBAT (80/20) remained almost unchanged. However, the impact strength of PLA/PBAT (70/30) was enhanced, increasing to 110% for 0.05 phr Perkadox. In case of the blends with TBT, SEM micrographs showed the decrease in the particle size of PBAT phase when adding TBT. Young's modulus and the tensile strength of all blend ratios were not different, but the elongation at break was improved when adding TBT owing to the transesterification reaction. For PLA/PBAT (80/20), the elongation at break was increased by 39%, whereas the elongation at break was increased by 15% for PLA/PLA (70/30). The impact strength of all blend ratios unaffected.

1. Introduction

Since the discovery of bioplastics, the growth and availability of some bio-based and/or biodegradable plastics manufacturers have become key factors to compete with existing non-biodegradable fossil-based plastics. These marketed bioplastics include poly (lactic acid) (PLA) under trade name, IngeoTM by NatureWorks, Sulzer Polylactide by Sulzer Chemtech, ECOPLAN by SK Chemicals, poly(butylene

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adipate-co-terephthalate) (PBAT) provided by BASF (Ecoflex®), Biocosafe 2003 by Xinfu Pharmaceutical Co. Ltd. and poly(butylene succinate) under trade name Bionolle (Showa Denko) or GsPLA (Mitsubishi Chemical). The combinations of these biodegradable polymers are also readily available as compound resins in a wide range of applications such as Ecovio® by BASF, Bioflex® (FKur). Among the bioplastics mentioned, the blends of PLA and PBAT have been extensively explored due to their complete biodegradable feature and mechanical balance.

PLA possesses high modulus and tensile strength, but it is brittle, resulting in limited applications [1, 2]. To improve its brittleness, many methods such as copolymerization, plasticization, blending with flexible biodegradable polymers (e.g. poly(butylene adipate-co-terephthalate)) [1, 2] have been explored. PBAT has been extensively investigated as an appropriate blend pair for enhancing brittleness of PLA as PBAT has high toughness and is fully biodegradable [1, 2]. However, PLA shows complete phase separation with PBAT, resulting in limited improvement in the toughness by physical blending [3, 4]. For such a system, depending on the required properties of the blends and products, whether PLA or PBAT becomes a major phase, the blend is less problematic.

The addition of reactive agents can improve compatibility between PLA and PBAT in blends; for instance, dicumyl peroxide (DCP) [5, 6], tetrabutyl titanate (TBT, $\text{Ti}(\text{BuO}_4)$) [4, 7, 8], bioxazoline [9], phthalic anhydride [9], acetyl tributyl citrate [10, 11], and glycidyl methacrylate (GMA) [12, 13].

Reactive agents can promote in-situ copolymerization through the free radical reaction using peroxide initiator. Coltelli M-B, et al. [5] studied reactive compatibilization between PLA and PBAT with various 2, 5-Dimethyl-2, 5-di (tert-butylperoxy) hexane contents. The results showed that mechanical properties (modulus and tensile strength) of the blends were improved, but the elongation at break was decreased due to the crosslinking reaction. The occurrence of crosslink was also confirmed by torque, melt volume-flow rate (MVR) and size-exclusion chromatography (SEC). Furthermore, the particle size of dispersed phase in reactive blends was lower than non-reactive blend due to improving interfacial adhesion between PLA and PBAT through free radical reaction. Nishida M, et al. [6] studied the effect of dialkyl peroxide on PLA/PBAT blends. The results showed that the elongation at break and the impact strength were improved when adding dialkyl peroxide at a ratio of PLA to PBAT to dialkyl peroxide being 60:40:1. It indicated that dialkyl peroxide resulted in improving ductility of the blends due to the crosslinking reaction. From these findings, peroxide could be used to modify the morphology and mechanical properties of PLA/PBAT blend.

Alternative to the free radical reaction is the transesterification reaction. Both reactions are reactive blending, so they are easy to process and low cost. Coltelli M-B, et al. studied the reaction time of transesterification for blending PLA, PBAT and TBT. The results showed that the particle size of dispersed phase in the blends with TBT was smaller than that of the blend without TBT and the elongation at break was improved due to the transesterification reaction. Moreover, the reaction time affected various properties of the blends. Lin S, et al. [4] studied PLA/PBAT with various TBT contents. The results showed that the tensile strength, the elongation at break and the impact strength were improved when adding TBT to the blends, particularly, PLA/PBAT blend with incorporation of TBT 0.5 wt.%. The compatibility between PLA and PBAT confirmed by SEM was also enhanced due to the transesterification reaction. Moreover, for dynamic mechanical analysis (DMA) results, storage modulus and glass transition temperature were improved. Girdthep S, et al. [8] studied PLA/PBAT (70/30) blends with TBT and kaolinite. TBT was added as compatibilizer to improve interfacial affinity between PLA and PBAT via transesterification. Kaolinite was added to increase the interlamellar space of the silicate layers. It was found that mechanical properties of PLA/PBAT blends were enhanced. Tensile strength was dropped and elongation at break and modulus were increased at TBT 0.5 phr, an optimal TBT concentration. SEM results showed that adding TBT could improve dispersion of PBAT in PLA phase. However, the reaction time of transesterification reaction is usually longer than that of the free radical reaction.

Therefore, this work aimed to study the two reactive systems involving free radical reaction using peroxide and transesterification reaction using TBT as a reactive agent for PLA/PBAT blends, where

PLA was used as a major phase with the composition of 80 and 70 percent by weight. The influences of both systems on the morphological and mechanical properties were separately discussed.

2. Experimental

2.1. Materials

PLA (4043D grade) was purchased from NatureWorks LLC, USA. PBAT (Ecoflex®) was purchased from BASF Chemical Company, Germany. Di (tert-butylperoxyisopropyl) benzene (Perkadox14s), having 40% of peroxide, was supplied by Akzo Nobel, Netherlands. Tetrabutyl titanate (TBT) was purchased from Sigma-Aldrich, USA.

2.2. Preparation of PLA/PBAT blends

PLA and PBAT were dried at 60°C for 5 hours prior to use. The weight ratios of PLA/PBAT were 80/20 and 70/30. The polymers and reactive agent (Perkadox) were weighted, premixed, and then fed into twin screw extruder using temperature 120/130/150/160/170/180/190/190°C and screw speed of 80 rpm. The amount of Perkadox (0.01, 0.03, 0.05 phr) was varied. Due to a slow reaction time, the experiments for transesterification catalyst were performed using an internal mixer to follow the reaction as a function of torques. The polymers and transesterification catalyst (TBT) were weighted, premixed, and added to internal mixer at 185°C and rotor speed of 60 rpm for 15 minutes. The amount of TBT (0.3, 0.5, 0.1 phr) was varied. The formulations consisting of Perkadox and TBT were referred as pX and TX, respectively and X denoted the quantity of reactive agents in phr.

2.3. Testing

Melt flow index (MFI) of all samples was tested at 190°C/2.16 kg, according to ASTM D1238. The fractured surface morphology of PLA/PBAT blends was examined by SEM (CamScan, MX-2000, UK). Mechanical properties were evaluated by tensile and impact testing. The tensile and impact specimens were prepared by compression moulding at 190°C. Tensile testing was carried out by universal testing machine (Instron, Model 5969, USA) equipped with a 5 kN load cell at a crosshead speed of 10 mm/min, according to ASTM D638. The specimen was type V. Notched Izod impact testing was tested according ASTM D256 (Zwick model pendulum impact tester B5102.202)

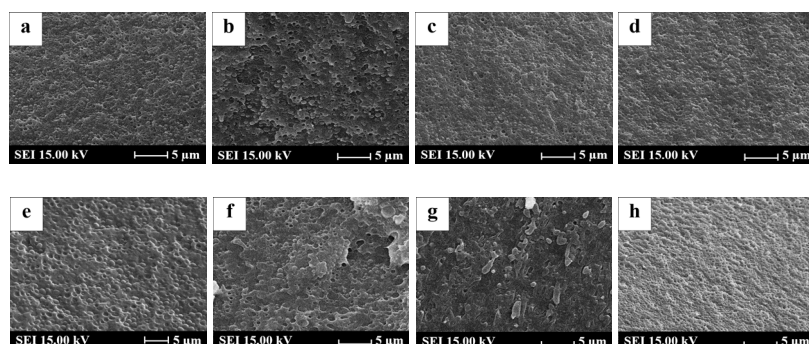


Figure 1. SEM micrographs of fractured surface (a) PLA/PBAT (80/20) (b) PLA/PBAT (80/20)+p0.01 (c) PLA/PBAT (80/20)+p0.03 (d) PLA/PBAT (80/20) + p0.05 (e) PLA/PBAT (70/30) (f) PLA/PBAT (70/30)+p0.01 (g) PLA/PBAT (70/30)+p0.03 (h) PLA/PBAT (70/30)+p0.05.

3. Results and discussion

3.1. PLA/PBAT blends with perkadox

3.1.1. Morphology. In case of PLA/PBAT (70/30) (figure 1(e)), PBAT particle sizes were larger than those of PLA/PBAT (80/20) (figure 1(a)). Upon increasing Perkadox contents, PBAT particles were still finely dispersed in PLA matrix and the size of PBAT particles of both blend ratios became

smaller. In case of PLA/PBAT (80/20), the size of PBAT particles reduced from about 0.6 to 0.2-0.4 μm . In case of PLA/PBAT (70/30), the size of PBAT particles also reduced from about 0.8 to 0.2-0.4 μm .

3.1.2. Melt flow index. MFI value of PLA/PBAT lied between that of their neat ones. For PLA/PBAT with Perkadox, the MFI values tended to decrease with the increase of Perkadox contents. This result could be observed for both blend ratios. The addition of Perkadox to the blends could cause lower MFI values since crosslinks could evolve between two polymers by Perkadox. However, with the same amount of Perkadox, PBAT contents increased in blends, so PLA/PBAT (70/30) led to higher MFI values.

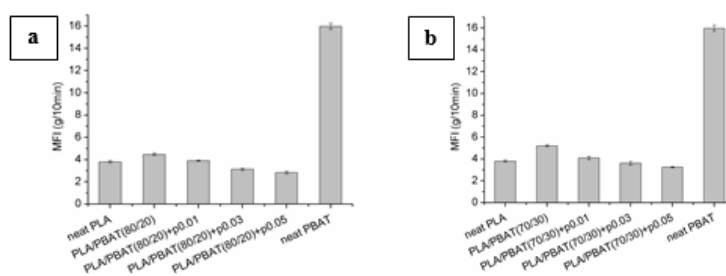


Figure 2. Melt flow index of neat PLA, neat PBAT and PLA/PBAT blends at various amounts of Perkadox (a) PLA/PBAT (80/20) blends and (b) PLA/PBAT (70/30) blends.

3.1.3. Tensile testing. Upon increasing PBAT contents in blends, Young's modulus and tensile strength decreased, but the elongation at break of the blends increased as demonstrated in figures 3(a) and 3(b), respectively. When the content of Perkadox in PLA/PBAT (70/30) increased, Young's modulus and tensile strength of the blends remained unchanged, whereas the elongation at break was slightly dropped when compared to PLA/PBAT without Perkadox probably due to the crosslinking reaction evolved by free radical reaction as indicated by the decrease in MFI values. As a result, blends with Perkadox were stiffer and more brittle than those without Perkadox. This finding was in good agreement with the elongation at break of PLA/PBAT (75/25) added 2, 5-Dimethyl-2, 5-di (tert-butylperoxy) hexane reported by Coltelli M-B, et al. [5]. For PLA/PBAT (80/20), when adding Perkadox, Young's modulus and tensile strength of blends were almost unchanged, but the elongation at break was slightly increased when compared to PLA/PBAT without Perkadox. The results could suggest that the interfacial adhesion between PLA and PBAT phases was improved.

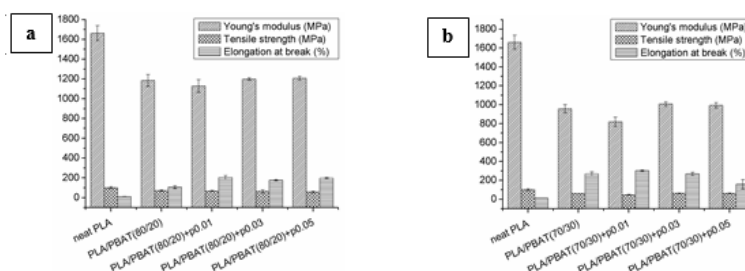


Figure 3. Young's modulus, tensile strength and elongation at break of neat PLA and PLA/PBAT blends (a) PLA/PBAT (80/20) blends and (b) PLA/PBAT (70/30) blends.

3.1.4. Impact testing. As expected, the impact strength of PLA/PBAT blend was higher than that of neat PLA due to the flexibility of chemical structure of PBAT. The addition of PBAT resulted in energy dissipation from PLA phase to PBAT phase because of the occurrence of very little adhesion between two phases [14]. The impact strength of PLA/PBAT (70/30) was almost two times higher than that of PLA/PBAT (80/20). The impact strength of PLA/PBAT (80/20) blends was insignificantly changed when adding greater amount of Perkadox (figure 4(a)). This result was similar to that reported by Nishida M, et al. [6]. They found that PLA/PBAT (80/20) with dialkyl peroxide 1 wt.% had the

similar impact strength to that of PLA/PBAT(80/20). However, the impact strength of PLA/PBAT (70/30) blends increased with the increasing amount of Perkadox. This may be due to the improvement of interfacial adhesion between PLA and PBAT phases (figure 4(b)). PLA/PBAT (70/30) + p0.05 had the highest impact strength of all samples. Its impact strength value was increased by about 110% (from 12.5 to 26.2 kJ/m²) when compared to non-reactive blend. The improvement of the impact strength by adding as high as 1 wt.% diakyl peroxide of 133% (from 10.0 to 23.3 kJ/m²) has been reported by other group [6]. Based on this finding, Perkadox was effective even at the very small amount.

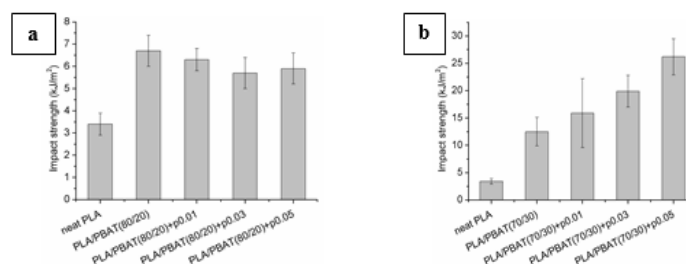


Figure 4. Impact strength of neat PLA and PLA/PBAT blends (a) PLA/PBAT (80/20) blends and (b) PLA/PBAT (70/30) blends.

3.2. PLA/PBAT blends with TBT

3.2.1. Morphology. SEM images of PLA/PBAT (80/20) blends (figures 5(a) and 5(b)) demonstrated more uniform PBAT phase than PLA/PBAT (70/30) blends (figures 5(c) and 5(d)). Adding TBT to both blend ratios, PBAT particles were smaller than the blends without TBT, which was in good agreement with Coltelli M-B, et al. [7]. They found that when adding TBT, the size of PBAT particles reduced from 0.95 to 0.75 μm (for PLA/PBAT (75/25) at 200°C and the mixing time 10 minutes in an internal mixer).

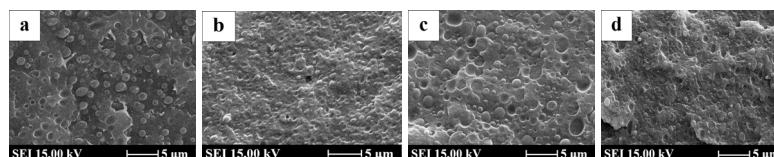


Figure 5. SEM micrographs of fractured surfaces. (a) PLA/PBAT (80/20), (b) PLA/PBAT (80/20)+T0.3, (c) PLA/PBAT(70/30) and (d) PLA/PBAT (70/30)+T0.3.

3.2.2. Melt flow index. From figure 6(a), the MFI values of PLA/PBAT (80/20) blends increased when increasing an amount of TBT, while those of PLA/PBAT (70/30) blends, however, remained almost constant (figure 6(b)). This suggested that the transesterification reaction did not change the viscosity of the blend, implying that the effect of TBT on the molecular weight was very small.

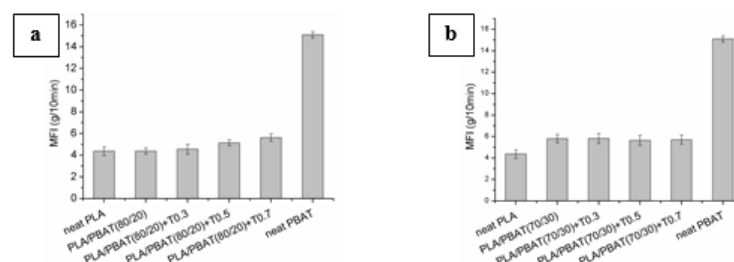


Figure 6. Melt flow index of PLA/PBAT blends with and without TBT. (a) PLA/PBAT (80/20) blends and (b) PLA/PBAT (70/30) blends.

3.2.3. Final torques. To ensure the complete reaction, torques of molten polymer blends were recorded in 15 minutes. The final torques were then taken to analyze the effect of TBT on the viscosity of blends. The final torques of PLA/PBAT blends with TBT were higher than that of PLA/PBAT blends without TBT. The results showed that the transesterification reaction could take place after 15 minutes (data not shown). Coltelli M-B [7] demonstrated that the reaction time of TBT in molten PLA/PBAT blend was around 20 minutes for the temperature of 200°C. For PLA/PBAT (80/20) blends, PLA/PBAT (80/20) + T0.3 had the highest final torque. For PLA/PBAT (70/30) blends, PLA/PBAT (70/30) + T0.5 had the highest final torque.

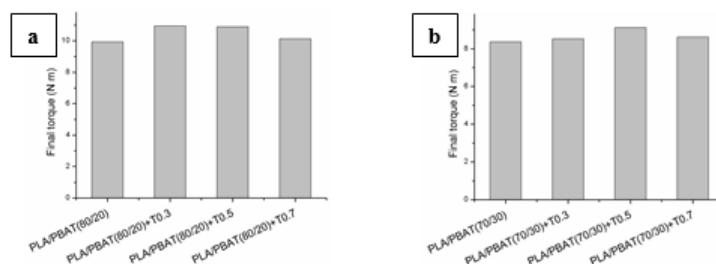


Figure 7. Final torques of PLA/PBAT blends with and without TBT (a) PLA/PBAT (80/20) blends and (b) PLA/PBAT (70/30) blends.

3.2.4. Tensile testing. Yong's modulus and tensile strength of PLA/PBAT blends with TBT were insignificantly different when compared to PLA/PBAT blends without TBT for both blend ratios. However, the elongation at break increased, particularly, PLA/PBAT (80/20) + T0.3 (from 188 to 262%) and PLA/PBAT (70/30) + T0.5 (from 191 to 221%) (figure 8(a)-(b)). These results indicated that the transesterification between PLA and PBAT reaction could occur [7] as also suggested in the final torque (figure 7). Girdthep S, et al. [11] found that the tensile strength of PLA/PBAT with and without TBT was not different, Young's modulus and the tensile strength were improved after the addition of TBT, particularly TBT 0.5 phr. In case of PLA/PBAT (80/20) with TBT less than 0.5 phr could improve the elongation at break of the blend, and the elongation at break of this blend was similar to that of PLA/PBAT (70/30) + T0.5.

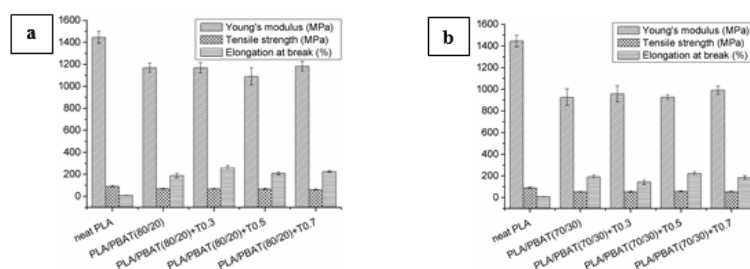


Figure 8. Young's modulus, tensile strength and elongation at break of PLA/PBAT with and without TBT (a) PLA/PBAT (80/20) blends and (b) PLA/PBAT (70/30) blends.

3.2.5. Impact testing. The impact strength of PLA/PBAT(80/20) blends dropped when increasing TBT content (figure 9(a)), which was in agreement with SEM images. In case of PLA/PBAT(70/30), the impact strength was not improved (figure 9(b)), which was in agreement with SEM images. The particle size of PBAT of PLA/PBAT(80/20)+T0.3 was larger than that of PLA/PBAT(80/20) without TBT (figure 10(a)-(b)). For PLA/PBAT(70/30), the particle sizes of PBAT of PLA/PBAT with and without TBT were not different. There were the cavities that were occurred by disengaging of dispersed phase from matrix (figure 10(c)-(d)). Furthermore, the interfacial adhesion between PLA and PBAT phases was poor despite adding TBT.

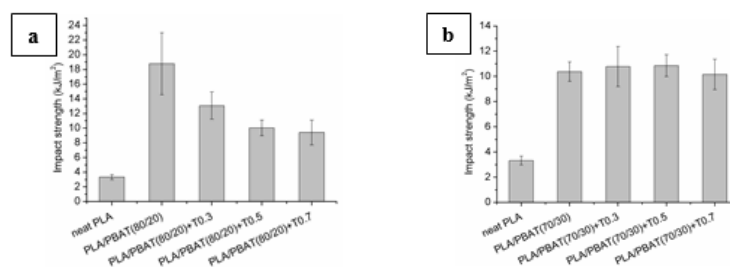


Figure 9. Impact strength of PLA/PBAT blends without and with TBT concentration (a) PLA/PBAT (80/20) blends and (b) PLA/PBAT (70/30) blends.

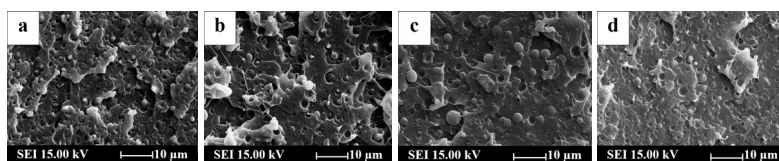


Figure 10. SEM micrograph of fractured surfaces from tensile testing (a) PLA/PBAT(80/20) (b) PLA/PBAT(80/20)+T0.3 (c) PLA/PBAT(70/30) (d) PLA/PBAT(70/30)+T0.3.

4. Conclusion

In case of PLA/PBAT blends with and without Perkadox, PLA, PBAT and Perkadox were blended in twin screw extruder. From SEM results, the particle sizes of PBAT phases of the blends with Perkadox were reduced from those of the blends without Perkadox for all blend ratios due to the improvement of interfacial adhesion between PLA and PBAT phases. The MFI values of all blend ratios were decreased when adding more Perkadox thanks to the crosslinking reaction. Although Young's modulus and the tensile strength of all blend ratios remained unchanged, the elongation at break tended to decrease when adding more Perkadox. The impact strength of PLA/PBAT (80/20) was unchanged even though the impact strength PLA/PBAT (70/30) was improved, increasing by 110% when adding Perkadox 0.5 phr. In case of PLA/PBAT blends with and without TBT, SEM results revealed that the particle sizes of PBAT phases of the blends with TBT were reduced when compared to those of the blends without TBT for all blend ratios due to the improvement of interfacial adhesion between PLA and PBAT phases through the transesterification reaction. Although Young's modulus and the tensile strength of all blend ratios were unchanged, the elongation at break tended to increase when adding TBT. The elongation at break of PLA/PBAT (80/20) was increased by 39% when adding TBT 0.3 phr while the elongation at break of PLA/PBAT (70/30) was increased by 15% when adding TBT 0.5 phr. The impact strength of all blend ratios was not improved.

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