A study on reactive blending of (poly lactic acid) and poly (butylene succinate co adipate)

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Abstract. This research aims to study the blending of Polylactic acid (PLA) and Polybutylene succinate co adipate (PBSA) in order to understand the role of peroxide in free radical reaction on the compatibilization between these two biodegradable polyesters. Various ratios of PLA/PBSA blends with and without reactive agents were prepared in the twin screw extruder. Two types of peroxides, Di (tert-butylperoxyisopropyl) benzene (DTBP) and 2, 5-Dimethyl-2, 5-(t-butylperoxy) hexane (DTBH), were used with various concentrations to compare. From the torques measurement, DTBP was more reactive with PLA and PBSA than DTBH. PLA and PBSA 80:20, 60:40, 50:50, 40:60, and 20:80% by weight were melt-blended in a twin screw extruder. The reactive polymer blends were also prepared for the same ratios of the blends with addition of 0.08 and 0.1 phr of DTBP. The mechanical, thermal, rheological, and morphological properties were investigated. The impact strengths of the non-reactive blend increased with the increasing in PBSA content. The optimal impact strength was obtained at 40%wt of PBSA with 0.1 phr of DTBP. Adding 0.08 and 0.1 phr of DTBP led to the co-continuous phase morphology of PLA/PBSA blends. The per cent crystallinity of PLA increased when blended with PBSA. PBSA might induce the crystallization of PLA.

1. Introduction
In the last two decades, biodegradable plastics based on renewable and non-renewable resources have been recognized as a solution to address the environmental pollution caused by the increase of non-degradable plastic wastes and the threat of oil depletion. Poly (lactic acid) (PLA) is one of the most popular biodegradable plastics being utilized in various applications due to its high tensile strength, good heat stability during processing, an excellent gloss and clarity. However, there are some drawbacks, including its brittleness and poor heat resistance when applied to the temperature above its glass transition temperature.

The simple approach to overcome the brittleness of PLA is the blending with others ductile biodegradable polymers, such as Poly (butylene succinate) (PBS), Poly (butylene succinate co adipate) (PBSA), Poly (caprolactone) (PCL), Poly (butylene adipate co butylene terephthalate) (PBAT). These choices of polymers have been readily studied. An important factor in polymer blends is the compatibility. Unfortunately, the above mentioned polymers and PLA are incompatible. PBSA is a promising biodegradable polymer because of its lower crystallinity and more polymer chain flexible so it is appropriate for various applications [1]. PBSA is commercially available aliphatic polyester

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with high flexibility, excellent impact strength, melt processibility, thermal, chemical resistance. Besides, PBSA has a low melting point of 90°C, which is more readily bio-degradable than others [2]. However, blending PLA with PBSA is not compatible so it is necessary to improve the compatibility between two phases. Sangmook Lee and Jae Wook Lee [2] investigated thermal properties and mechanical properties of binary blend of PLA and PBSA. They found that polymer blends had lower thermal stability than pure polymers. The modulus and tensile strength of polymer blends decreased when the content of PBSA increased. On the other hand, the impact strength of polymer blends was seriously increased higher than the rule of mixing.

Compatibilization through the in situ formation of compatibilizer in polymer blends has become increasingly important alternative to replace the method of adding block or graph copolymers [3]. Vincent Ojijo et al. [4] blended PLA/PBSA in a presence of triphenyl phosphate (TPP); they found that the torque values were increased after adding the TPP. When increased the TPP content, the dispersed phase size was reduced and PLA and PBSA were linked so they were improved the compatibility. Deyun Ji et al. [5] prepared the polymer blends of PLA/PBS in a reactive blending by using dicumyl peroxide (DCP) as a reactive agent. Some cross linked/blanched structures were formed according to the rheological measurement and gel fraction results. PLA-PBS copolymers of the reactive acted as a compatibilizer for PLA and PBS phase so the compatibility between PLA and PBS phase were improved [5].

The blended between PLA and PBSA is incompatible so the properties of PLA/PBSA blends could be deteriorated [4]. From the previous research, adding additives (e.g. triphenyl phosphate, dicumyl peroxide) could improve the compatibility and dispersity of polymer blends [4, 5]. Moreover there is no research that used the peroxides as the reactive agent for PLA/PBSA blends and it was found that PBS which had the same functional groups as PBSA could react with peroxide so it might indicate that PBSA can also reacts with peroxides. Thus the properties of PLA/PBSA might improve with a presence of Peroxides. The effect of Di (tert-butylperoxyisopropyl) benzene (DTBP) to PLA/PBSA blends has not been reported. Therefore, in this study, it aimed to study the properties of polymer blends (PLA/PBSA) in non-reactive and reactive blends. Peroxide (DTBP) was used as a reactive agent for PLA/PBSA blends. The mechanical, rheological, thermal, and morphological of non-reactive and reactive polymer blends were investigated.

2. Experimental

2.1. Materials
Poly (lactic acid) (PLA) was purchased from Nature Works, LLC, USA and Poly (butylene succinate co adipate) (PBSA grade; Bionolle® 3001D) was purchased from Showa High Polymer Co., Ltd., Japan. Both of polymers were in the form of pellet dried at 60°C for 5 hours before processing. Di (tert-butylperoxyisopropyl) benzene (DTBP) (Perkadox14s) having 40% of peroxide and 2, 5-Dimethyl-2, 5-(t-butylperoxy) hexane (DTBH) (Luperox 101 XL45) having 50% of peroxide were purchased from Akzo Nobel and Arkema Inc., respectively.

2.2. Melt-blend of PLA or PBSA with reactive agents
To investigate the reactivity between polymers and two types of peroxides (DTBP and DTBH), PLA and PBSA were melt-blended with each peroxide at 190°C in an internal mixer with screw speed 60 rpm. The torque values were detected in 10 minutes. The concentrations of peroxide varied from 0.1 to 1 phr.

2.3. Preparation of polymer blends.
The ratios of PLA: PBSA 80:20, 60:40, 50:50, 40:60, and 20:80 were weighted and melt-blended in a twin screw extruder. The temperature profile from feeding zone to die were 130/140/150/160/170/180/190°C and the screw speed was set at 80 rpm. The reactive blends were prepared by blending both of polymers with peroxide selected from 2.2, in this case0.08 and 0.1 phr of DTBP were used in the twin screw extruder with the same temperature profile as non-reactive PLA/PBSA blends. The symbol PBSA20 referred to 20%wt PBSA in the blend. The concentrations of Di (tert-butylperoxyisopropyl) benzene (DTBP) and 2, 5-Dimethyl-2, 5-(t-butylperoxy) hexane (DTBH) were written as Pxx and Lxx respectively (where xx is the concentration).
2.4. Melt flow index
Melt Flow Index (MFI) of polymer blends and neat polymers were investigated according to ASTM D1238. PLA/PBSA blends were characterized at 190°C, using 2.8 kN of load.

2.5. Fourier Transform Infrared Spectroscopy (FT-IR)
Fourier transformed infrared spectra of samples were detected over the range 400-4000 cm⁻¹, using Vertex70, Bruker, Germany. The samples were mixed with KBr and laminated.

2.6. Morphology
The morphology of non-reactive and reactive polymer blends was studied by Scanning Electron Microscope (SEM, made by Hitachi). The specimens were prepared from fractured surface of the impact testing specimens.

2.7. Mechanical properties
The modulus, elongation at break, and tensile strength of polymer blends were determined using Instron Crop, model 5969 with a load cell of 5 kN, according to ASTM D638-type IV with a rate at 10 mm/min at room temperature. For Impact testing, the specimens were tested according to ASTM D256 and using RESIL IMPACTOR, PIANEZZA-TORINO, Italy with a load 2.75 Jules.

2.8. Thermal Properties
Differential Scanning Calorimeter (DSC) was used to investigate the glass transition temperature and melting temperature of polymer blends. The samples were tested in the heat-cool-heat mode under the nitrogen atmosphere, with the heating and cooling rate at 5°C/min. The temperature was scanned from -60°C to 200°C. The crystallinity of polymer blends were calculated from followed equation [6].

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\%X_c = \frac{(\Delta H_m - \Delta H_{cc}) \times 100}{\Delta H_f^o \text{ fraction}}
\]

Where \(\Delta H_m\) is the enthalpy of fusion and \(\Delta H_{cc}\) is the enthalpy of crystallization which obtained from the second heating of DSC. \(\Delta H_f^o\) is the enthalpy of completed crystallization and the fraction means PLA or PBSA weight ratios of the polymer blend.

3. Results and Discussions

3.1. Effect of peroxide types on torque values of neat PLA and PBSA
PLA and PBSA were dried-mixed with DTBP (P) and DTBH (L) and transferred to an internal mixer at the same mixing temperature and rotor speed to investigate the reactivity of each polymer and reactive agent. Figure 1 showed the torque values of PLA after adding DTBP and DTBH. The torque values of PLA increased when the concentration of DTBP and DTBH reached 1 phr. For the same amount of peroxides, DTBP was more reactive with PLA than DTBH in agreement with final torques. Torques of PBSA mixed with peroxides was shown in figure 2, the torque values of PBSA increased with increased amount of peroxide. At 0.1 phr of peroxides, the torque value was lowest and it was highest when added 1 phr of peroxides for both DTBP and DTBH. The increase in torque values indicated an increase in melt viscosity. It could be speculated that there were possible crosslinking reactions during the melt-blending [5]. When compared DTBP and DTBH, DTBP was more reactive with PBSA than DTBH due to the higher final torque value as seen in figure 2. Thus, 0.1 phr of DTBP was selected as a reactive agent of PLA/PBSA blends.

3.2. PLA/PBSA blends

3.2.1. Melt Flow Index (MFI). Table 1 showed Melt Flow Index (MFI) of polymer blends in non-reactive and reactive blends. The MFI of the blends lied between neat PLA and PBSA as shown in table 1. After adding DTBP at 0.08 and 0.1 phr, MFI of reactive polymer blends decreased, implying the increase in viscosity of polymer blends. Peroxides could act as the crosslink promoter as observed in the increase in torque values.
Figure 1. Torque-time of PLA mixed with peroxides (DTBP (P), DTBH (L)) with various contents.

Figure 2. Torque-time of PBSA mixed with peroxides (DTBP (P), DTBH (L)) various contents.

Table 1. Melt flow index of polymer blends.

| Formulation | MFI (g/10 min) | DTBP 0.08phr | DTBP 0.1phr |
|-------------|----------------|---------------|--------------|
| Neat PLA    | non-reactive   | 4.13±0.33     | -            |
| PBSA20      | 3.92±0.47      | 3.24±0.29     | 2.58±0.37    |
| PBSA40      | 4.12±0.59      | 1.88±0.23     | 1.50±0.33    |
| PBSA50      | 3.89±0.48      | 1.55±0.14     | 0.96±0.31    |
| PBSA60      | 3.46±0.45      | 1.09±0.17     | 0.65±0.19    |
| PBSA80      | 3.92±0.39      | 0.46±0.20     | 0.25±0.09    |
| Neat PBSA   | 2.55±0.18      | -             | -            |

3.2.2. Fourier Transformation Infrared Spectroscopy (FT-IR). As seen in the figure 3, FT-IR spectra of PLA showed peaks at 2997.29 and 2945.91 cm⁻¹ which was corresponded to −CH₂ stretching vibration and peaks at 1752.92 cm⁻¹ and 1183.08 cm⁻¹ were assigned to −C=O and C-O stretching vibration respectively. FTIR spectra of PBSA located at 1744.42 and 1181.73 cm⁻¹ were assigned to C=O and C-O respectively. For the blends, the characteristic peaks of PLA and PBSA were appeared about 2900, 2800, and 1700 cm⁻¹ respectively. Besides, it was found that the peaks of −CH₂, C=O, and C-O of blends in a presence of DTBP shifted towards lower wavenumber. It might suggest that the interaction between PLA and PBSA existed upon blending. However, very low degree of possible crosslinking reaction was difficult to be detected by FTIR due to peaks overlapping.

Figure 3. FT-IR spectra of neat PLA, neat PBSA and non-reactive and reactive PLA/PBSA blends.

3.2.3. Morphology. Figure 4 showed SEM micrographs of non-reactive and reactive polymer blends from the fractured surface of impact specimens. Without adding DTBP, as shown in figures 4(a-e), the dispersed phase particles were larger in sizes (the particle size was 30 microns) and the particle sizes of dispersed phase increased with PBSA contents. It indicated that PLA and PBSA in non-reactive blends were not compatible. However, at 80% wt of PBSA, the separation between two phases was not clearly observed. When adding 0.08 and 0.1 phr of DTBP, the morphology of the blends changed as seen in figures 4(a′-e′) and figures 4(a″-e″). It was found that co-continuous
phase occurred upon adding the DTBP in 40\%wt of PBSA. In this case, PBSA became the matrix because the addition of peroxides resulted in higher viscosity of PBSA as compared to PLA so PLA was sheared easily and became the small dispersed phase. The increase of peroxides caused the better compatibility between PLA and PBSA.

3.2.4. Mechanical properties. As seen in figure 5, the impact strengths of non-reactive polymer blends remained almost unchanged. When PBSA content was 80\%wt, the impact strength increased dramatically and was even higher than the line of mixing rule. It indicated that there were better compatibility and dispersity in PLA/PBSA blends as seen in SEM micrographs (discussed in 3.2.3). The improvement of impact strength of polymer blends could be more pronounced when adding 0.08 and 0.1 phr of DTBP. Especially, when adding 0.1 phr of DTBP for 40\%wt. of PBSA, it was found that the impact strength reached 35 kJ/m\(^2\) (7 times higher than that of non-reactive blends at the same ratio). DTBP acted as an initiator for the possible partial crosslink reaction between PLA and PBSA, hence improving interfacial adhesion between the polymers. The impact strength increased with PBSA contents. At 40\%wt. of PBSA with 0.1 phr of DTBP, the inversion phase might occur as the PBSA had higher viscosity than PLA and could become the matrix. Thus, PBSA40 with a presence of 0.1 phr of DTBP had the similar impact strength as neat PBSA and its impact strength was higher than line of mixing rule.

The modulus of polymer blends decreased when PBSA contents increased as seen in figure 6 and the tensile strength showed the similar trends (figure 7) because PBSA is tougher than PLA. In

![Figure 4. SEM micrographs of fractured surface from impact testing (a-e) non-reactive PLA/PBSA blends, (a'-e') adding 0.08 phr of DTBP, and (a''-e'') PLA/PBSA with adding 0.1 phr of DTBP. (Under 2000x magnification).]
addition, it was found that adding 0.08 and 0.1 phr of DTBP caused the modulus and tensile strength of polymer blends to drop. The elongation at break of polymer blends increased when PBSA contents increased as shown in figure 8. For both non-reactive and reactive blends, the elongations at break were higher than the line of mixing rule. This implied that PBSA could improve the brittleness of PLA because of the elastic characteristic in PBSA. However, it was found that the elongation at break of polymer blends slightly decreased when adding 0.1 phr of DTBP.

Figure 5. Impact strength of polymer blends.  
Figure 6. Modulus of polymer blends.  
Figure 7. Tensile strength of polymer blends.  
Figure 8. Elongation at break of polymer blends.  
Non-reactive, \(0.08\) phr, and \(0.1\) phr of DTBP

Table 2. Thermal properties of polymer blends obtained from 2\(^{nd}\) heating of DSC thermograms.

| Formulation   | \(T_g\) (°C) | \(T_c\) (°C) | \(T_m\) (°C) | \(H_m\) (J/g) | \(\%X_c\) |
|---------------|--------------|--------------|--------------|---------------|-----------|
|               | PBSA         | PLA          | PBSA         | PLA           | PBSA      | PLA       | PBSA      | PLA       |
| neat PLA      | -            | 61.91        | -            | -             | 147.4     | 153.1     | -         | 28.26     | -         | 4.108     |
| PBSA20        | -50.69       | 60.6         | -            | -             | 91.57     | 146.6     | 152.6     | 11.09     | 27.48     | 39.05     | 19.44     |
| PBSA40        | -44.85       | 62.03        | 59.45        | -             | 82.33     | 92.28     | 146.9     | 152.5     | 16.39     | 17.6      | 28.86     | 12.22     |
| PBSA50        | -44.3        | 60.37        | 59.09        | -             | 82.06     | 92.52     | 147.3     | 152.7     | 17.96     | 12.18     | 25.3      | 5.763     |
| PBSA60        | -42.77       | 59.76        | 59.26        | -             | 81.98     | 92.5      | 147.5     | -         | 23.09     | 10.98     | 27.1      | 7.5       |
| PBSA80        | -43.16       | 56.89        | 59.42        | -             | 81.84     | 92.27     | 146.4     | 151.6     | 26.45     | 5.71      | 23.28     | 6.129     |
| PBSA20+P0.08  | -            | 60.45        | 65.49        | -             | 91.06     | 145.2     | 152.9     | 10.29     | 26.53     | 36.23     | 18.8      |
| PBSA40+P0.08  | -45.63       | 60.24        | 64.73        | -             | 85.05     | 91.62     | 146.1     | 152.9     | 14.47     | 17.94     | 25.48     | 11.52     |
| PBSA50+P0.08  | -43.26       | 60.44        | 65.73        | -             | 86.18     | 92.09     | 146.4     | 153.3     | 17        | 11.93     | 23.94     | 7.806     |
| PBSA60+P0.08  | -44.21       | 59.67        | 65.67        | -             | 85.21     | 92.11     | 146.1     | 153.1     | 20.86     | 14.02     | 24.48     | 11.18     |
| PBSA80+P0.08  | -43.42       | -            | 68.43        | -             | 88.11     | 144.7     | 152.3     | 46.47     | 4.66      | 40.91     | 8.118     |
| PBSA20+P0.1   | -            | 60.42        | 65.79        | -             | 91.04     | 145.7     | 153.1     | 6.63      | 21.84     | 23.35     | 11.68     |
| PBSA40+P0.1   | -45.33       | 60.33        | 65.38        | -             | 85.23     | 91.48     | 146       | 152.9     | 15.64     | 15.63     | 27.54     | 7.258     |
| PBSA50+P0.1   | -43.86       | 60.01        | 67.04        | -             | 87.18     | -         | 145.9     | 153       | 17.78     | 9.95      | 25.04     | 6.473     |
| PBSA60+P0.1   | -43.68       | 60.16        | 67.25        | -             | 87.95     | -         | 145.7     | 152.9     | 19.83     | 7.59      | 23.27     | 8.161     |
| PBSA80+P0.1   | -43.16       | -            | 68.57        | -             | 88.95     | -         | 144.8     | 152.3     | 25.69     | 4.04      | 22.61     | 9.14      |
| neat PBSA     | -43.16       | -            | 60.04        | -             | 82.98     | 92.58     | -         | 51.8      | -         | 36.48     | -         |

\(^1\)Heat of fusion of PLA and PBSA are 93 J/g [6] and 142 J/g [7], respectively.
3.2.5. Thermal properties. Table 2 showed the results of DSC from second heating scans. It was found that the glass transition temperature of PBSA and PLA were about -43°C and 61°C respectively and there were no differences of the results after blending them together. It suggested that PLA/PBSA blends were immiscible. When considering the cool crystallization temperatures (T_c), T_c of all blends with 0.08 and 0.1 phr increased, especially when PBSA contents increased. However, PLA did not show the cool crystallization temperature because of its slow crystallization rate. The melting temperature (T_m) of PBSA was 92°C. After PBSA was blended with PLA, there were no differences of T_m between pure polymer and polymer blends. Moreover, PBSA showed two peaks of melting temperature corresponding to re-melting of newly formed crystalline. PLA showed T_m which remained constant for both non-reactive and reactive blends. The addition of DTBP did not affect the melting temperature of polymer blends. The percent crystallinity (%X_c) of PLA in non-reactive blends was found to be increased. It might be due to the fact that PBSA was able to crystallize easily so it might induce the crystallization of PLA. Adding 0.08 and 0.1 phr of DTBP caused the decrease of the percent crystallinity of PLA in PLA/PBSA blends because possible crosslink might hinder the crystallization of PLA. The percent crystallinity of PBSA could not be accurately measured because the heat of fusion of PBSA overlapped with the heat of cold crystallization of PLA.

4. Conclusion
In this research, it aimed to study the properties of polymer blends in non-reactive and reactive blending. The effect of two types of peroxides and amount of peroxides on torque values was analyzed and it was found that DTBP was more reactive with PLA and PBSA than DTBH under specified blending condition as DTBP revealed higher torque value. For the impact testing, adding 0.1 phr of DTBP into PBSA40 could increase the impact strength dramatically. The interfacial adhesion and viscosity of PLA/PBSA blends could be improved. SEM micrographs showed the morphology close to co-continuous phase with a presence of DTBP. Furthermore, the elongation at break of polymer blends was improved when PBSA contents increased for both non-reactive and reactive blends. For thermal properties, blending the PLA with PBSA could increase the percent crystallinity of PLA. The percent crystallinity of PLA in reactive blends decreased when compared with non-reactive blends for all ratios.

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