Effect of peroxide and chain extender on mechanical properties and morphology of poly (butylene succinate)/poly (lactic acid) blends

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Abstract. Poly (butylene succinate) (PBS) and poly (lactic acid) (PLA) are biodegradable polymers with high potential to replace commodity fossil-based polymers in a wide range of applications. However, these two polymers are immiscible in most ratios, but partially miscible when one of the two is a major phase. In this study, a one-step process in a twin-screw extruder was used to prepare the blends between poly (butylene succinate) (PBS) as a matrix and poly (lactic acid) (PLA) as a dispersed phase. To improve mechanical properties and morphology of blends, two reactive agents, peroxide (Perkadox) and multifunctional epoxide chain extender (Joncryl) were selected and compared. All samples were characterized for melt flow index (MFI), morphology, tensile, and impact properties. The results showed that the mechanical properties and morphology of PBS/PLA blends were improved when using both reactive agents. It was demonstrated that the increased mechanical properties resulted from good interfacial adhesion between PBS and finely dispersed PLA particles. The addition of 0.075 phr Perkadox to PBS/PLA (75:25 and 80:20) blends increased elongation at break by 7.2% and 38.4%, respectively compared with the blends without reactive agents. The results from gel content also revealed the graft copolymer existed at the interface when reactive agents were added. In the case of using multifunctional epoxide chain extender, the impact strength of the blends increased.

1. Introduction

In recent years, environmental pollution and the great depletion of non-renewable fossil resource have been increasingly concerned. The accumulation of non-biodegradable plastic wastes disposed daily leads to land and air pollution. One possible solution to this problem is to replace the commodity non-biodegradable fossil-based polymers with the renewable polymers or biodegradable polymers, which are readily susceptible to microbial action. Such biodegradable polymers are produced and processed to a wide spectrum of products, offering an alternative to fossil-based plastics [1-3]. Among biodegradable polymers, poly (butylene succinate) (PBS) is a popular choice due to its good...
mechanical strength and wide availability in an industrial scale. It is a renewable and fully-degradable plastic. It has high flexibility, impact strength, and thermal and chemical resistance but has low melt strength and is still expensive. Blending PBS with other biodegradable polyester can allow the fine-tuning of process ability of raw materials and properties of products. For most of the commercially biodegradable polymers, PLA is an interesting blend pair for PBS. PLA possesses high mechanical properties and is inexpensive. Moreover, PLA has recently been applied in various end-use applications [4-7].

A blend between PBS and PLA is partially miscible with the blend ratio of PBS/PLA up to 80/20 wt% [1]. PLA can offer strength and stability of PBS. However, the elongation at break of the blends decreases with the increasing PLA content [1, 6]. Mechanical properties of PBS/PLA blends strongly rely on the interfacial adhesion. Therefore, effective compatibilizers must be located at the interface for giving a low interfacial tension and a fine morphology of dispersed phase in the blend.

In order to achieve good compatibility of aliphatic polyesters, many methods such as non-reactive and reactive blending, copolymer synthesis and the addition of additives [8] were proposed. The superior compatibility of biodegradable polymer could be produced by adding reactive agents or grafting chemicals onto polymer backbone [9]. Many authors have reported the use of reactive agents in PBS/PLA blends such as dicumyl peroxide (DCP) [2], 2,5-dimethyl-2,5-dinitro (tertbutylperoxy) hexane [10], isocyanate [11], Ti(OiPr)₄ [12], Ti(OBu)₄ [12], and multifunctional epoxide [13]. The main advantages of reactive blending process include one-step process, cost-effectiveness and easy-to-handle features. The reactive can be selected relevant to polymers and processing parameters. Therefore, the aim of this work was to study the effect of two reactive agents on the mechanical properties and morphology of PBS/PLA (75:25 and 80:20). Two types of reactive agents, namely, peroxide (Perkadox 14-40B-PD) and multifunctional epoxide chain extender (Joncryl™ ADR-4368) with varying contents, were selected for comparison. Mechanical properties and morphology of PBS/PLA (75:25 and 80:20) were investigated and discussed. Gel content was determined to confirm the possible reactions.

2. Experimental

2.1. Materials

PBS (GS Pla FZ91PD) with MFI of 11 g/10 min (190°C, 2.16 kg) was purchased from the Mitsubishi Chemical Corporation (Japan). PLA (4043D) with a MFI of 2 g/10 min (190°C, 2.16 kg) was purchased from Nature Works LLC (USA). Di (tert-butylperoxyisopropyl) benzene (Perkadox 14-40B-PD), was purchased from Akzo Nobel (Netherlands). The peroxide initiator was absorbed on silica and calcium carbonate powder having reactive content of about 40%. The chain extender (Joncryl™ ADR-4368) was purchased from BASF The Chemical Co. (Thailand). The chain extender in solid flake had high epoxy functionality.

2.2. Preparation of PBS/PLA blends

PBS and PLA pellets were first dried at 60°C for 5 hours before further use. The ratios of PBS and PLA were 75:25 and 80:20 by weight. PBS, PLA and reactive agents were weighted and premixed prior to transferring to a twin-screw extruder (SHJ-25, China). The extrusion temperature was controlled with temperature profile being 100/130/140/150/160/170/180/195°C from feed zone to die exit. The screw speed was set at 100 rpm. The extruder was cooled in the water bath, then granulated and dried at 60°C for 12 hours. Two reactive agents systems, free radical reaction (Perkadox) and condensation reaction (Joncryl), were used for comparison. Reactive agents at various loading per 100 g of PBS/PLA blends were 0.0025, 0.0050, and 0.0075 phr for Perkadox system and 0.5, 1.0, and 1.5 phr for Joncryl system, respectively. PBS/PLA blend with Perkadox was referred to as Px and Joncryl as Jx, where x was the amount of reactive agents per 100g of blends. For instance, P0.0025 refers to a blend with 0.0025 phr of perkadox. A non-reactive PBS/PLA blend was prepared by using the identical procedure for comparison and denoted as PBS/PLA.
2.3. Characterization

2.2.1. Melt flow index. Melt flow index (MFI) of all samples was performed on a melt flow indexer (Intro D7053, KAYENNESS) operating at 190°C with 2.16 kg load according to ASTM D1238.

2.2.2. Morphology. Scanning electron microscope (SEM) (Camscan MX-2000) was used to characterize the phase morphology and compatibility of PBS/PLA blends. The fracture surface was coated with sputtered gold and an accelerating voltage of 15 kV was used to produce the SEM photographs.

2.2.3. Mechanical properties. Notched Izod impact strength was tested according to ASTM D256 (ZwickB5102.202, Izod type). Tensile properties were measured using Universal Testing Machine (Instron 5969, Instron) according to ASTM D638, specimen type I. The specimens were tested at a cross-head speed of 50 mm/min.

2.2.4. Gel content analysis. To investigate the change in physical properties due to possible reactions, gel content test was measured using 1 g of PBS/PLA blends (with various reactive agents), which was thoroughly shaken with 20 ml dichloromethane and then left to rest at room temperature for 18 hours. PBS and PLA were removed from extraction residues. The residues were filtered through a 120-mesh sieve. Finally, the obtained residues were dried in an oven before calculating gel contents in each sample and performing FTIR analysis. The gel content (%) was calculated via equation (1).

\[
%\text{gel content} = \frac{W_2 - W_3}{W_3} \times 100
\]  

Where \(W_2\) denoted the weight of the sample and the cage after extraction and drying, \(W_2\) was the weight of cage, and \(W_3\) referred to weight of original sample.

3. Results and discussion

3.1. Melt flow index

From figure 1, MFI value of PBS/PLA (80:20) blend was similar to that of PBS/PLA (75:25) blend. MFI value of PBS/PLA (75:25) blends was 6.92 g/10min whereas PBS/PLA blends with reactive agents (P0.0025, P0.0050, P0.0075, J0.5, J1.0, and J1.5) expressed lower MFI values. Interestingly, MFI value was significantly decreased in the case of the blend with Perkadox (P) 0.0075 phr consisting of higher PLA content (grey bar, PBS/PLA(75:25)) (from 6.92 to 1.42 g/10 min), while the addition of Joncryl (J) 1.5 phr in the same composition of PBS/PLA(75:25) decreased the MFI value to 1.65 g/10 min. This indicated that some reactions in the blend with Perkadox and Joncryl were likely to occur.

![Figure 1. MFI of PBS/PLA blends at various contents of reactive agents.](image-url)
3.2. Morphology

SEM micrographs of PBS/PLA (75:25) blend were shown in figure 2. The dispersion of PLA particles within the PBS matrix was less than 1 µm. The voids between PBS matrix and dispersed PLA particles could be observed in figure 2(a), indicating the poor interface between two polymers. In the case of PBS/PLA (75:25) blend at low contents of Perkadox between 0.0025-0.0075 phr (figures 2(b), 2(c) and 2(d), respectively), PLA particles were finely and uniformly dispersed in PBS matrix and showed a better interfacial adhesion than the blend without Perkadox. Considering the addition of Joncryl between 0.5-1.5 phr (figures 2(e)-2(g) for PBS/PLA (75:25) blend, PLA particles were dispersed in PBS matrix with fine particle sizes. Compared with the systems consisting of Perkadox with Joncryl, Perkadox system demonstrated a better interfacial adhesion, whereas Joncryl system only provided a fine dispersion phase. Similar results were also observed for SEM micrographs of PBS/PLA (80:20) blend at various contents of reactive agents in figure 3. Therefore, the addition of two reactive agents, namely, Perkadox and Joncryl, to PBS/PLA blends is likely to improve the morphology compared with non-reactive PBS/PLA blend.

![Figure 2](image1.png)

**Figure 2.** SEM micrographs of the fracture surface of PBS/PLA(75:25) blends at various contents of reactive agents(a) non-reactive agent, (b) Perkadox 0.0025 phr, (c) Perkadox 0.0075 phr, (d) Perkadox 0.0100 phr, (e) Joncryl 0.5 phr, (f) Joncryl 1.0 phr, and (g) Joncryl 1.5 phr.

![Figure 3](image2.png)

**Figure 3.** SEM micrographs of the fracture surface of PBS/PLA(80:20) blends at various contents of reactive agents(a) non-reactive agent, (b) Perkadox 0.0025 phr, (c) Perkadox 0.0075 phr, (d) Perkadox 0.0100 phr, (e) Joncryl 0.5 phr, (f) Joncryl 1.0 phr, and (g) Joncryl 1.5 phr.

3.3. Mechanical properties

According to two selected reactive systems, the effect of reactive agents on the mechanical properties of PBS/PLA blends was investigated. The impact strength was shown in figure 4. From figure 4, the
impact strengths of PBS/PLA 75:25 and 80:20 blends were 5.98 and 6.97 kJ/m² respectively. The impact strength increased with the increasing Perkadox and Joncryl contents. The reactive agents systems, having Perkadox content between 0.0025 and 0.0075 phr, and having Joncryl content between 0.5 and 1.5 phr, clearly improved the impact strengths of PBS/PLA blends. This could be due to the free radical reaction of peroxide (Perkadox) with PBS/PLA to form the long branched structures or lightly crosslinked structures, whereas multifunctional epoxides of Joncryl could react with PBS/PLA providing the long linear of reconnected PBS/PLA chain. Therefore, they exhibited the difference in the improvement of impact strength compared with non-reactive agents.

The modulus, tensile strength, and elongation at break were characterized as shown in figures 5-7. Modulus, tensile strength, and elongation at break increased with the increasing Perkadox contents. From figure 5, modulus of PBS/PLA 75:25 and 80:20 blends were 653 and 636 MPa, respectively. A Perkadox system improved the modulus, tensile strength, and elongation at break of PBS/PLA blends, whereas for the Joncryl system, modulus remained almost unchanged with the increasing Joncryl contents while tensile strength and elongation at break decreased. In the case of the addition of Joncryl, the modulus, tensile strength, and elongation at break of PBS/PLA blends were unaffected.

![Figure 4](image1.png) **Figure 4.** Impact strengths of PBS/PLA blends at various contents of reactive agents.

![Figure 5](image2.png) **Figure 5.** Modulus of PBS/PLA blends at various contents of reactive agents.

![Figure 6](image3.png) **Figure 6.** Tensile strength of PBS/PLA blends at various contents of reactive agents.

![Figure 7](image4.png) **Figure 7.** Elongation at break of PBS/PLA blends at various contents of reactive agents.

### 3.4. Gel content tests

It was evident that with the addition of Perkadox or Joncryl, the melt viscosity changed significantly. This implied possible reactions such as crosslink or branching. Gel content analysis was then performed to prove the physical changes of PBS/PLA blends with reactive agents. Any changes in chemical structures can result in the poor dissolution in the good solvent. Figure 8 represented the gel contents of PBS/PLA blends at various contents of reactive agents. Crosslinked polymers would give more gel contents in polymer blends, which were obtained after removing PBS and PLA by dichloromethane. The gel was not dissolved in dichloromethane. All of the blends showed low gel content (less than 10%), but it increased with the added amount of reactive agents. A small gel fraction
could arise from possible crosslinked phase, branching structures and some graft copolymers in the blends.

![Figure 8](image)

**Figure 8.** Gel contents of PBS/PLA blends at various contents of reactive agents.

The gel fractions of PBS/PLA blend from the extraction method were characterized by Fourier Transform Infrared Spectroscopy (FTIR), and compared with the PBS and PLA as shown in figures 9 and 10. The FTIR spectrum of PBS showed the characteristic at peak 1739 cm\(^{-1}\) and 1170 cm\(^{-1}\) corresponding to carbonyl (C=O) groups and C-O stretching, respectively. The FTIR characteristic peaks of PLA were about 3157 cm\(^{-1}\) and 1406 cm\(^{-1}\) assigning to –OH stretch, and C-O, respectively. The FTIR spectra of the gel fractions from the reactive blends showed both characteristics of PBS and PLA. It indicated that the gel fraction contained a small portion of possible PBS-g-PLA (graft copolymer). This graft copolymer might be located at the interface of PBS and PLA, which led to the better interfacial adhesion between two polymers when reactive agents were added. Consequently, mechanical properties were improved.

![Figure 9](image)

**Figure 9.** FTIR spectra of PBS/PLA (75/25) blend at various contents of (a) Perkadox and (b) Joncryl.

![Figure 10](image)

**Figure 10.** FTIR spectra of PBS/PLA (80/20) blend at various contents of (a) Perkadox and (b) Joncryl.
4. Conclusion
The addition of two reactive agents, Perkadox and Joncryl, into PBS/PLA blends improves the mechanical properties and morphology. The peroxide is likely to react with PBS/PLA via free radical reaction to form the long branched structures or lightly crosslinked structures whereas multifunctional epoxides (Joncryl) is prone to react with PBS/PLA to form the long linear of reconnected PBS/PLA chain. Therefore, they exhibit the differences in the improvement of impact strength and morphology compared with non-reactive agents. The results from gel content test and FTIR spectra reveal the formation of graft-copolymer at the interface of PBS and PLA when reactive agents are added. The slightly crosslinked polymers could be formed as suggested by low gel content. In addition, the addition of both reactive agents in PBS/PLA blends also improves the impact strength and morphology. Therefore, the reactive agents have the great potential to be used in PBS/PLA blends.

Acknowledgments
The authors would like to gratefully thank National Research Council Thailand (NRCT) and Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, and Silpakorn University, Thailand for financial supports.

References
[1] Bhatia A, Gupta R K, Bhattacharya S N and Choi H J 2007 Korea-Aust. Rheol. J 19 125-31
[2] Wang R, Wang S, Zhang Y, Wan C and Ma P 2009 Polym. Eng. Sci. 26-33
[3] Sotho K 2013 Properties of Poly (Butylene Succinate) Base Blends via Reactive Extrusion (Silpakorn University: Faculty of Engineering and Industrial Technology)
[4] Corporation M C GS Pla properties sheet. Available at: https://www.pttpm-techinfo.com/DownloadProduct.aspx, 2013
[5] LLC N 2010 Material Safety Data Sheet: 4043D. Available at: www.natureworksllc.com/media/Technical_Resources/Technical_Data_Sheets/TechnicalDataSheet_4032D_films_pdf, 2015
[6] Yokohara T and Yamaguchi M 2008 Eur. Polym. J. 44 677-85
[7] Wilcox-Barsalou M 2010 Two concepts of Bioplastics–Degradability and Renewability. Available at: plasticsandtheplanet.com/archives/343, October 18, 2010
[8] Bicerano J 2010 A Practical Guide to Polymeric Compatibilizers for Polymer blends. Available at: www.plas2006.com/uploadfile/20063112235119.doc, 2010
[9] Ma P, Hristova-Bogaerds G D, Lemstra P J, Zhang Y and Wang S 2012 Macromol. Mater. Eng. 297 402-10
[10] Coltelli M-B, Bronco S and Chinea C 2010 Polym. Degrad. Stabil. 95 332-4
[11] Yang S-L, Wu Z-H, Yang W and Yang M-B 2008 Polym. Test. 27 957-63
[12] Moura I, Nogueira R, Bounor-Legare V and Machado A V 2012 Mater. Chem. Phys. 134 103-10
[13] Al-Itry R, Lamnawar K and Maazouz A 2002 Polym. Degrad. Stabil. 97 1898-914