

การวิเคราะห์ผลของวัสดุเชิงประกอบระหว่างพอลิแลคติกแอซิดและพอลิบิวทิลีน ซัคซิเนต เมื่อเติมสารช่วยยืดสายโซ่โมเลกุล

Characterization of Polymer Composites between Poly (lactic acid) and Poly (butylene succinate) with Chain Extender

อรปรียา เวียงอินทร์¹, ยศฐา ศรีเทพ^{2*}

Onpreeya Veang-in¹, Yottha Srithep^{2*}

Received: 31 October 2016 ; Accepted: 12 January 2017

บทคัดย่อ

งานวิจัยนี้ได้ทำการศึกษสมบัติทางกลและปรับปรุงความเข้ากันได้ของพอลิแลคติกแอซิด (PLA) และพอลิบิวทิลีนซัคซิเนต (PBS) ซึ่งเป็นพอลิเมอร์ย่อยสลายได้ตามธรรมชาติ ผสมสารยืดสายโซ่โมเลกุลโดยเครื่องเอ็กซ์ทรูเดอร์สกรูเดี่ยวที่อุณหภูมิ 160-190 องศาเซลเซียส จากนั้นทำการฉีดขึ้นรูปชิ้นงานที่อุณหภูมิ 190 องศาเซลเซียส โดยศึกษาผลกระทบของสารยืดสายโซ่โมเลกุลที่ปริมาณร้อยละ 0-4 โดยน้ำหนัก ที่มีผลต่อสมบัติทางกล พฤติกรรมทางความร้อนและ สัณฐานวิทยาของ PLA โดยผสม PBS ที่อัตราส่วนร้อยละ 10-50 โดยน้ำหนัก แล้วทำการวิเคราะห์ทดสอบวัสดุด้วยวิธี Differential Scanning Calorimetry เพื่อศึกษาการเปลี่ยนแปลงของอุณหภูมิแก้ว (T_g) อุณหภูมิหลอมเหลว (T_m) และเปอร์เซ็นต์ความเป็นผลึกของสาร ($\% \lambda_c$) ของวัสดุผสม ซึ่งพบว่าเมื่อเพิ่มปริมาณสารยืดสายโซ่โมเลกุลส่งผลให้ค่า T_g , T_m และ $\% \lambda_c$ ของวัสดุผสมมีแนวโน้มลดลง เมื่อศึกษาลักษณะทางสัณฐานวิทยาของพื้นผิววัสดุผสมโดยใช้กล้องจุลทรรศน์อิเล็กตรอน (SEM) พบว่ามีความแตกต่างทางสัณฐานวิทยาอย่างชัดเจนขึ้นอยู่กับอัตราส่วนผสม และพบว่าเกิดการแยกเฟสระหว่าง PLA และ PBS เกิดขึ้นเมื่อปริมาณ PBS เพิ่มขึ้น อย่างไรก็ตามสารยืดสายโซ่โมเลกุลสามารถปรับปรุงความเข้ากันได้ของวัสดุผสมระหว่าง PLA และ PBS ได้เป็นอย่างดี สำหรับตัวอย่าง PLA ผสม PBS ร้อยละ 50 โดยน้ำหนัก เมื่อทำการทดสอบแรงดึงพบว่าวัสดุเกิดการยืดตัวที่จุดขาดเพิ่มขึ้น 600% และมีความเสถียรภาพทางความร้อนที่เพิ่มขึ้นอย่างมีนัยสำคัญที่ปริมาณ สารยืดสายโซ่โมเลกุลร้อยละ 4 โดยน้ำหนัก แต่ค่าโมดูลัสและความต้านทานแรงดึงลดลง ในขณะที่ต้องการใช้งานทั้งความต้านทานแรงดึงและความเหนียวควรใช้ PLA และ PBS ที่ผสมกับสารยืดสายโซ่โมเลกุลร้อยละ 2 โดยน้ำหนัก ซึ่งให้ผลว่ามีความต้านทานแรงดึงและความเหนียวของวัสดุในระดับปานกลาง

คำสำคัญ: พอลิแลคติกแอซิด พอลิบิวทิลีนซัคซิเนต สารยืดสายโซ่โมเลกุล พอลิเมอร์ผสม

Abstract

Poly (lactic acid) (PLA) and poly(butylene succinate) (PBS) for biodegradable polymers composites with chain extenders were melt blended in a single screw extruder at 160-190°C. The blended materials were then processed at 190°C by injection molding to produce tensile specimens. The effect of chain extenders (0 to 4 wt%) on mechanical and thermal properties of PLA and PBS (10 to 50 wt%) blends was studied. Differential scanning calorimetry was used to study glass transition temperature (T_g), melting temperature (T_m) and degree of crystallinity ($\% \lambda_c$) of the blends. Adding chain extender resulted in the decrease of T_g , T_m and $\% \lambda_c$ of both PLA and PBS. The morphology of fractured surface was examined using scanning electron microscopy (SEM) and showed clear phase differences depending on blend compositions. Phase separation between PLA and PBS occurred as PBS composition increased. However, chain extender improved miscibility of the PLA/PBS blends. For PLA/50%PBS

¹ นิสิตปริญญาโท, ²ผู้ช่วยศาสตราจารย์, สาขาวิชาวิศวกรรมการผลิต, คณะวิศวกรรมศาสตร์ มหาวิทยาลัยมหาสารคาม จังหวัดมหาสารคาม 44150

¹ Graduate student, ²Asst. Prof., Department of Manufacturing Engineering, Faculty of Engineering, Mahasarakham University, Mahasarakham 44150, Thailand., ^{2*}Corresponding author, Email: yottha.s@msu.ac.th

sample, tensile tests showed the elongation at break increased by 600% and thermal stability increased significantly with added 4 wt% chain extender but the Young's modulus and tensile strength decreased. Applications requiring both tensile strength and ductility should use PLA/PBS blends with 2 wt% of chain extender, which provides moderate tensile strength and ductility of the PLA.

Keywords: poly(lactic acid), poly(butylene succinate), chain extender, composite

Introduction

Biodegradable polymers from renewable sources such as poly(lactic acid) (PLA), poly(butylene succinate) (PBS) or degradable polymers from petroleum sources such as poly(butylene adipate/terephthalate) (PBAT), poly(ethylene terephthalate/succinate) (PETS) and poly(ϵ -caprolactone) (PCL) have been studied by various researchers.¹⁻³ PLA is a biodegradable thermoplastic polyester derived from biomass, such as sugar, corn and beet, which possesses good physical and mechanical properties combined with biocompatibility and biodegradability.^{4,5} Particular interest is the reinforcement of PLA because the thermal properties, toughness, water vapor and gas barrier properties of PLA are inferior to those of conventional petroleum based polymers.^{6,7} One strategy to tailor the properties of PLA is combining the polymer with reinforcing elements.

The blending of conventional polymers has been extensively used to develop new polymeric materials. Blending PLA with other polymers is a practical and economic way to toughen PLA. Elastomers have commonly been considered as efficient tougheners for plastics. The elastomer particles behave as stress concentrators enhancing the fracture energy absorption of brittle polymers and ultimately result in a toughened material. Numerous elastomers have been blended with PLA, such as thermoplastic polyurethane (TPU). Such immiscible blends exhibit different types of heterogeneous morphology, which depends on the blend composition, interfacial tension, processing condition and rheological properties of the component.⁸

PBS is biodegradable aliphatic polyester produced by polycondensation of 1,4-butanediol with succinic acid.⁹ It has high flexibility, impact strength, thermal and chemical resistance.¹¹ It can be blended easily with PLA. Several PLA/PBS blends have been investigated.³ However, simple blending of PLA and PBS may produce a phase-

separated PLA/PBS mixture; therefore efforts have been made to improve the compatibility between PLA and PBS.¹²

We aimed to produce a blend of PLA and PBS by addition of an epoxy based chain extender. We focused on the influence of a chain extender on the mechanical and thermal properties of PLA/PBS blends. Such a blend would be expected to provide a better compatibility.

Experimental details

Materials

PLA 3051D, a NatureWorks LLC product, was designed for injection molding applications where the requirements are clarity with heat deflection temperatures lower than 55 °C, Melt Flow Index is 1.12 g/10 min (155 °C, 2.16 kg) were measured following ASTM D1238, T_m about 150 – 165 °C and T_g about 55-65 °C.

The other biodegradable polyester used PBS (gradeAZ71TN), supplied by Mitsubishi Chemical Corporation, Japan. PBS melting point is 115°C. Its density is 1.26 g/cm³ and Melt Flow Index is 220 g/10 min (155 °C, 2.16 kg).

Chain extender (Joncryl® ADR 4368-C from BASF (USA)) is a compound of hydroxyl, carboxylic acid, anhydride, amine and epoxy groups. Figure 1 shows schematically the multi-functional chain extension concept.¹³

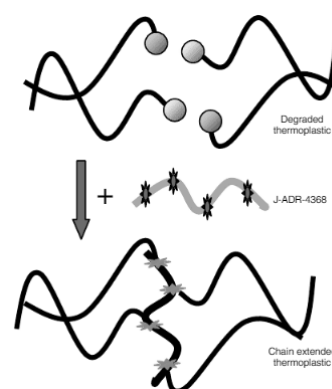


Figure 1 Schematic representation and the principal of chain extension

Blend preparation

Before blending, PLA and PBS were dried in vacuum oven at 80°C for 3 hours to remove moisture. The PLA, PBS and PLA/PBS (90/10, 70/30, 50/50) blends with 0, 2 and 4 wt% chain extender (C) were processed at 100 rpm and 190°C in a single screw extruder (HAAKE PolyLab OS system). Thick tensile bars (ASTM D638 Type I) were prepared by injection molding using a Plastic Injection Molding Machine (ING-58T) at 190°C. Sample characteristics are listed in Table 1.

Tensile testing

Tensile properties were measured following ASTM D638-10 at a crosshead speed of 50 mm/min. The static tensile modulus, strength and strain-at-break were measured at room temperature (~25°C) and atmospheric conditions (relative humidity ~50 ± 5%) on a universal testing machine (Narin Instrument Co. Ltd., Model: NRI-TS500-2S). Five specimens of each sample group were tested and the average results were reported.

The experimental data were compared with a theoretical model to predict the Young's modulus, tensile strength and elongation at break of the composite materials. The model used the classical Rule of Mixtures approach where the Young's modulus, tensile strength and elongation at break was calculated from:¹⁴

$$T = T_L X_L + T_B X_B \quad (1)$$

where T is the composite modulus, tensile strength or elongation at break, T_L is the PLA's modulus, tensile strength or elongation at break, T_B is the PBS's modulus, tensile strength or elongation at break, X_L is the matrix volume fraction and X_B is the PBS volume fraction.¹⁵

Scanning electron microscope (SEM)

The morphology of the sample surface was recorded with a JEOL JSM-6460LV scanning electron microscope (SEM) operated at 10 kV. Samples of neat PLA, neat PBS and PLA/PBS blends with fractured surfaces were prepared by brittle fracture in liquid nitrogen and all specimens were sputter-coated with a thin layer of gold (20 nm) prior to examination.

Differential scanning calorimetry (DSC)

The crystallinity of the PLA matrix phase usually influences the mechanical properties of the blends, so thermal analysis used a differential scanning calorimeter (DSC, PerkinElmer Instruments, DSC 4000) under a nitrogen atmosphere.

About 5 mg. samples cut from the molded tensile bars and sealed in aluminum pans then heated from -10 to 200°C at a rate of 10 °C/min. The melting temperature (T_m), apparent melting enthalpy (ΔH_f) and enthalpy of cold crystallization (ΔH_{cc}) were determined from DSC curves. Parameters T_m and ΔH_f were taken as the peak temperature and the area of the melting endotherm, respectively.

Crystallinity of PLA (λ_c (PLA)) and PBS (λ_c (PBS)) blends in the samples was estimated from the first heating cycle using:

$$\% \lambda_c (\text{PLA}) = \left[\frac{\Delta H_m(\text{PLA})}{\Delta H_f^0(\text{PLA})} \right] \times \frac{100}{W} \quad (2)$$

$$\% \lambda_c (\text{PBS}) = \left[\frac{\Delta H_m(\text{PBS})}{\Delta H_f^0(\text{PBS})} \right] \times \frac{100}{W} \quad (3)$$

where $\Delta H_f^0(\text{PLA})$ is the enthalpy of melting per gram of 100% crystalline (perfect crystal) (93 J/g)¹⁶ and PBS is 110.3 J/g¹⁷ and w is the weight fraction of PLA or PBS in the blends.

To determine the original crystallinity of the injection molded PLA which has low crystallization rate, the extra heat released during heating (i.e. enthalpy of cold crystallization) was subtracted from the total endothermic heat flow during melting of the whole crystallites.¹⁸ Thus, the modified equation for the crystallinity of the injection-molded can be written:

$$\% \lambda_c (\text{PLA}) = \left[\frac{\Delta H_m(\text{PLA}) - \Delta H_{cc}(\text{PLA})}{\Delta H_f^0(\text{PLA})} \right] \times \frac{100}{W} \quad (4)$$

Thermogravimetric Analysis (TGA)

TGA used a PerkinElmer Instruments (TGA4000) from 30 to 600°C at a heating rate of 10 °C/min under nitrogen. Approximately 10 mg of each sample was used for each test. The loss of weight was recorded and normalized against the initial weight. The thermal degra-

dation temperatures were defined from the decomposition temperatures at 5% weight loss ($T_{5\%}$).

Results and discussion

Tensile testing

Tensile testing was tested by a Universal Testing Machine (UTM) to investigate the influence of PBS on Young's modulus, tensile strength and elongation at break.

Figure 2 (a) shows the change of Young's modulus as more PBS was blended into PLA. The results clearly indicate that an increase in PBS content resulted in a gradual reduction of Young's modulus. The highest and lowest moduli were 27.5 MPa for neat PLA and 12.5 MPa for neat PBS. According to Bhatia et al.¹⁹, the gradual reductions of Young's modulus with increasing PBS is related to the compatibility of PLA/PBS blends, the higher portion of PBS results in lower compatibility of PLA/PBS blends. After adding 50 wt% PBS the Young's modulus decreased to around 15 MPa, after adding 2 wt% chain extender to the composite material, the Young's modulus further decreased slightly and then significantly when adding 4 wt% chain extender in (Figure 2 (b)).

Figure 2 (c) shows the influence of PBS on tensile strength. The tensile strength of neat PLA was 61 MPa and neat PBS was 30 MPa. Similar to Young's modulus, increasing the PBS portion reduced tensile strength gradually. According to Bhari K et al.⁹, the reductions of tensile strength with an increasing content of PBS are related to the compatibility of PLA/PBS blends, the higher content of PBS results in lower compatibility of PLA/PBS blends. Excessive chain extender reduces the tensile strength, so, for example an increase from 2 to 4 wt% chain extender in the 50 wt% PBS blend led to a decrease to 22 MPa from 41MPa (Figure 2 (d)). The combined blending of PLA with PBS and the incorporation of the chain extender imparted both ductility and melt strength to the system.²⁰

Figure 2 (e) shows that the elongation at break of neat PLA was 13% and PBS was 21% and increased with content of PBS in the blends. The elongation at break of PLA/PBS blends mixed with chain extender greatly increased with an increase in chain extender content see figure 2 (f). The blend with 50% PBS increased elongation at break up to 15.5% compared to PLA at 13%, ie a 17% increase in elongation. Compared with PLA/50%PBS blends without chain extender, we found that PLA/50%PBS blends with 4wt% of chain extender elongation at break increased by 600%. However, the elongation at break increased by only 200% when adding 2 wt% chain extender. This result is consistent with Radheshkumar et al.²¹ and Chou et al.²², who investigated the influence of compatibilizer content on the mechanical behavior of the blends. They reported that the compatibilizer can improve the ductility of PLA/PBS blends, because increasing compatibilizer content results in higher compatibility of PLA/PBS blends.

Even though the chain extender improved the ductility of PLA/PBS blends, in contrast, excessive chain extender also resulted in the reduction of the tensile modulus of PLA/PBS blends such as the sample with 4 wt% of chain extender. The use of chain extender therefore depended upon the application of PLA/PBS blends as a working material, for example, PLA/PBS blends with 4 wt% of chain extender is suitable only when high ductility PLA/PBS blends are needed. Applications requiring both tensile strength and ductility should use PLA/PBS blends with 2wt% of chain extender, which provides moderate tensile strength and ductility of the PLA.

Figure 3 compares Young's modulus, tensile strength and elongation at break from experimental data to the rule of mixtures model. Experimental data closely followed the mixing rule line. Figure 3(a) and (b) show that both Young's modulus and tensile strength decreased with the increase of PBS content in the blends and Figure 3(c) shows the elongation at break which increased with higher PBS content. Similar results have been reported by Bhatia et al.¹⁹

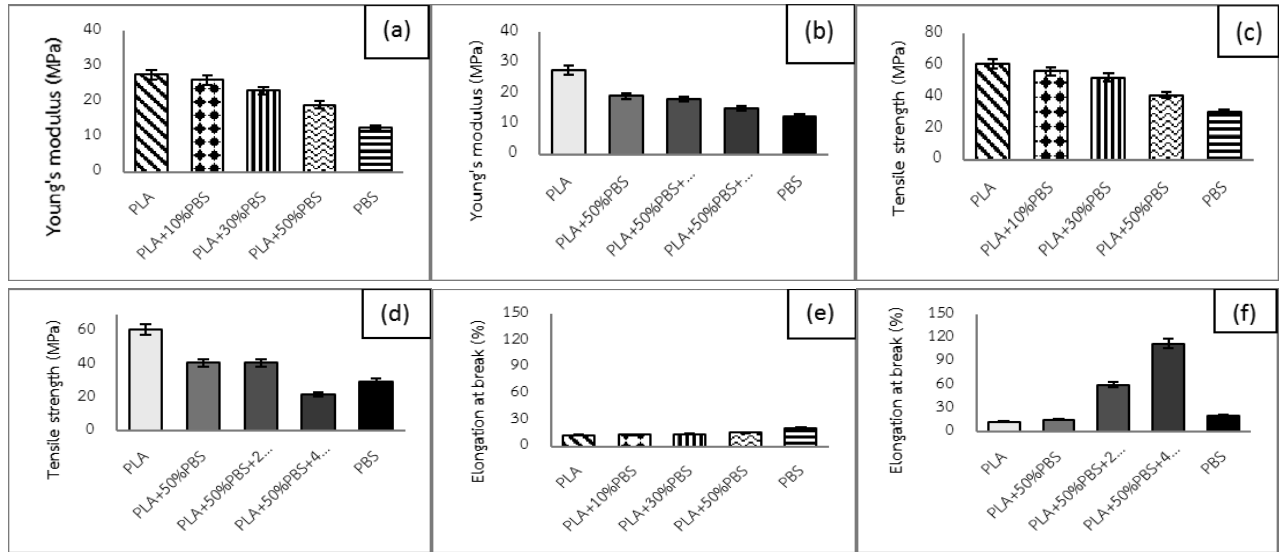


Figure 2 Mechanical properties of PLA, PBS, PLA/PBS and its PLA/PBS/chain extender composites (a) Young's modulus without chain extender, (b) Young's modulus with chain extender, (c) tensile strength without chain extender, (d) tensile strengths with chain extender, (e) elongation at break without chain extender and (f) elongation at break with chain extender

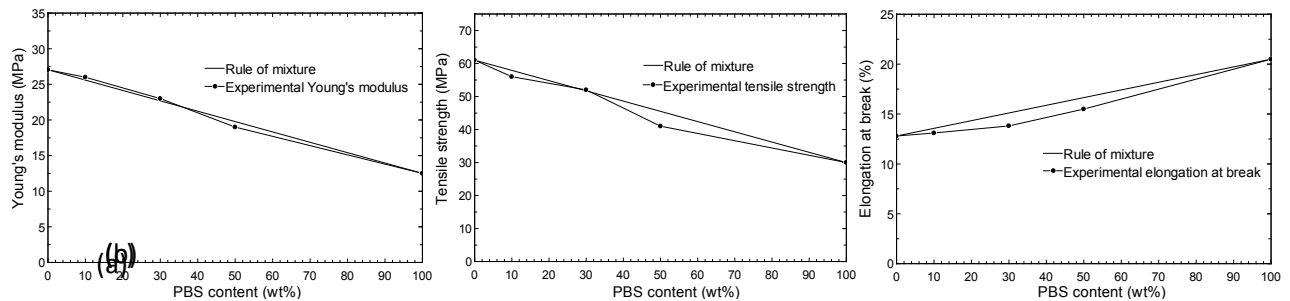


Figure 3 (a) Young's modulus, (b) tensile strength and (c) elongation at break from rule of mixtures Model and experiment

Scanning electron microscopy (SEM)

Figure 4 shows SEM micrographs of fractured surfaces of neat PLA, neat PBS, PBS/PLA blends and PBS/PLA blends adding chain extender under 100x magnification. As shown in Figure 4(a), the neat PLA showed a smooth fracture surface, indicating a typical brittle fracture and correspondingly low impact strength. Meanwhile, fractured neat PBS (Figure 4 (b)) showed rougher surfaces revealing more ductile behavior.¹⁷

With the different amounts of PBS, the blends presented the different impact fracture morphologies. Figures 4(c), (e) and (g), showing PBS content increasing from 10 wt% to 50 wt%: at 50 wt%, larger PBS particles appeared on the fracture surface, showing that PBS promoted phase separation. This was attributed to the

combination of low interfacial adhesion between PLA and PBS phases and much higher viscosity of the PLA dispersed phases in the relatively lower viscosity PBS matrix. Whereas for 10 wt% and 30 wt% blends, the fracture surface was smoother revealing brittle behavior and good dispersion of PBS in the PLA matrix was observed.¹⁹

When the chain extender content was increased to 4 wt% (Figure 4 (d), (f) and (h)), it was found that PLA dispersed phases were smaller compared to blends without chain extender. The ability to mix better caused the chain extender to make a homogeneous composite material. However, the morphology of the PLA/50%PBS blend with 4 wt% chain extender presents more uniform phases than that without chain extender and PBS particles were more evenly distributed, which resulted in polymer

blend toughness increase compared to lower PBS content blends. Clearly, the phase structure of the PLA/PBS/chain extender ternary blend played an important role in enhancing PLA toughness. As the content of chain extender increased, PBS and PLA became more phase compatible, with significantly improved interfacial adhesion between the PLA matrix and the PBS phase and the fracture surface became more homogeneous.²³

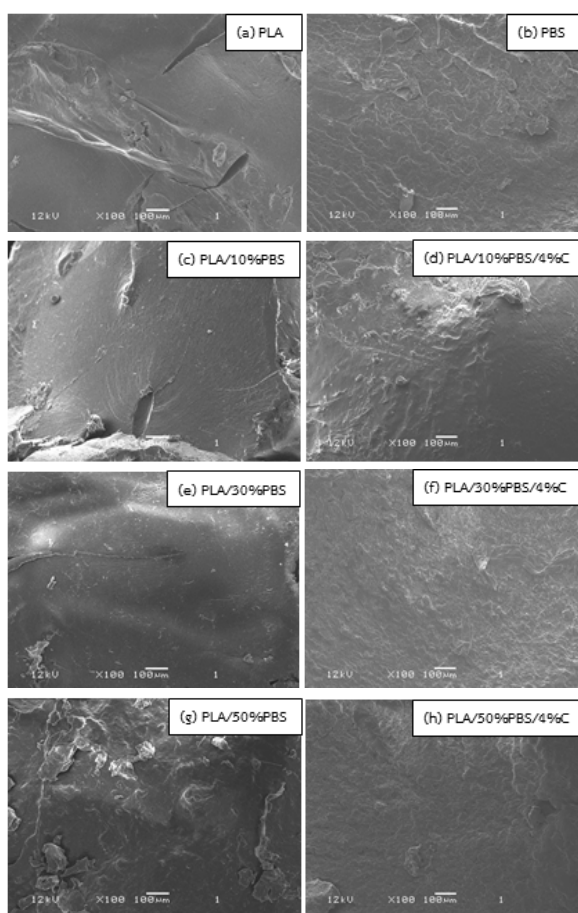


Figure 4 SEM micrographs of fractured surfaces of neat PLA, neat PBS, PLA/PBS and its PLA/PBS/chain extender composites

Differential scanning calorimetry (DSC)

Figure 5 shows DSC curves recorded during heating of PLA, PBS and PLA/PBS blends. The glass-transition temperature (T_g), the cold crystallization temperature (T_{cc}), the cold crystallization enthalpy of fusion (ΔH_{cc}), the melting temperature (T_m), the enthalpy of fusion (ΔH_m) and the percentage of crystallinity ($\% \lambda_c$) for all blends are summarized in Table 1.

The temperatures observed around 110 °C for PBS and 156 °C for PLA for all PLA/PBS blend specimens are the melting points. As shown in Table 1, T_m of neat PLA was about 156.1 °C and neat PBS about 110.7 °C. When PLA and PBS were mixed, we found two melting points (see figure 5 (a)), caused by separation of the mixed material: the first point is the melting point of the PBS and the second is that of PLA. T_m of PLA and PBS remained alike as the amount of PBS increased. In Figure 5 (b), (c) and (d), when adding chain extender, the T_m of both PLA and PBS decreased. Increase in chain extender content made the two melting points become closer together, because of enhanced homogeneity of PLA and PBS. The melting enthalpy of fusion (ΔH_m) of neat PLA was 28.4 J/g and neat PBS was 79.3 J/g. Increasing 10 to 50 wt% of PBS in PLA led to decreased ΔH_m (PLA) but ΔH_m (PBS) increased. When adding chain extender in the blend materials, the ΔH_m of both PLA and PBS decreased.

As shown in Figure 5(a) and Table 1, the shoulders around 60 to 80 °C in the DSC thermograms reveal the glass transition temperature of the PLA. We found that the T_g of neat PLA was 57.9 °C. Similar to other reports¹⁹, the blends of PLA/PBS were partially miscible as seen in lower T_g of PLA at higher PBS content. Increasing 10 to 50 wt% of PBS in PLA caused gradual reductions of T_g from 61.6 to 57.4 °C. Adding chain extender to PLA/PBS blends resulted in reduced T_g of the composite materials.

Moreover, the T_{cc} of neat PLA was 108.5°C. Increasing the PBS content in PLA decreased both T_{cc} and ΔH_{cc} and became invisible at 50 wt% PBS. The increased PBS from 10 to 30 wt% decreased T_{cc} from 96.4 °C to 95.9 °C and ΔH_{cc} from 21.1 J/g to 15.1 J/g. When the chain extender was added to the composites, the T_{cc} occurred at lower temperature and ΔH_{cc} became lower. The interfacial reaction between the epoxide group and the carboxyl end group of PLA and PBS occurred at the interface, which made the composites chain rearrangement (motion) more difficulty and retarded cold crystallization.

Table 1 DSC data for PLA/PBS blends adding chain extender

Sample	T _g (°)	T _m (PBS) (°)	ΔH _m (PBS) (J/g)	T _{cc} (°)	ΔH _{cc} (PLA) (J/g)	T _m (PLA) (°)	ΔH _m (PLA) (J/g)	%λ _c (PLA)	%λ _c (PBS)
PLA	57.9	-	-	108.5	19.9	156.1	28.4	9.1	-
PBS	38.6	110.7	79.3	-	-	-	-	-	71.9
PLA/10%PBS	61.5	108.8	4.7	96.4	21.07	154.6	20.3	0.9	4.3
PLA/10%PBS/2%C	61.2	106.4	4.3	94.8	16.2	154.5	18.9	2.9	3.9
PLA/10%PBS/4%C	50.2	107.8	4.0	84.8	14.3	150.3	17.4	3.3	3.6
PLA/30%PBS	60.2	110.1	20.1	95.9	15.1	154.6	19.6	4.8	18.2
PLA/30%PBS/2%C	49.0	108.1	15.8	89.0	13.0	150.8	16.1	3.3	14.3
PLA/30%PBS/4%C	41.7	107.0	9.6	87.0	8.8	150.6	10.5	1.8	8.7
PLA/50%PBS	57.4	110.3	35.9	-	-	154.8	12.1	13.1	32.5
PLA/50%PBS/2%C	55.2	109.3	28.5	-	-	151.6	11.7	12.5	25.8
PLA/50%PBS/4%C	53.8	107.8	27.5	-	-	150.2	11.0	11.8	25.0

The %λ_c of neat PLA was only 9.1% while neat PBS was 71.9%. This is because during injection molding, the crystallization process of PLA was partially hampered due to the high cooling rate and exhibited a cold crystallization peak during the DSC test when the specimens are re-heated and regained some mobility to re-crystallize. Increasing 10 to 50 wt% of PBS into PLA, we found that the %λ_c (PLA) increased, %λ_c (PBS) decreased. When adding chain extender to the blends, the %λ_c of both PLA and PBS decreased. In general, when chain extender was introduced in the blending system the chain-extending reaction among PLA would make the molecular weight of PLA increase; on the other hand, the reaction between PLA and PBS restricted the movements of PLA and PBS chains. As the mobility of the chains decreased, the materials were more difficult to crystallize than that without chain extender.

Thermal stability of the polymer was measured by TGA, where the weight loss due to the loss of degradable products was monitored as a function of temperature. Figure 5 shows thermograms of PLA, PBS and PLA/50% PBS with and without chain extender blends. From TGA curves in Figure 5, we found that the

decomposition temperature of PBS was slightly higher than PLA. PLA with 50 wt% PBS reached slightly higher thermal stability compared to pure PLA. Therefore, when PBS content is higher, dispersion of PBS leads to slightly higher degradation temperatures than that of neat PLA. When adding chain extender, the decomposition temperatures of material composite increased.

As shown in Table 2, the decomposition temperatures at 5% weight loss (T_{5%}) were 344.9 °C for PLA/50%PBS blend and 346.2 °C for PLA/50%PBS/4%chain extender blend. This is similar to Pilla et al.²⁴, indicating that the PLA-chain extender has a better thermal stability than pure PLA system. According to Srithep et al.²⁵, the melt flow index of the blends increased with increasing the content of the chain extender in polyester which means the increase of molecular weight and caused higher thermal stability because chain extender can be connect molecules of the material cause molecular weight and strength increases. As a result, thermal stability increased.

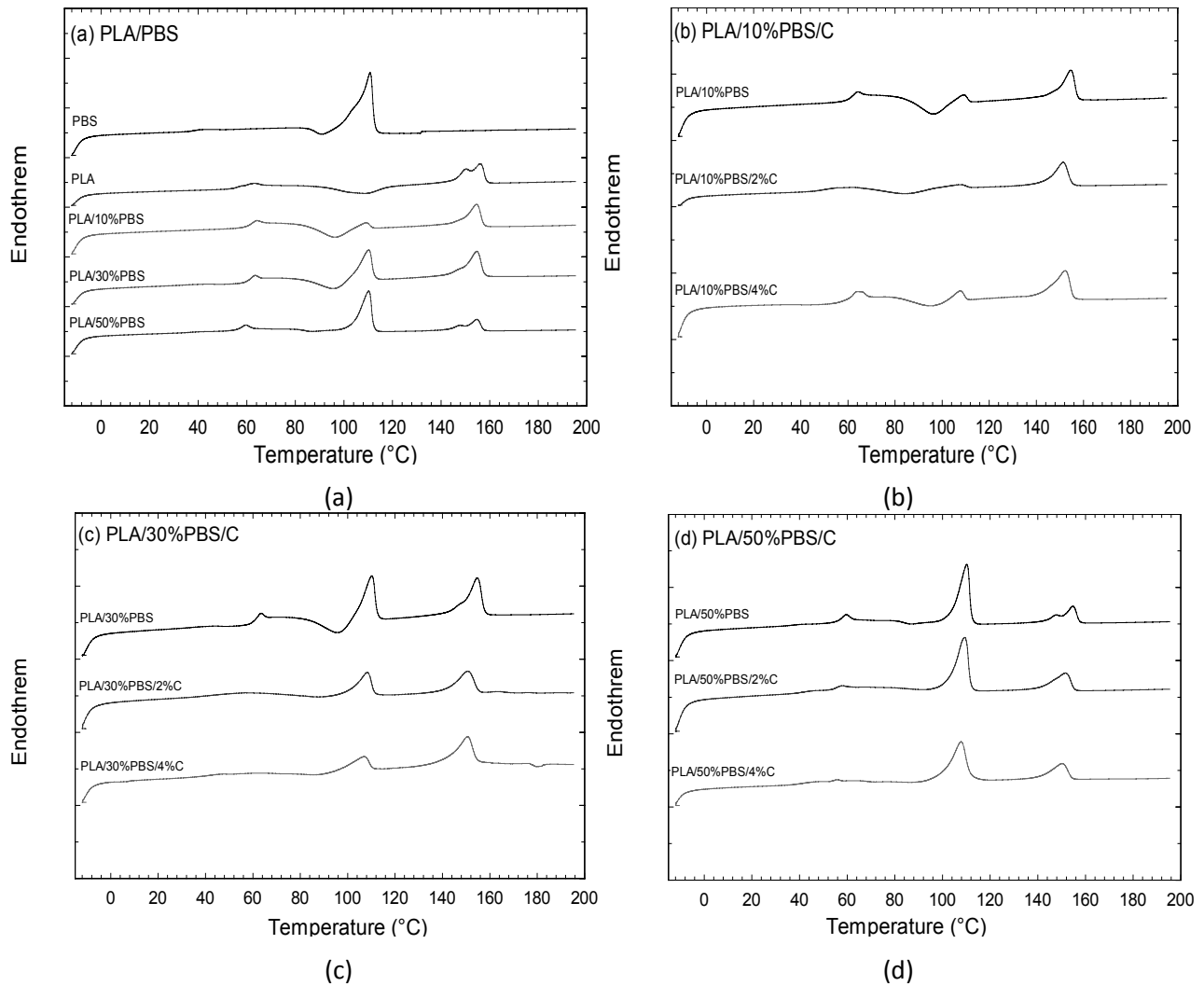


Figure 5 DSC thermograms for various blends (a) PLA/PBS (b) PLA/10%PBS/chain extender (c) PLA/30%PBS/chain extender (d) PLA/50%PBS/chain extender

Thermal stability

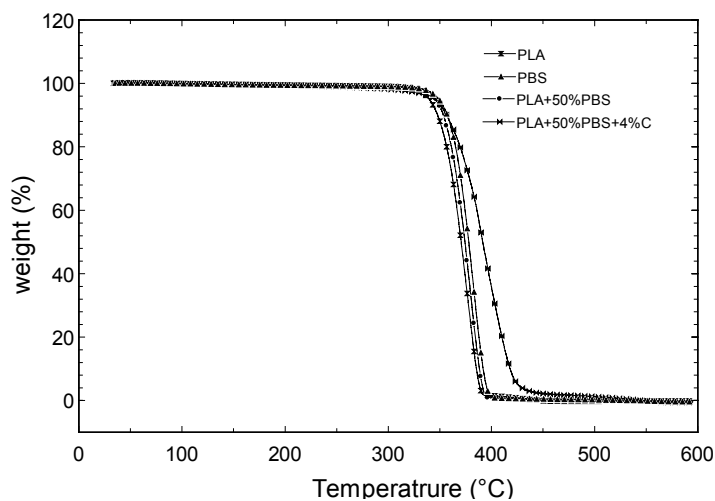


Figure 6 TGA curves for PLA, PBS, PLA/PBS adding chain extender

Table 2 Degradation temperatures of PLA, PBS and PLA/PBS adding chain extender

Sample	T _{5%} (°)
PLA	339.7
PBS	348.8
PLA+50%PBS	344.9
PLA+50%PBS+4%C	346.2

Conclusion

Adding chain extender led to mixed morphology of interacting particles within the polymer matrices. From thermal analysis, 4 wt% chain extender demonstrated greatest thermal stability. SEM studies demonstrated that higher concentrations of chain extender enhanced miscibility for PLA/PBS polymer blends. For DSC studies, T_g, T_m, ΔH_m and %λ_c of the composite material decreased, due to the higher flexibility of the PBS, that, combined with PLA, is a strong but brittle polymer, so that PLA based blends will be more flexible and tougher. Elongation at break significantly increased, while tensile strength and Young's modulus of the blends were reduced with excessive chain extender.

Acknowledgements

We thank the Faculty of Engineering Maharakham University for facilities and the Graduate School of Maharakham University for the research grant.

References

1. Fujimaki T. Processability and properties of aliphatic polyesters, 'BIONOLLE', synthesized by polycondensation reaction. *Polym Degrad Stab* 1998(59):209-14.
2. Garlotta D. A Literature Review of Poly(Lactic Acid). *Polym Degrad Stab* 2001;9(2):63-84.
3. Park JW, Im SS. Phase behavior and morphology in blends of poly(L-lactic acid) and poly(butylene succinate). *J Appl Polym Sci* 2002;86(3):647-55.
4. Vink ETH, Rabago KR, Glassner DA, Gruber PR. Applications of life cycle assessment to Nature Works™ polylactide (PLA) production. *Polym Degrad Stab* 2003;80(3):403-19.
5. Fortunati E, Armentano I, Zhou Q, Puglia D, Glassner A et al. Microstructure and nonisothermal cold crystallization of PLA composites based on silver nanoparticles and nanocrystalline cellulose. *Polym Degrad Stab* 2012;97(10):2027-36.
6. Petersen K, Nielsen P, Olsen M. Physical and Mechanical Properties of Biobased Material Starch, Polylactata and Polyhydroxybutyrate. *Starch* 2001 (53):356-61.
7. Bastioli C. Global Status of the Production of Biobased Packaging Materials. *Starch* 2001;53(8): 351-5.
8. Han JJ, Huang HX. Preparation and Characterization of biodegradable polylactide/thermoplastic polyurethane elastomer blends. *J Appl Polym Sci* 2011;120(6): 3217-23.
9. Bhari K, Mitomo H, Enjoji T, Yoshii F, Makuuchi K. Radiation crosslinked poly(butylene succinate) foam and its biodegradation. *Polym Degrad Stab* 1998; 62(3):551-7.
10. Doi Y, Kasuya K, Abe H, Koyama N, Ishiwatari S, Takagi K et al. Evaluation of biodegradabilities of biosynthetic and chemosynthetic polyesters in river water. *Polym Degrad Stab* 1996;51(3):281-6.
11. Sinha Ray S, Okamoto K, Okamoto M. Structure-property relationship in biodegradable poly (butylene succinate)/ layered silicate nanocomposites. *Macromolecules* 2003;36(7):2355-67.
12. Homklin R, Hongsriphan N. Mechanical and Thermal Properties of PLA/PBS Cocontinuous Blends Adding Nucleating Agent. *Energy Procedia* 2013;34:871-9.
13. Frenz V, Scherzer D, Villalobos M, Awojulu AA, Edison M, Meer R. Multifunctional Polymers as Chain Extenders and Compatibilizers for Polycondensates and Biopolymers. . ANTEC 2008:1682-6.
14. Srithep Y, Turng LS, Sabo R, Clemons C. Nanofibrillated cellulose (NFC) reinforced polyvinyl alcohol (PVOH) nanocomposites properties, solubility of carbon dioxide, and foaming. *Cellulose* 2012;19(4): 1209-23.
15. Bulota M, Jääskeläinen AS, Paltakari J, Hughes M. Properties of biocomposites: influence of preparation method, testing environment and a comparison with

- theoretical models. *J Master Sci* 2011;46(10): 3387-98.
16. Suksut B, Deeprasertkul C. Effects of Nucleating Agents on Physical Properties of Poly(lactic acid) and Its Blend with Natural Rubber. *J Polym Environ* 2011;19(1):288-96.
 17. Homklin R, Hongsriphan N. Mechanical and Thermal Properties of PLA/PBS Cocontinuous Blends Adding Nucleating Agent. *Energy Procedia* 2013;34:871 – 9
 18. Srithep Y, Nealey P, Turng LS. Effects of annealing time and temperature on the crystallinity and heat resistance behavior of injection molded poly (lactic acid). *Polym Eng Sci* 2013;53(3):580-8.
 19. Bhatia A, Gupta RK, Bhattacharya SN, Choi HJ. Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate) (PBS) blends for packaging application. *Korea-Aust Rheol J* 2007; 19(3):125-31.
 20. Eslami H, Kamal MR. Effect of a chain extender on the rheological and mechanical properties of biodegradable poly(lactic acid)/poly[(butylene succinate)-co-adipate] blends. *J Appl Polym Sci* 2013;129(5): 2418-28.
 21. Radheshkumar C, Munstedt H. Morphology and mechanical properties of antimicrobial polyamide/silver composites. *Mater Lett* 2005;59(14-15): 1949-53.
 22. Chou PM, Zulkifli A, Sreekantan S. Evaluation of the flexural properties and bioactivity of bioresorbable PLLA/PBSL/CNT and PLLA/PBSL/TiO₂ nanocomposites. *Compos Eng* 2012;43(3):1374-81.
 23. Chen L, Qiu X, Xie Z, Hong Z, Suna J, Chena X et al. Poly(L-lactide)/starch blends compatibilized with poly(L-lactide)-g-starch copolymer. *Carbohydr Polym* 2006;65(1):75-80.
 24. Pilla S, Kramschuster A, Yang L, Lee J, Gong S, Turng LS. Microcellular injection-molding of polylactide with chain-extender. *Mater Sci Eng C* 2009;29(4): 1258–65.
 25. Srithep Y, Javadi A, Pilla S, Turng LS, Gong S, Clemons C et al. Processing and characterization of recycled poly (ethylene terephthalate) blends with chain extenders, thermoplastic elastomer, and/or poly (butylene adipate co terephthalate). *J Polym Eng Sci* 2011;51(6):1023-32.