

# Preparation of Polymer Blends between Poly (L-lactic acid), Poly(butylene succinate-co-adipate) and Poly(butylene adipate-co-terephthalate) for Blow Film Industrial Application

W. Pivsa-Art, S. Pavasupree, N. O-Charoen, U. Insuan, P. Jailak and S. Pivsa-Art

**Abstract**— The preparation of polymer blends of poly(lactic acid) (PLA), Poly(butylene-succinate-co-adipate)(PBSA) and poly(butylene adipate-co-terephthalate) (PBAT) were studied with the objectives to apply to blown film extrusion method. The blends were prepared using twin-screw extruder. The ratio of PLA and PBSA was fixed at 80/20 and the PBAT content was investigated with 0, 10, 20, 30, 40 and 50 wt%. The speed of screw was 80 rpm with the die temperatures of 220, 200, and 180 °C. It was found that the melt flow index (MFI) and tensile strength of blends decreased with increasing amount of PBAT, whereas the percentage strain showed contrastive results. The maximum tensile strength and impact strength were reached with the blend of equal amount 20 wt% of PBAT. Then, the correspondent condition was used in the blown film extrusion process. The morphology investigation using scanning electronic microscopy (SEM) of PLA/PBSA/PBAT blends showed an excellent compatibility between the three polymers.

**Keywords**— Blown film extrusion, Poly(lactic acid) (PLA), Poly(butylene succinate-co-adipate) (PBSA), Poly(butylene adipate terephthalate) (PBAT), Polymer blend

## 1. INTRODUCTION

The rapid growth of plastic production is considered as a serious source of environment pollution from their wastes. Approximately 100 million tons of plastics are produced each year. Within a short period of time almost half of them are disposed to the environment [1]. In recent years, researcher have paid attention on discovering an alternative way to solve the problems by replacing the commodity synthetic polymers with biodegradable polymers. Among various kinds of biodegradable plastics discovered, poly(lactic acid), PLA, is the most promising polymer due to its excellent mechanical properties and biodegradability behavior [2].

PLA is a kind of linear aliphatic biodegradable thermoplastic polyester produced from renewable resources with excellent properties comparable to many petroleum-based plastics [3,4]. The extrusion grade PLA has high modulus (over 3 GPa) and strength (over 50 MPa) comparable to that of many petroleum-based plastics. But its high glass transition temperature (about 60 °C) and low toughness limit its application. The neat PLA is hard to be designed for film extrusion [5,6,7]. Therefore, it is needed to blend PLA with other biodegradable polymers having more flexible properties to improve PLA properties suitable for film applications. In addition, their blend system has attracted many interests because it complements brittleness of the PLA with an elastomeric property polymer. Poly(butylene

succinate-co-adipate) (PBSA) is a commercially available aliphatic polyester synthesized from diacids and diols with high flexibility, excellent impact strength, melt processibility, thermal, chemical resistance and low melting point of 90°C, which is more readily biodegraded than PLA [9]. PBSA has excellent processability and can be moulded into a variety of products using conventional equipment applicable to polyolefins [10]. However, in the literature review found that the PBSA can be used in the polymer blends less than 20 wt%. Therefore, the polymer blend shows brittle behavior. Poly(butylene adipate terephthalate) (PBAT) is an elastomeric polymer using to improve mechanical properties. So combining the high toughness of PBAT and the relatively low price of PLA can result in a novel blend [11]. PBAT is synthesized by esterification of 1,4-butanediol with aromatic dicarboxylic acid and then polycondensation with succinic acid, is attractive while its other properties such as melt viscosity, softness and gas barrier properties are not sufficient for its application to various final products [8].

In this study we have prepared PLA/PBSA/PBAT blends to obtain biodegradable polymers with good impact resistance and investigated various aspects of the thermal, rheological, and mechanical properties in these blend systems. As a result of blending PLA/PBSA/PBAT were subjected to blow film process.

## 2. EXPERIMENTAL

### 2.1 Materials

Poly(lactic acid) (PLA) (PLA 4042D) was purchased from the Natureworks LLC in pellet form exhibits a density of 1.26 g/cm<sup>3</sup>, melt flow index (MFI) of 4-8 g/10min, a number average molecular weight of 120,000 g/mol, a glass transition temperature and melting point of 51 and 150 °C, respectively. Poly(butylenes adipate-co-terephthalate) (PBAT, Ecoflex FBX 7011) was purchased from BASF Corporation in pellet form having a density of 1.23 g/cm<sup>3</sup>, melt flow index (MFI) of 2 g/10min and a number average molecular weight of 24,400 g/mol.

---

W. Pivsa-Art, S. Pavasupree, N. O-Charoen, U. Insuan, P. Jailak and S. Pivsa-Art are with the Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Klong 6, Thanyaburi, Pathumthani 12110, Thailand, E-mail: weraporn@hotmail.com

## 2.2 Preparation of PLA/PBSA/PBAT blends

The compounds of PLA/PBSA/PBAT blends were prepared using a twin-screw extruder. The extruder had a screw diameter of 26 mm, and an  $L/D$  ratio of 40 with five controlled temperature zones which were set to range from 180 (next to the feeding segment) to 220 °C (die adaptor). The screw speed was maintained at 80 rpm for all runs. Before extrusion, PLA, PBSA and PBAT resin were dried at 80 °C for 8 hours in an oven in order to remove any trace of moisture to prevent potential hydrolytic degradation during the melt processing in the extruder. The mixture of PLA/PBSA/PBAT was manually premixed by tumbling in a plastic zip-lock bag, and subsequently fed into the extruder for melt compounding. The extrudate was cooled in a water bath and subsequently granulated by a pelletizer. The polymer sheets (thickness 2 mm) of polymer blends were prepared by compression molding.

## 2.3 Thermal properties

The differential scanning calorimetry (DSC) is used to evaluate the thermal properties of the PLA/PBSA/PBAT blends. The samples were analyzed using a Shimadzu DSC-50Q under  $N_2$  atmosphere at heating rate at a constant 10 °C/min and heated to 200 °C. The thermogram signal was derived from the temperature difference between the sample and the reference. The sample of 5-10 mg was placed in a crimped aluminium pan. The melting temperature,  $T_m$  was calculated from the midpoint of the base-line shift of the DSC thermogram

## 2.4 Rheology properties

The melt flow index of a polymer melt was carried out using an ASTM D 1238 standard. The flow rate is determined as a function of applied load with the mass flow rate expressed in gram mass per 10 minutes. The extrusion took place isothermally in 10 min under constant temperature through a die of standard size. The sample of 5 g as a power or a pellet is heated for 5 minutes in the barrel and extruded through the die under a constant load 2.16 kg. The melt flow index of PLA/PBSA/PBAT blends was measured at 190 °C.

## 2.5 Mechanical properties

The tensile properties were determined according to ASTM D 638 (Type I) using dumbbell shape specimens. The test was carried out on a universal testing machine (LLOYD Instruments LR 10K Plus) with a crosshead speed of 50 cm/min. The elongation of specimens was obtained from the extensometer. The Izod impact strength was determined according to ASTM D256 by using the Impact Tester GOTECH GT 7045. The report value was the average of three replicates for each property test.

## 2.6 Scanning electron microscopy (SEM)

The morphology of the fracture surface of the PLA/PBSA/PBAT blends were also investigated using a JEOL model JSM-6400 scanning electron microscope at 10 kV. The specimens were fractured under cryogenic condition using liquid nitrogen. Then, the specimens were mounted on a SEM stub using a double-side tape and the fracture surface of specimens was sputtered with a thin gold layer.

## 3. RESULTS AND DISCUSSION

### 3.1 Thermal properties

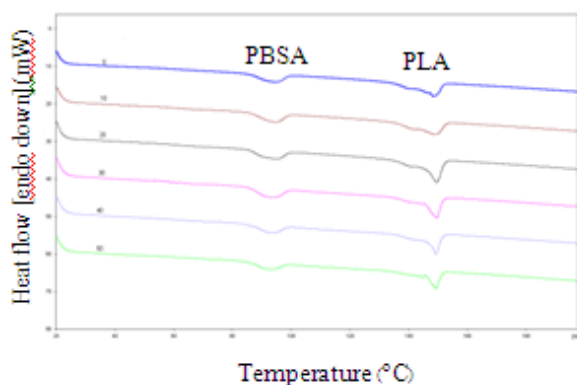
The results of DSC thermogram for the PLA/PBSA/PBAT blends were presented in Fig. 1. They showed two endothermic peaks for the second heating. Thermal properties of the blends were summarized in Table 1. PLA is a highly crystalline polymer exhibiting a melting point ( $T_m$ ) of 151.3 °C, while for PBSA, which is a less crystalline polymer, the corresponding value is 92.7 °C. The melting temperature ( $T_m$ ) of the PBAT is *ca.* 106.0 °C. A direct proof of polymer miscibility in blend can be obtained by observing the behavior of the  $T_m$  with the blend composition. Increasing PBAT contents in the blends resulted in two different behaviors [12].

The  $T_m$  of PLA decreased from 151.3° to 148.6 °C for PLA/PBSA blends containing 80/20 wt% due to active interaction between PLA and PBSA chains after added PBAT to the blends. This could be an indication of partial miscibility of the two polymers. On the other hand, the  $T_m$  of the blend showed slightly higher than pure PBAT, which was found to increase with increasing PBAT content. The blends showed overlap of melting endotherm and re-crystallization exotherm. Fig. 1 shows exothermic peaks which are attributed to crystalline reorganization during heating. These newly formed crystallites melted on continuous heating. The re-crystallization temperature of PLA phase increased with increasing PBAT content. Re-crystallization of the initially amorphous PLA fraction can take place only at higher  $T_m$ , whereas the mobility of the PLA chain is sufficiently high to reorganize into a new crystalline conformation. However, pure PLA does not show any apparent re-crystallization peak. This behavior is very similar to typical plasticized thermoplastics. PLA content in PLA:PBSA blends also shows exothermal peak shift of PBSA towards higher temperature [13]. But the shifts in the blends are not so noticeable, which indicates immiscibility. In the entire composition range investigated, two distinct melting peaks were observed, indicating that each component crystallized individually. The results demonstrate that for up to 20 wt% of PBSA in PLA, miscibility is possible and beyond that they become immiscible.

**Table 1** Melting temperature of PLA/PBSA/PBAT blends

PBAT content (wt%)	Melting temperature, $T_m$ (°C)		
	Peak 1 (PLA)	Peak 2 (PBSA)	Peak 3 (PBAT)
PLA	151.3	-	-
PBSA	-	92.7	-
PBAT	-	-	106.0
0 <sup>a</sup>	148.6	94.2	-
10 <sup>a</sup>	149.1	94.5	-
20 <sup>a</sup>	149.5	94.5	-
30 <sup>a</sup>	149.6	93.6	-
40 <sup>a</sup>	149.3	93.5	-
50 <sup>a</sup>	149.4	92.5	-

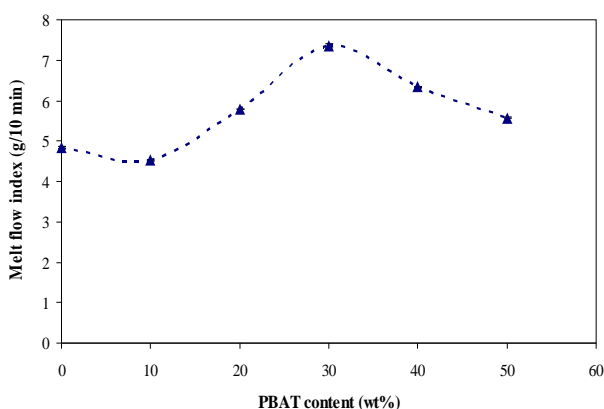
<sup>a</sup>PLA/PBSA = 80/20



**Fig. 1** DSC thermogram of PLA/PBSA/PBAT blends at various PBAT content: 0, 10, 20, 30, 40 and 50 wt% on heating rate of 10 °C/min

**3.2 Rheology properties**

The melt flow indexes of the PLA/PBSA/PBAT blends are presented in Fig 2. The melt flow index (190°C/2.16 kg) values of PLA, PBSA, PBAT and PLA/PBSA (80/20) of 8.46, 2.34, 4.06 and 4.83 g/10 min, respectively. The melt flow index of PLA/PBSA/PBAT blends at various PBAT contents of 10, 20, 30, 40 and 50 wt% shown in, 4.53, 5.79, 7.36, 6.34 and 5.57 g/10 min, respectively. The melt flow index of PLA/PBSA/PBAT blends due to increase with increasing of PBAT content. Decrease of viscosity when adding PBAT increase.



**Fig. 2** DSC thermogram of PLA/PBSA/PBAT blends at various PBAT content 0, 10, 20, 30, 40 and 50 wt% on heating rate 10 °C/min

**3.3 Mechanical properties**

Table 2 represents the typical tensile properties and impact strength obtained from PLA/PBSA/PBAT blends at different wt% of PBAT loading (10, 20, 30, 40 and 50 wt%) It is observed that the tensile strength, Young’s modulus (E) of PLA/PBSA (80/20) is 20.39 MPa, 1756.33 MPa with an elongation at break of 2.06% respectively. Incorporation of PBAT, results in a trend to increase in the tensile strength, Young’s modulus (E) and elongation at break of PLA/PBSA matrix. PLA/PBSA/PBAT biodegradable blends exhibits optimum increase of 40.71 MPa in tensile strength at 20 wt% of PBAT contents and 6.94% increase in elongation and 1561.34 MPa in Young’s modulus (E) at 20 wt% of

PBAT contents. This is probably due to improved interaction between the carbonyl group of PBAT and PLA/PBSA (80/20) matrix. However, increase in PBAT contents loading from 30 to 50 wt% results in phase separation and leading to structure crack formation and failure in the blends. The addition of PBAT in the PLA/PBSA matrix should be in the range of 10 to 20 wt% which indicates polymer homogeneous and increase the modulus of PLA/PBSA blends. In amount of PBAT in range of 30-50 wt% showed decreasing of tensile strength, elongation and young modulus of the blends.

Impact strength of PLA/PBSA/PBAT blends with PBAT contents was shown in Table. 2. Interestingly, we could observe that when PBAT content is at 20 wt%, the impact strength of the blends showed much higher value at higher PBAT content increase , it was much lower than the line. Like a typical rubber toughening system, a remarkable improvement of about two and half times of pure PLA in impact strength can be realized by using only 10-30 wt% PBAT in PLA.

**Table 2** Mechanical properties of PLA/PBSA/PBAT blends

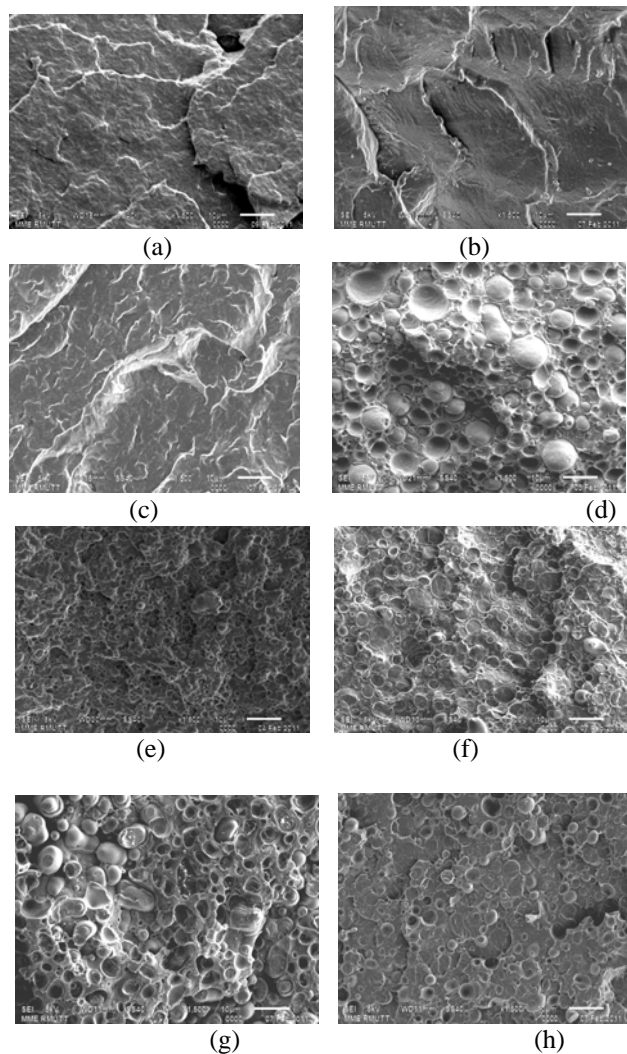
PBAT content (wt%) <sup>a</sup>	Tensile strength (MPa)	Elongation at break (%)	Young's Modulus (MPa)	Impact strength (J/m)
0	20.39 (2.37) <sup>b</sup>	2.06 (0.54)	1756.33 (100.29)	2.99 (0.35)
10	36.32 (2.12)	6.94 (1.92)	1561.34 (28.32)	20.58 (3.63)
20	40.71 (6.28)	5.55 (1.45)	1551.99 (73.23)	26.97 (2.52)
30	32.80 (0.84)	4.00 (0.54)	1336.72 (71.49)	13.90 (4.42)
40	27.08 (1.40)	3.44 (0.09)	1264.46 (35.04)	7.67 (1.57)
50	21.80 (0.99)	3.68 (0.34)	1044.77 (17.66)	7.80 (1.52)

<sup>a</sup> PLA/PBSA=80/20, <sup>s</sup>standard deviation

**3.4 Morphology**

The morphology of the blends was investigated with high-resolution Scanning electron microscopy (SEM), operated at an acceleration voltage of 10 kV. The blends were fractured in liquid nitrogen. SEM images of the blends are shown in Fig. 3. SEM images of fractured surfaces show the morphology of the PLA, PBSA, PBAT, PLA/PBSA (80/20 wt%) and PLA/PBSA/PBAT blends. From Figs.3 (a) it is brittle behavior of PLA, (b) and (c) show ductile behavior of PBSA and PBAT, respectively. The Fig. 3(d) phase separation is an evident in the blends of PLA/PBSA (80/20) and the blends of PLA/PBSA/PBAT at various PBAT content. In Fig. 3(e, f) shows smooth surface with less phase separation morphology. The dispersed phases of PBSA particles were relatively small due to the increase of PBAT content. The particle size became larger

while increasing the amount of PBAT (Fig. 3(g, h)), which may be due higher viscosity of PBAT than PLA at low shear rate shown in Fig. 6(h). The results indicate the traditional morphology of immiscible blend system.



**Fig. 3** SEM photographs of the PLA/PBSA/PBAT blends: (a) PLA, (b) PBAT, (c) PBSA, (d) without the addition of PBAT (PLA/PBSA=80/20 wt%), (e) addition of 10 wt% of PBAT, (f) addition of 20 wt% of PBAT (g) addition of 30 wt% of PBAT, (h) addition of 40 wt% of PBAT and (i) addition of 50 wt% of PBAT (magnification x1500)

For the addition of PBAT at 10, 20 and 30 wt% (Fig. 1b), the fracture surface of the PLA/PBSA/PBAT blends exhibited the partial compatibility with little phase separation between PLA/PBSA and PBAT resulting to good mechanical properties. To consider the addition of PBAT into the PLA/PBSA blends, it was observed that the fracture surface of the PLA/PBSA/PBAT became smoother which is the characteristic of the ductile materials.

#### 4. Conclusions

The thermal analysis using differential scanning calorimetry of PLA/PBSA/PBAT blend showed the separation of each melting temperature of both polymer compositions. From the morphology study it was found that both polymers (PLA and PBSA) showed only few compatible parts and phase separation could be clearly

seen. Polymer blend of PLA/PBSA of 80/20 wt% shows good distribution of compositions after added PBAT 10-30 wt% and good mechanical properties. The polymer blend of PLA/PBSA (80/20 wt%) and various PBAT of 20 wt% showed highest of tensile strength of 40.71 Mpa and impact strength 26.9 7J/m. This implied that PBAT could act as the interfacial agent to improve the mechanical properties of the blends.

#### Acknowledgement

The authors gratefully acknowledge National Innovation Agency (NIA) Research Fund by The National Project on Bioplastics and Biodegradable Materials, Kasetsart University (Project code: C14-52), Department of Materials and Metallurgical Engineering, Department of Chemical and Materials Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi (RMUTT).

#### REFERENCES

- [1] Huang, S. J. 1985. *Encycl Polym Sci Eng 2: Biodegradable polymers*. Wiley-Interscience, New York.
- [2] Shu-Ying Gu., Ke Zhang., Jie Ren and Hui Zhan., 2008. Melt rheology of polylactide/poly(butylene adipate-co-terephthalate) blends, *J Carbohydrate Polymers* 74, pp. 79-85.
- [3] Martin, O. and Averous, L. 2001. Poly(lactic acid): Plasticization and properties of biodegradable multiphase systems. *Polymer*, 42(14), pp. 6209-6219.
- [4] Fang, Q. and Hanna, M. A. 1999. Rheological properties of amorphous and semicrystalline poly(lactic acid) polymers. *Industrial Crops and Products*, 10(1), pp. 47-53.
- [5] Ogata, N. Jimenez, G. Kawai, H. and Ogihara, T. 1997. Structure and thermal/mechanical properties of poly(L-lactide)-clay blend. *Journal Polymer Science*, B35(2), pp. 389-396.
- [6] Bhatia A, Gupta RK, Bhattacharya SN, Choi HJ (2007) Compatibility of biodegradable poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) blends for packaging application. *Korea-Australia Rheol J* 19: pp.125-131.
- [7] Wu TM, Chiang MF, 2005. Fabrication and characterization of biodegradable poly(lactic acid)/layered silicate nanocomposites. *Polym Eng Sci* 45: pp.1615-1621.
- [8] Jiang L, Wolcott MP, Zhang J, 2006. Study of biodegradable polylactide/poly(butylene adipate-co-terephthalate) blends. *Biomacromolecules* 7, pp. 199-207.
- [9] Fujimaki T., 1998. Processability and properties of aliphatic polyesters, 'BIONOLLE', synthesized by polycondensation reaction. *Polymer degradation and stability*; 59(2): pp. 209e14.
- [10] Tserki, V. Matzinos, P. Pavlidoo, E. Panayiotou, C. 2006. Biodegradable aliphatic polyesters. Part II. Synthesis and characterization of chain extended poly(butylenes succinate-co-butylene adipate), *Polymer degradation and stability*, 91, pp. 377-384.
- [11] Francesca Signori, Maria-Beatrice Coltelli and Simona Bronco., 2009, Thermal degradation of poly(lactic acid) (PLA) and poly(butylenes adipate-co-terephthalate) (PBAT) and their blends upon

melt processing, *Journal of Polymer Degradation and Stability* 94, pp. 74–82.

- [12] Sweet, G. E. and J. P. Bell, 1972, Multiple endotherm melting behavior in relation to polymer morphology, *Journal of Apply Polymer Science. Part A-2: Polymer Physics*, 10: pp.1273-1283.
- [13] Miyata, T. and T. Masuko, 1998, Crystallization behaviour of poly(L-lactide), *Polymer*, 39, pp.5515-5521.