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## Effect of Additive on Crystallization and Mechanical Properties of Polymer Blends of Poly(lactic acid) and Poly[(butylene succinate)-*co*-adipate]

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### Abstract

The effect of additive on crystallization and mechanical properties of poly(lactic acid) (PLA) and poly(butylene succinate-co-adipate) (PBSA) blend was studied. PLA and PBSA were blended in a twin screw extruder, which incorporated poly(butylene adipate-co-terephthalate) (PBAT) as an additive in PLA/PBSA blend. The ratio of PLA/PBSA was 80/20. The contents of PBAT were varied from 0 to 50 wt%. The thermal properties and crystallization behavior of PLA/PBSA/PBAT blends were analyzed by differential scanning calorimetry. The effect of PBAT contents on non-isothermal crystallization kinetic of the composites was investigated by using Avrami equation. Tensile strength and impact performance of the PLA/PBSA/PBAT blends decreased when increasing PBAT contents. It can be noted that the addition of 20 wt% PBAT showed the maximum impact performance of the PLA/PBSA blends.

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### 1. Introduction

In the present day, the rapid growth of plastic production is considered as a serious situation of environment pollution from their wastes. Approximately 100 million tons of plastics are produced each

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year. Within a short period of time almost half of them are disposed to the environment [1]. In recent years, researchers have paid attention on discovering an alternative way to solve the problems by replacing the commodity synthetic polymers with biodegradable polymers. Biodegradable polymers are prompt for using instead of non-degradable of petroleum-based polymer with considering on the environment problems and awareness [2-3]. Commercially biodegradable polymers are including poly(lactic acid) (PLA), poly(hydroxyl butylate-co-valerate) (PHBV), poly(butylenes succinate) (PBS) and poly(butylenes adipate-co-terephthalate) (PBAT). 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 [4]. However, the properties of individual biodegradable polymers are still restrain and unsuitable for industrial applications. Blending of various biodegradable polymers or addition of natural or synthetic additives would enhance properties of biodegradable polymers for applying in various industries [5-6].

This research focuses on preparing polymer blends with superior properties from biodegradable polymers. Binary blends of PLA/PBSA were used as the main matrix. The effect of the third components PBAT contents as modifying additive on morphological, thermal properties, crystallization behavior and mechanical performance of ternary blends of PLA/PBSA/PBAT was investigated.

## 2. Experimental

### 2.1. Materials and Preparations

PLA (4042D, NatureWorks, LLC, USA.) was purchased from Freshbag Co., Ltd., Thailand. PBSA (Bionelle®) was supplied by Showa High Polymer Co., Ltd., Japan. PBAT (Ecoflex FBX7011) was purchased from BASF The Chemical Company, China.

All polymers were dried in an oven at 80 °C for 8 hours before compounding. The ratio of PLA/PBSA blend was set constantly at 80/20, 80 wt% of PLA and 20 wt% of PBSA. PBAT contents were varied at 0-50 wt%. The various contents of PBAT in the PLA/PBSA blends will be referred as PBAT0, PBAT10, PBAT20, PBAT30, PBAT40 and PBAT50 for PBAT contents of 0-50wt%. The composition of the blends is shown in Table 1. PBAT were compounded with PLA and PBSA in a twin screw extruder (KEDSE 20/40, Brabender, Germany). The barrel temperature was set at 150-190 °C with screw speed of 80 rpm. After pelletized, PLA/PBSA/PBAT ternary blends were compression molded to perform a 3 mm-thick sheet at temperature of 190 °C for 4 minutes. The cooling time was set at 6 minutes.

Table 1. Blend compositions.

PLA/PBSA Blends	PBAT contents (wt%)	Sample designation
80/20	0	PLA/PBSA/PBAT0
	10	PLA/PBSA/PBAT10
	20	PLA/PBSA/PBAT20
	30	PLA/PBSA/PBAT30
	40	PLA/PBSA/PBAT40
	50	PLA/PBSA/PBAT50

## 2.2. Characterization

Thermal properties of the ternary blends were carried out by using a differential scanning calorimetry (PerkinElmer, Q8000 Diamond DSC). The specimens were heated from 30 to 200 °C at heating rate of 20 °C/min under nitrogen. The crystallization kinetic of non-isothermal crystallization of ternary blends was performed according to the Avrami equation [7-9] as following:

$$X(t) = 1 - \exp(-kt^n) \quad (1)$$

$$\log[-\ln(1 - X(t))] = \log k + n \log t \quad (2)$$

$$k = \frac{\ln 2}{(t_{1/2})^n} \quad (3)$$

where  $X(t)$  = relative crystallinity  
 $k$  = crystallization rate constant  
 $n$  = Avrami exponential  
 $t$  = time (min)  
 $t_{1/2}$  = half time crystallization (min)

The morphology of the fracture surface of the ternary blends was investigated using a scanning electron microscope (JEOL JSM-6400).

Tensile testing was performed according with ASTM D638 by using LLOYD (T30K) universal testing machine. The extension rate was 50 mm/min.

Izod impact strength of the blends was carried out according with ASTM D256 by CEAST impact tester.

## 3. Results and Discussion

### 3.1. Thermal properties of PLA/PBSA/PBAT blends

The results of DSC thermogram for the PLA/PBSA/PBAT blends are presented in Fig.1 and Fig.2. Thermal properties of the blends were summarized in Table 2. Fig.1 shows melting thermograms of neat PLA, neat PBSA, neat PBAT and PLA/PBSA/PBAT blend. The results present melting temperature ( $T_m$ ) of PLA, PBSA and PBAT at 151.3 °C, 92.7 °C and 116.4 °C, respectively. After blending PLA/PBSA with various contents of PBAT, DSC thermograms of the blends exhibit two melting peaks of PBSA and PLA at temperature about 94 °C and 149 °C for PBSA and PLA, respectively. Hence, PLA and PBSA show some miscibility, which exhibited the shift of both melting temperatures toward each other. A direct proof of polymer miscibility in blend can be obtained by observing the behavior of the  $T_m$  with the blend composition [10]. There was no change in melting temperatures of PLA and PBSA when blending with various contents of PBAT as shown in Fig.2. However, PBAT influences on the shape of the melting thermogram of both PLA and PBSA in the blends, which would effect on the crystal size forming in PLA and PBSA.

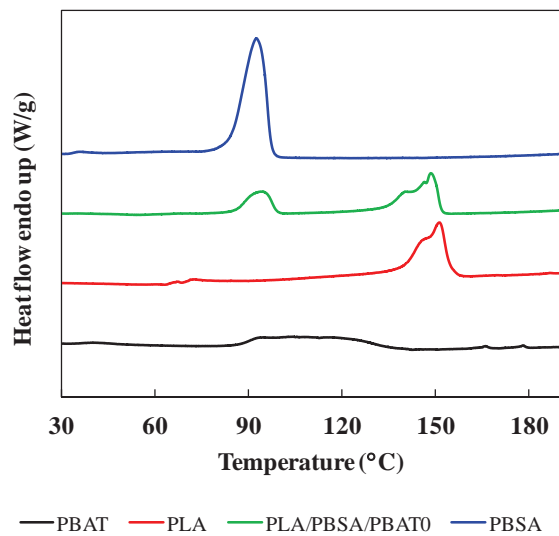


Fig.1. DSC melting thermograms of PLA, PBSA, PBAT and their blends.

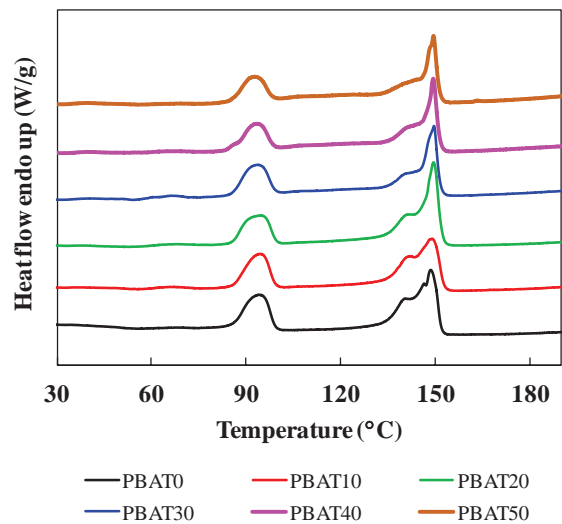


Fig.2. DSC melting thermograms of PLA/PBSA/ PBAT blends at various contents of PBAT.

Table 2. Melting temperature of PLA, PBSA and PBAT in neat polymer and in the blends.

Sample	Melting temperature (°C)		
	PBSA	PBAT	PLA
PLA	-	-	151.3
PBSA	92.7	-	-
PBAT	-	116.4	-
PBAT0	94.2	-	148.6
PBAT10	94.3	-	149.0
PBAT20	94.5	-	149.5
PBAT30	93.6	-	149.6
PBAT40	93.5	-	149.3
PBAT50	92.5	-	149.4

### 3.2. Crystallization behavior of PLA/PBSA/PBAT blends

The effect of PBAT contents on the crystallization kinetic of PLA/PBSA/PBAT blends were investigated by non-isothermal crystallization. The crystallization kinetic parameters were analyzed with the Avrami equation. Fig.3 shows relative crystallinity of PLA and PBSA phase in neat polymer and the blends with various contents of PBAT at 0, 20 and 50 wt%. The half time crystallization ( $t_{1/2}$ ) could be determined from the relative crystallinity. The results are tabulated in Table 3. It can be seen that crystallization of PBSA in the blends would be occurred earlier than PLA with regardless on PBAT contents. Fig.4 illustrates the Avrami plot of PLA and PBSA phase in neat polymer and the blends. The kinetic parameters of Avrami exponential ( $n$ ) and crystallization rate constant ( $k$ ) are presented in Table 3. PBAT influenced on crystallization of PLA and PBSA in the blends with indicated by these kinetic parameters. In addition, Avrami exponent of specimens would inform the mechanism of the growing crystal during the crystallization, which related to the heterogeneous nucleation [7-9]. From the results, the value of Avrami exponent,  $n$  for neat PLA and PBSA is 2.15 and 2.72, respectively. On the other hand, the  $n$  values of PLA and PBSA in the blends are about 1.5-1.9 and 3.0-3.4 for PLA and PBSA phase in the blends, respectively. All  $n$  values indicated a three-dimension spherulite growth of heterogeneous nucleation [7-8]. The addition of PBAT in the blends can act as heterogeneous nucleation and increase the heterogeneity in the crystallization process of PLA and PBSA. The crystallization rate constant,  $k$  increased when increasing PBAT contents in the blends. Moreover, PBAT exhibited greater influenced on crystallization of PBSA than PLA, which indicated by higher  $k$  values. Therefore, PBSA would crystallize faster than PLA.

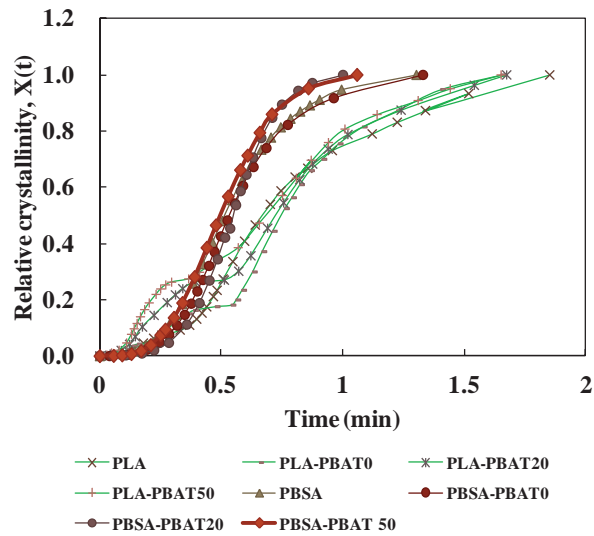


Fig.3. Relative crystallinity from non-isothermal crystallization of PLA, PLSA phase in neat polymer and their blends with various contents of PBAT.

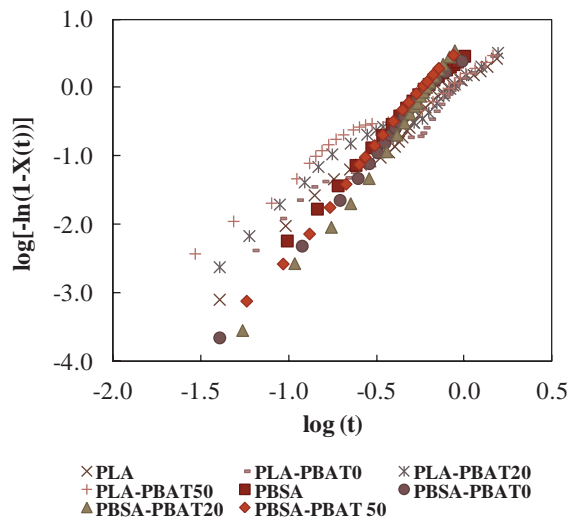


Fig.4. Avrami plot from non-isothermal crystallization of PLA, PLSA phase in neat polymer and the blends with various contents PBAT.

Table 3. Non-isothermal crystallization kinetic parameter of PLA and PBSA phase in neat polymer and the blends with PBAT.

Sample	Polymer	$t_{1/2}$ (min)	n	k ( $\text{min}^{-1}$ )
PLA	PLA	0.68	2.15	1.59
PLA/PBSA/PBAT0		0.74	1.93	1.24
PLA/PBSA/PBAT20		0.72	1.78	1.62
PLA/PBSA/PBAT50		0.68	1.55	1.20
PBSA	PBSA	0.51	2.72	4.33
PLA/PBSA/PBAT0		0.54	3.08	4.62
PLA/PBSA/PBAT20		0.57	3.48	4.92
PLA/PBSA/PBAT50		0.50	3.18	6.31

### 3.3. Morphology of PLA/PBSA/PBAT blends

Fig.5. shows SEM images of tensile fractured surfaces of PLA, PBSA, PBAT, and their blends at various contents of PBAT. From the results, it can be seen a smooth surface of brittle behavior of PLA as shown in Fig.5 (a) while there is some elongate part of ductile surface of PBSA and PBAT as presented in Fig.5. (b) and (c), respectively. Fig.5. (d) to (h) show the phase separation occurred in PLA/PBSA blends without and with PBAT. The results indicate the traditional morphology of immiscible blend system. PBSA was a dispersed phase on PLA matrix. The dispersed phases of PBSA particles were relatively small due to the increase of PBAT contents. The PBSA particle size became smaller when increasing the amount of PBAT. It might be due to less interfacial tension between PLA and PBSA when adding PBAT in the blends.

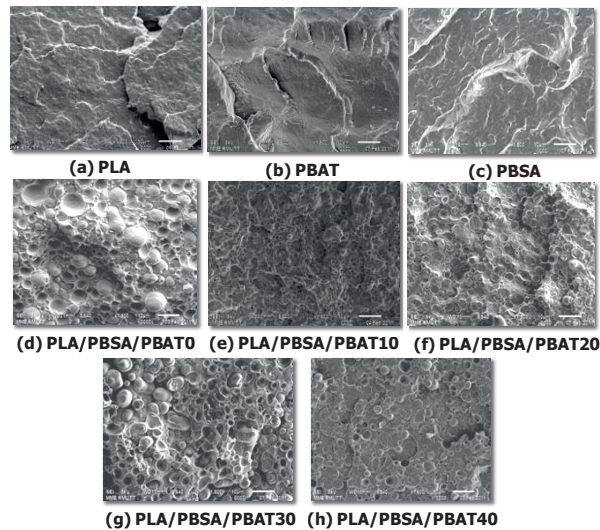


Fig.5. SEM photographs of neat PLA, neat PBSA, neat PBAT and their blends with PBAT 0-40 wt%.

### 3.4. Mechanical properties of PLA/PBSA/PBAT blends

Fig.6. exhibits tensile strength of PLA/PBSA/PBAT blends. The adding of PBAT up to 20 wt% could improve tensile strength of the blends. Nevertheless, tensile strength of the blends decreased when increasing PBAT contents, which might be due to the increment of ductile segment and poor load transferring at higher contents of PBAT. Fig.7 shows impact strength of the blends with various contents of PBAT. The impact strength of the blends increase when adding PBAT contents up to 20 wt%. It might due to the improvement of crystallization and rubber toughening effect. However, the drastically drop of impact strength could be attributed to some crack formation occur from the phase separation. It can be noted that a remarkable improvement of about two and half times of pure PLA in impact strength can be realized by using only 10-20 wt% PBAT in the blends.

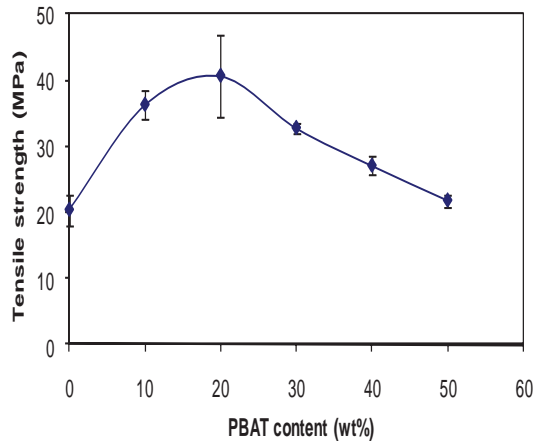


Fig.6. Tensile strength of PLA/PBSA/PBAT blends at PBAT contents 0-50 wt%.

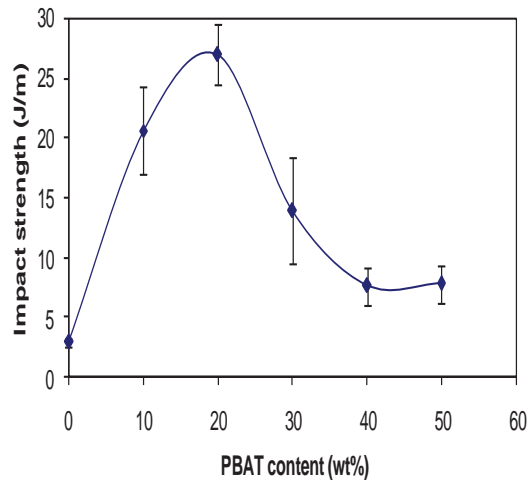


Fig.7. Impact strength of PLA/PBSA/PBAT blends at PBAT contents 0-50 wt%.



#### 4. Conclusion

In this research, we used PBAT biodegradable polymer as an additive for modifier the properties of PLA/PBSA blends. PLA and PBSA blends showed some miscibility, which was indicated by the shifted of melting temperature towards each other. However, the blends still presented phase separation when blending with PBAT. PBAT influenced on both of PLA and PBSA crystallization. The crystallization kinetic parameters informed that the crystallization process of PLA and PBSA are heterogeneous nucleation with three-dimension spherulite growth when incorporation with PBAT. The highest tensile strength and impact strength of the blends was obtained at PBAT 20 wt%.

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