

MECHANICAL AND MORPHOLOGICAL PROPERTIES OF POLY (LACTIC ACID)/POLY (BUTYLENE ADIPATE-CO-TEREPHTHALATE)/CALCIUM CARBONATE COMPOSITE

A. Teamsinsungvon^{1,2}, Y. Ruksakulpiwat^{1,2}, K. Jarukumjorn^{1,2*}

¹ School of Polymer Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand,

² Center for Petroleum, Petrochemical and Advanced materials, Chulalongkorn University, Bangkok, Thailand

* Corresponding author (kasama@sut.ac.th)

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1 General Introduction

Poly (lactic acid) (PLA), a linear aliphatic polymer, is known as a biodegradable thermoplastic polymer with widely potential applications [1, 2]. PLA has a number of interesting properties including biodegradability, biocompatibility, high strength, and high modulus [3]. For this reasons, PLA is a candidate for producing package materials. However, its high brittleness and low toughness limit its application [4]. To overcome these limitations, blending PLA with flexible polymers is a practical and economical way to obtain toughened PLA. Poly (butylene adipate-co-terephthalate) (PBAT), an aliphatic-aromatic copolyester, is considered a good candidate for the toughening of PLA due to its high toughness and biodegradability [5]. Binary blends of PLA and PBAT exhibited higher elongation at break but lower tensile strength and modulus than the pure PLA due to the addition of a ductile phase. Therefore, the addition of filler to PLA/PBAT blends led to a modulus approaching that of the pure PLA. Unfortunately, PLA blends and PLA filled with natural materials e.g. natural fiber, calcium carbonate (CaCO₃) have poor mechanical properties due to the poor interfacial adhesion. Maleic anhydride grafted PLA (PLA-g-MA) has been used to improve the interfacial adhesion between PLA and other polymers [6, 7, 8] or PLA and fillers [9, 10, 11]. CaCO₃ is selected in this study since it yields a cost reduction in polymer and can influence mechanical properties. The objective of this work was to investigate the effects of PLA-g-MA and CaCO₃ on mechanical, morphological, and thermal properties of PLA/PBAT blend.

2 Experimental

2.1 Materials

PLA used in this study was Natureworks PLA 4042D. PBAT was BASF Ecoflex FBX 7011. Calcium carbonate (CaCO₃) with an average particle size of 1.20-1.40 μ m (HICOAT 810) was supplied from Sand and Soil Co., Ltd. PLA-g-MA prepared in-house was used as a compatibilizer. The grafting level (%G) of the PLA-g-MA was 0.41% [12].

2.2 Preparation of blend and composite

PLA and PBAT pellets were dried at 70°C for 4 hrs before mixing. All blends and composite were prepared using a co-rotating intermeshing twin screw extruder (Brabender DSE 35/17D). A temperature profile was 160/165/170/165/160°C. Screw speed was 25 rpm. After exiting die, the extrudates were cooled in air before being granulated by a pelletizer. The test specimens were prepared by a compression molding machine (LabTech, LP20-B). The compression condition was processed at the temperature of 170°C and pressure of 100 MPa. The designation and composition of the blends and composite are shown in Table 1.

Table 1. Designation and composition of blend and composite

Designation	PLA [%wt.]	PBAT [%wt.]	CaCO ₃ [%wt.]	PLA-g-MA [phr]
PLA	100	-	-	-
PBAT10	90	10	-	-
cPBAT10	90	10	-	2
30CaCO ₃	90	10	30	2

2.3 Characterization of blend and composite

2.3.1 Mechanical properties

Tensile properties were obtained according to ASTM D638 using an Instron universal testing machine (UTM, model 5565) with a load cell of 5 kN.

Impact test was performed according to ASTM D256 using an Atlas testing machine (model BPI).

2.3.2 Morphological properties

Morphologies of all blends and composite were examined by a scanning electron microscope (JEOL, model JSM-6400). Acceleration voltage of 10 kV was used to collect SEM images of sample. The samples were freeze-fractured in liquid nitrogen and coated with gold before analysis.

2.3.3 Thermal properties

Thermal properties of PLA, PLA/PBAT blends, and PLA/PBAT/CaCO₃ composite were investigated using a differential scanning calorimeter (Perkin Elmer, DSC7). All samples were heated from 25°C to 200°C with a heating rate of 5°C/min (heating scan) and kept isothermal for 2 min under a nitrogen atmosphere to erase previous thermal history. Then, the sample was cooled to 25°C with a cooling rate of 20°C/min and heated again to 200°C with a heating rate of 5°C/min (2nd heating scan).

Thermogravimetric analysis of PLA, PLA/PBAT blends and PLA/PBAT/CaCO₃ composite were examined using a thermogravimetric analyzer (Perkin Elmer, SDT 2960). Thermal decomposition temperature of each sample was examined under nitrogen atmosphere. The sample with a weight between 10 to 20 mg was used for each run. Each sample was heat from room temperature to 600°C at a heating rate of 10°C/min. The weight change was recorded as a function of temperature.

3 Results and discussion

3.1 Mechanical properties

Mechanical properties of PLA, PLA/PBAT blends, and PLA/PBAT/CaCO₃ composite are listed in Table 2. Young's modulus, tensile strength, elongation at break, and impact strength values were normalized against those of pure PLA (643.95 MPa, 55.49 MPa, 11.89%, and 1.58 kJ/m² for Young's modulus, tensile strength, elongation at break, and impact strength, respectively) are shown in Fig. 1.

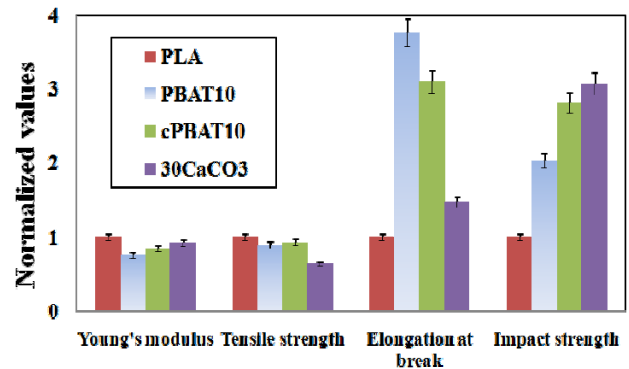


Fig.1. Mechanical properties of PLA, PLA/PBAT blend, compatibilized PLA/PBAT blend, and PLA/PBAT/CaCO₃ composite (values normalized against the Young's modulus, tensile strength, elongation at break, and impact strength of pure PLA)

The addition of PBAT into PLA resulted in a noticeable improvement of PLA ductility. Moreover, adding PLA-g-MA increased tensile strength and impact strength of the PLA/PBAT blend due to improved interfacial adhesion between PLA and PBAT through the formation of miscible blends between PLA parts of PLA-g-MA and PLA [9]. When CaCO₃ was incorporated into the compatibilized blend Young's modulus increased but tensile strength and elongation at break

Table 2. Tensile properties and impact strength of PLA, PLA/PBAT blends, and PLA/PBAT/CaCO₃ composite.

Designation	Tensile strength [MPa]	Elongation at break [%]	Young's modulus [MPa]	Impact strength [kJ/m ²]
PLA	55.49±1.22	11.89±1.92	643.95±83.13	1.58±0.16
PBAT10	49.40±1.37	44.72±8.51	487.10±36.77	3.21±0.18
cPBAT10	51.67±1.85	36.85±1.74	543.65±24.19	4.45±0.33
30CaCO ₃	35.58±2.02	17.56±2.91	593.34±40.77	4.85±0.61

decreased. The reduction of tensile strength of the compatibilized blend may be due to the agglomeration of CaCO_3 as shown in Fig.2 (e and f).

3.2 Morphological properties

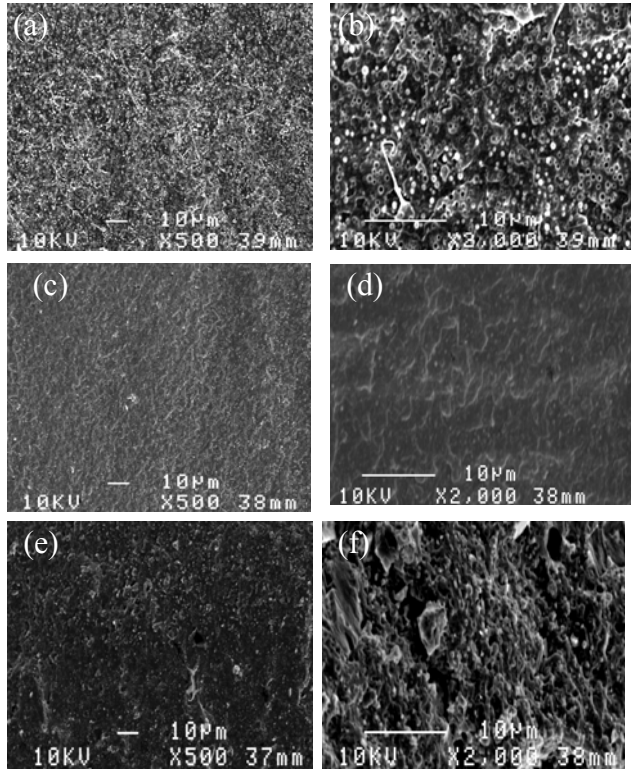


Fig.2. SEM micrographs of (a) PLA/PBAT blend (x500), (b) PLA/PBAT blend (x2000), (c) cPLA/PBAT blend (x500), (d) cPLA/PBAT blend (x2000) (e) 30CaCO₃ composite (x500), and (f) 30CaCO₃ composite (x2000)

SEM micrographs of the fracture surface of PLA/PBAT blend, compatibilized PLA/PBAT blend, and PLA/PBAT/CaCO₃ composite are shown in Fig. 2. Fig. 2(a) and (b) present PLA/PBAT blend

without PLA-g-MA. Large PBAT phase domains were found. In a case of the compatibilized PLA/PBAT blend, the dispersed phase was finely dispersed in the matrix as shown in Fig. 2(c and d) due to improved interfacial adhesion between matrix and dispersed phase. This resulted in the improvement of the mechanical properties of the PLA/PBAT blend. With the addition of CaCO₃ to compatibilized blend, agglomerates of CaCO₃ were observed as shown in Fig. 2(e) and (f). This may be because PLA-g-MA content was not enough to improve both the interfacial adhesion between PLA and PBAT in the blend and the distribution of CaCO₃ in the blend resulted in PLA/PBAT/CaCO₃ composite with poor tensile strength, elongation at break.

3.3 Thermal properties

DSC thermograms of PLA, PLA/PBAT blends and PLA/PBAT/CaCO₃ composite are shown in Fig.3. DSC data of PLA, PLA/PBAT blends, and PLA/PBAT/CaCO₃ composite are listed in Table 3. Neat PLA displayed a glass transition temperature (T_g) at 57.63°C, cold crystallization temperature (T_c) at 112.20°C, and melting temperature (T_m) at 148.67°C accompanied with shoulder-melting peak at 155.17°C. The incorporation of PBAT decreased T_c of PLA by approximate 5°C and narrowed the peak width, indicating enhancement of crystalline ability of PLA [5]. However, T_g and T_m of PLA/PBAT blend did not change when compared with PLA. With incorporation of PLA-g-MA, T_g , T_c , and T_m of PLA/PBAT blend did not change while heat of melting (ΔH_m) increased. This result suggested that PLA-g-MA improved compatibility of PLA/PBAT blend [14]. Adding CaCO₃ resulted in a decrease in heat of crystallization (ΔH_c) of the compatibilized PLA/PBAT blend. The observed

Table 3. DSC data of PLA, PLA/PBAT blends, and PLA/PBAT/CaCO₃ composite.

Designation	T_g [°C]	T_c [°C]	ΔH_c [Jg ⁻¹]	T_{m1} [°C]	T_{m2} [°C]	ΔH_m [Jg ⁻¹]
PLA	57.63	112.20	27.02	148.67	155.17	24.65
PBAT10	57.70	107.61	23.32	148.08	154.91	19.29
cPBAT10	57.44	107.19	23.22	148.11	154.35	21.05
30CaCO ₃	57.05	107.19	15.66	147.33	154.33	15.91

T_g ; glass transition temperature, T_c ; cold crystallization temperature, ΔH_c ; heat of crystallization, T_m ; melting temperature, ΔH_m ; Heat of melting.

reduction in the ΔH_c was probably attributed to the lesser polymer content in the composite available for crystallization [15].

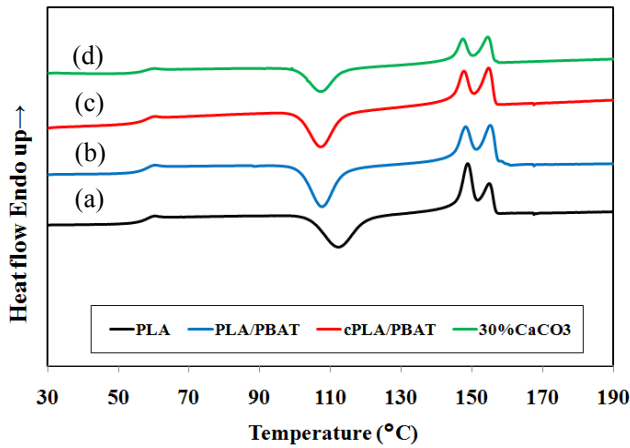


Fig.3 DSC thermograms of (a) PLA, (b) PLA/PBAT blend, (c) compatibilized PLA/PBAT blend, and (d) PLA/PBAT/CaCO₃ composite (the second heating, heating rate 5°C/min)

Table 4. Degradation temperature of PLA, PLA/PBAT blends and PLA/PBAT/CaCO₃ composite as determine from TGA results.

Designation	T ₅ [°C]	T ₅₀ [°C]	T _f [°C]
PLA	333.70	362.01	387.96
PBAT10	333.71	363.30	428.80
cPBAT10	340.76	363.72	434.18
30CaCO ₃	287.97	324.77	434.81

TGA thermograms of PLA, PLA/PBAT blends, and PLA/PBAT/CaCO₃ composite are presented in Fig.4. Thermal degradation at 5% weight loss (T₅), thermal degradation at 50% weight loss (T₅₀) and final degradation temperature (T_f) of PLA, PLA/PBAT blends and PLA/PBAT/CaCO₃ composite are listed in Table 4. T₅, T₅₀, and T_f of neat PLA were at 333.70°C, 362.01°C, and 387.96°C, respectively. The addition of PBAT into PLA increased T_f of PLA indicating the improvement of thermal stability of PLA. Furthermore, the compatibilized PLA/PBAT blend

showed higher T₅, T₅₀, and T_f than PLA/PBAT blend. This suggested that thermal stability of the blend was enhanced with addition of PLA-g-MA. PLA and PLA/PBAT blends left no char residue at 600°C. For the PLA/PBAT/CaCO₃ composite, T₅ and T₅₀ was lower than that of the blend. This indicated that thermal stability of PLA/PBAT blend significantly decreased with the compounding with CaCO₃. Because the basic nature of CaCO₃ had catalyzed the depolymerization of the ester bonds of PLA, thus it was responsible for the reduced thermal stability [16]. Moreover, the composite left the char residual at 30.22%.

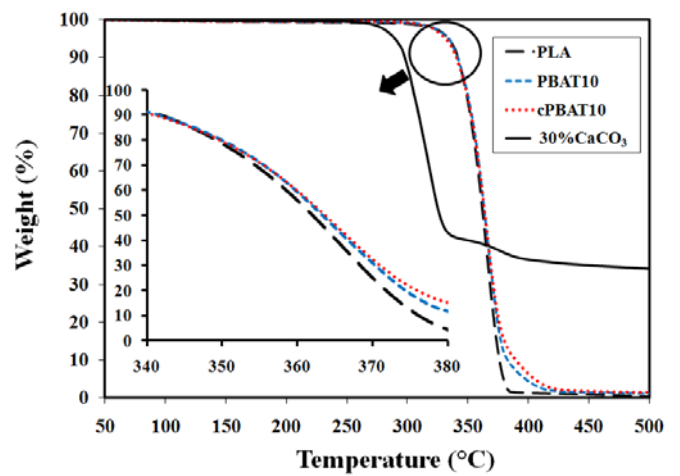


Fig.4 TGA thermograms of PLA, PLA/PBAT blend, and PLA/PBAT/CaCO₃ composite

Conclusions

PLA/PBAT blend exhibited higher elongation at break and impact strength but lower tensile strength and Young's modulus than PLA. PLA-g-MA enhanced the adhesion between PLA and PBAT leading to the improvement of the mechanical properties of PLA/PBAT blend. With the addition of CaCO₃, tensile strength and elongation at break of the PLA/PBAT blend decreased while Young's modulus and impact strength increased. The incorporation of PBAT decreased T_c of PLA indicating enhancement of crystalline ability of PLA. With presence of PLA-g-MA, T_g, T_c, and T_m of the PLA/PBAT blend did not change while ΔH_m increased. The incorporation of CaCO₃ resulted in a decrease in ΔH_c of the compatibilized PLA/PBAT blend. The thermal stability of PLA/PBAT blend improved with adding PLA-g-MA. However, CaCO₃

resulted in a reduction of thermal stability of compatibilized PLA/PBAT blend.

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