

## Mechanical, thermal and morphological properties of poly(lactic acid)/ethylene-butyl acrylate copolymer nanocomposites

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**Abstract.** This paper reports a melt blend of poly(lactic acid) (PLA)/ethylene-butyl acrylate copolymer (EBAC) with organoclay content at 3 phr. The mechanical, thermal and morphological properties of PLA/EBAC blends and nanocomposites were investigated. The morphological analysis revealed EBAC phase dispersed as a spherical domain in PLA matrix and the domain size of EBAC dispersed phase increased with increasing EBAC content. The addition of organoclay could improve the miscibility of PLA/EBAC blends due to the decrease of domain size of EBAC dispersed phase. The mechanical properties indicated that the strain at break and impact strength of PLA increased when added EBAC, but Young's modulus and tensile strength decreased. Storage modulus increased with the addition of organoclay to the PLA/EBAC blends. The thermal properties found that the incorporation of organoclay in the PLA/EBAC blends did not effect on the glass transition temperature and melting temperature values relative to PLA. The degradation temperature of PLA improved with the addition of EBAC. This indicated that EBAC has more thermal stability and degradation temperature than PLA. From X-ray diffraction patterns displayed the characteristic peak in PLA/EBAC/organoclay nanocomposites appeared at the lower angle, which indicated the dispersed clay is intercalated in the polymer matrix. However, second-order diffraction peak appeared at the higher angle indicated that there was partially the conventional composite.

### 1. Introduction

Poly(lactic acid) (PLA) is a well-known biodegradable polymer and an eco-friendly material. PLA is linear aliphatic thermoplastic polyester, which can be synthesized by condensation of lactic acid or ring opening polymerization of lactide [1-2]. Another feature that makes PLA interesting is the fact that it can be processed similarly to polyolefins, and PLA has high strength, high modulus and transparency. However, the main drawbacks with PLA properties are too brittle, low-melt viscosity, softens at relative low temperatures, low-heat distortion temperature and low thermal stability compared to commercial polymers, thus PLA led to its restricted applications [3-5]. For more applications of PLA, it needed to improve the mechanical and thermal properties of PLA.

Some researchers have studied to improve the weak properties of PLA by blending with thermoplastic starch (TPS), natural rubber, plasticizers, and other more flexible polymers [4-7] and reinforcing materials [8-10]. However, the main problems with PLA toughening through plasticizers or rubber are the reduction in strength and modulus properties of the PLA blends can be observed [4,6,11-12]. Thus, the improvement of the reduced mechanical properties of PLA blends may be improved by the addition of clay due to clay has a high aspect ratio that it often exhibits remarkable



improvement in material properties, resulting from the increased surface area between the polymer matrix and clay platelets [13]. Moreover, several studies have reported that organically modified clay or organoclay played the role as a compatibilizer for enhance the miscibility of immiscible polymer blends by effectively reducing the domain size of the dispersed phase [14-17]. For instance, Ray et al. [14] studied the effect of organoclay on the morphology and properties of poly(propylene) (PP) and poly[(butylene succinate)-co-adipate] (PBSA) blends. The results found that the presence of organoclay improved the tensile properties and thermal stability of virgin blends, and scanning electron microscopy (SEM) study observed the morphology of PP/PBSA blend was significant changed after adding organoclay. Mallick *et al.*, (2010) [15] studied the morphology and properties of poly(methyl methacrylate) (PMMA)/high-density polyethylene (HDPE) blends with organoclay. They reported that the average domain sizes of the dispersed HDPE phase in PMMA/HDPE (70/30 w/w) blends decreased in presence of organoclay. The incorporation organoclay increased the tensile strength and storage modulus of the PMMA/HDPE blends. Thus, the addition of organoclay to improve the miscibility and properties of PLA blends is interesting.

Some literatures have investigated the addition of organoclay to improve the properties of PLA blends for extend applications. For example, the study of Hasook *et al.*, (2006) [13] investigated the effect of organoclay on the mechanical properties of PLA/poly( $\epsilon$ -caprolactone) blends. They found that Young's modulus of PLA/organoclay composites was higher than that of neat PLA. The elongation of the PLA/PCL/organoclay composites also improved. Thus, the presence of organoclay can improve the strength and modulus of the PLA blends.

This work studied the influence of organoclay on mechanical, thermal and morphological properties of PLA/ethylene-butyl acrylate copolymer (EBAC)/organoclay composites. The composites with varying contents of organoclay were prepared by a melt mixing technique in an internal mixer and molded by compression molding.

## 2. Materials and Methods

### 2.1. Materials

PLA with the melt flow index (210°C/2.16 kg) of 6.0 g/10 min and specific gravity of 1.24 was produced by NatureWorks LLC, USA, under the trade name of "Ingeo™ Biopolymer 2003D". The ethylene-butyl acrylate copolymer (EBAC) has the melt flow index (190°C/2.16 kg) of 3.95 g/10 min and density of 0.926 g/mL. EBAC with 28.10 wt% of buthyl acrylate was produced by DuPont Company. The nanoclay surface modified with 25-30 wt% of octadecylamine (organoclay) was purchased from Aldrich Company.

## 2.2. Sample Preparation

Before blending, PLA was dried in an oven at 80°C for 4 h, and organoclay was dried at 80°C 24 h to eliminate moisture. EBAC was not dried before blending process. PLA/EBAC blends were prepared by melt blending in an internal mixer at 180°C and a rotor speed of 80 rpm for 15 min. The EBAC contents were 5, 10, 10 and 30 wt%. PLA/EBAC blends with organoclay content 3 phr were prepared in a same condition. PLA/EBAC first melted for 5 min and then organoclay was added and continuous mixed for 10 min. After compounding, PLA/EBAC blends without and with organoclay were dried in an oven at 80°C for 1 h for reject moisture. Afterward the blends and composites were compression molded at 180°C for testing.

## 2.3. Sample Characterization

The morphology of impact fractured surfaces of PLA/EBAC blends without and with organoclay was investigated by scanning electron microscope (SEM) instruments (Maxim 2000S, CamScan Analytical, UK) at 15 kV accelerating voltage after gold coating.

The impact strength of PLA/EBAC blends without and with organoclay was measured using a noted Izod impact tester (Zwick/material testing August-Nagelstr.11.D-89079 Ulm) at room temperature. The impact test was performed according to ASTM D 256. Tensile test was conducted according to ASTM D 638 with a universal tensile testing machine (LR 50k from Lloyd instruments, UK) at a crosshead speed of 50 mm/min. Each value obtained represented the average of five samples.

The thermomechanical properties (storage modulus) of PLA/EBAC blends without and with organoclay was measured in bending film mode at a constant vibration frequency of 1 Hz, a temperature ranges of 30-140°C, and a heating rate of 5°C/min in a nitrogen atmosphere with a dynamic mechanical analyzer (DMA) (Pyris Diamond DMA, Perkin Elmer, USA). The glass transition temperature was detected by using the peak of  $\tan \delta$  from DMA test.

Differential scanning calorimetry (DSC) characterization (Pyris I, Perkin Elmer, USA) was performed to investigate the glass transition temperature of the composites. The temperature was in the range of 50-200°C at a heating rate of 10°C/min in a nitrogen atmosphere for the heating scan then the analysis performed from the heating scan. The degradation temperature of PLA/EBAC blends without and with organoclay was measured by thermogravimetric analysis (TGA) (SDT Q600, TA Instruments, UK). The temperature was in the range of 30-600°C at a heating rate of 10°C/min under nitrogen atmosphere.

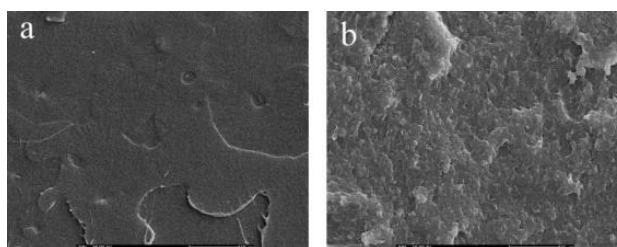
### 3. Results and Discussion

#### 3.1. Morphology

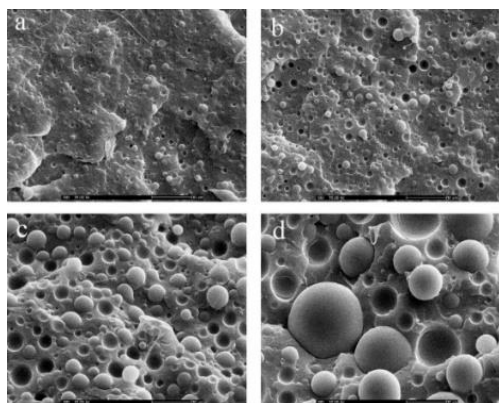
Figure 1 shows the SEM micrographs of the impact fractured surfaces of pure PLA and PLA/organoclay (100/3) composites, respectively. Figure 1(a) shows the impact fractured surface of pure PLA presented a smooth surface, characteristic of a brittle semicrystalline polymer [6]. While impact fractured morphology of PLA/organoclay composites in Figure 1(b) was relatively rough.

Figure 2(a-d) shows SEM micrographs of impact fractured surface of PLA/EBAC blends with increasing EBAC contents from 5 to 20% (w/w). The micrographs of the blends were clearly demonstrated a two-phase separation of the dispersed phase and matrix phase. This indicates that PLA/EBAC blends are completely immiscible, where minor phase of EBAC disperses as spherical domains in PLA matrix. Moreover, the domain size of dispersed EBAC phase increased with increasing EBAC content. In general, in an immiscible blend system especially at high content of dispersed phase, polymers always coagulate individually due to their different chemical structures and high molecular weights [6]. Additionally, the microvoids surrounding the EBAC droplets indicate weak interfacial adhesion in the blends because of the immiscible nature of the polymers. Because of the high interfacial tension between the two polymers, the spherical morphology is anticipated because of the minimization of the interfacial area [18].

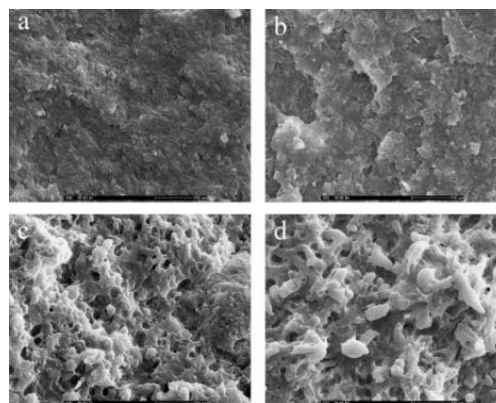
Figure 3 shows the SEM micrographs of the impact fractured surfaces of PLA/EBAC/organoclay composites. The addition of organoclay in the PLA/EBAC blend reduced the spherical domain sizes of dispersed EBAC phase significantly when compared with the blends absence organoclay. The spherical shape of dispersed EBAC phase was changed to elongated structure at high EBAC concentration. This indicated that the compatibility between PLA and EBAC was improved when organoclay was added. Thus, the organoclay plays an important role as compatibilizer in reducing the spherical domain of EBAC of PLA blends.



**Figure 1.** SEM micrographs of impact fractured surface of (a) PLA and (b) PLA/organoclay (100/3).



**Figure 2** SEM micrographs of PLA/EBAC blends (a) 95/5, (b) 90/10, (c) 80/20, and (d) 70/30.



**Figure 3** SEM micrographs of PLA/EBAC/organoclay composites (a) 95/5/3, (b) 90/10/3, (c) 80/20/3, and (d) 70/30/3.

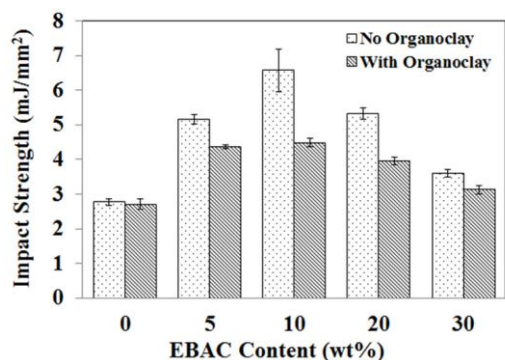
### 3.2. Mechanical Properties

Figure 4 shows the impact strength of PLA/EBAC blends without and with organoclay at various EBAC contents. The impact strength of neat PLA was  $2.77 \text{ mJ/mm}^2$ . The impact strength of PLA/EBAC blends increased with increasing EBAC content up to 10% (w/w), this behavior was also observed in the PLA/natural rubber blends [4]. When the NR content reached 10% (w/w), impact strength of the PLA/EBAC blends was  $6.57 \text{ mJ/mm}^2$ , which is about two times higher than that of neat PLA. However, when EBAC content was increased to 20% and 30% (w/w), impact strength of PLA/EBAC blends was decreased to  $5.32$  and  $3.60 \text{ mJ/mm}^2$ , respectively, but it was still higher than that of neat PLA. This suggests that the optimum content of EBAC in PLA is 10% (w/w). The decrease in impact strength of PLA/EBAC blends at high EBAC content may be due to the enlargement of the dispersed EBAC caused by the coagulation of EBAC phase as shown in SEM micrographs. From the results indicated that EBAC could improve the impact strength of PLA. The impact strength of PLA/organoclay (100/3) was  $2.71 \text{ mJ/mm}^2$  and the addition of organoclay decreased the impact strength of PLA/EBAC blends every concentration EBAC. However, the impact strength of PLA/EBAC/organoclay composites increased with increasing EBAC content up to 10% (w/w) same as the trend of PLA/EBAC blends, and it was still higher than that of neat PLA. This implied that the addition of organoclay did not improve the impact strength of PLA/EBAC blends.

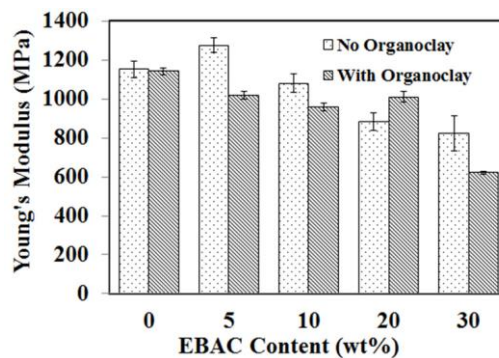
Figure 5 shows Young's modulus of PLA/EBAC blends without and with organoclay at various EBAC contents. The Young's modulus of neat PLA was  $1,152.08 \text{ MPa}$ . Young's modulus of PLA increased when added EBAC content of 5% (w/w) and Young's modulus of PLA/EBAC blends decreased with increasing EBAC content when EBAC contents were 10, 20 and 30% (w/w). Thus, the reduction in Young's modulus was due to the result of the rubbery nature of EBAC and a weak interfacial adhesion between PLA and EBAC phases as previous shown in SEM micrographs [4]. The Young's modulus of PLA/organoclay (100/3) was  $1,141.14 \text{ MPa}$  and the addition of organoclay



decreased the Young's modulus of PLA/EBAC blends every concentration EBAC and Young's modulus of PLA/EBAC/organoclay composites showed the trend like as Young's modulus of PLA/EBAC blends. This implied that the addition of organoclay did not improve Young's modulus of PLA/EBAC blends.



**Figure 4.** Impact strength of PLA/EBAC blends without and with organoclay 3 phr.



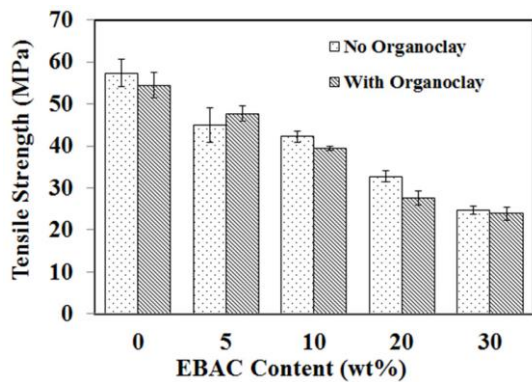
**Figure 5.** Young's modulus of PLA/EBAC blends without and with organoclay 3 phr.

Figure 6 shows the tensile strength of PLA/EBAC blends without and with organoclay at various EBAC contents. The tensile strength of neat PLA was 57.36 MPa. The tensile strength of PLA/EBAC blends decreased with increasing EBAC content. Thus, the reduction in tensile strength was due to the result of the rubbery nature of EBAC and a weak interfacial adhesion between PLA and EBAC phases as previous shown in SEM micrographs [4]. The tensile strength of PLA/organoclay (100/3) was 54.45 MPa and the addition of organoclay slight decreased the tensile strength of PLA/EBAC blends all concentration EBAC. This result indicated that the addition of organoclay did not improve the tensile strength of PLA/EBAC blends.

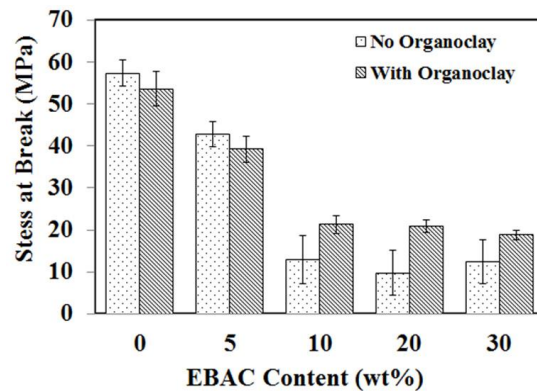
Figure 7 shows the stress at break of PLA/EBAC blends without and with organoclay at various EBAC contents. The stress at break of neat PLA was 57.36 MPa. The stress at break of PLA/EBAC blends decreased with increasing EBAC content. Thus, the reduction in stress at break was due to the result of nature of EBAC and a poor interfacial adhesion between PLA and EBAC phases [4]. The stress at break of PLA/organoclay (100/3) was 53.61 MPa and the addition of organoclay slight decreased the stress at break of PLA/EBAC blends at EBAC 5% (w/w), while the addition of organoclay increased the stress at break of PLA/EBAC blends in a range of 10-30% (w/w).

Figure 8 shows the strain at break of PLA/EBAC blends without and with organoclay at various EBAC contents. The strain at break of neat PLA and PLA/organoclay were 9.37% and 10.53%, respectively. The strain at break of PLA/EBAC blends increased with increasing EBAC content and the strain at break of the blends increased to 64.26% when EBAC content was 30% (w/w) [4]. The results indicated that EBAC could improve the strain at break of PLA. The incorporation of organoclay increased the strain at break of PLA/EBAC blends in a range of EBAC content 10%-20%

(w/w), while the other EBAC content showed the strain at break of PLA/EBAC/organoclay composites was small change.



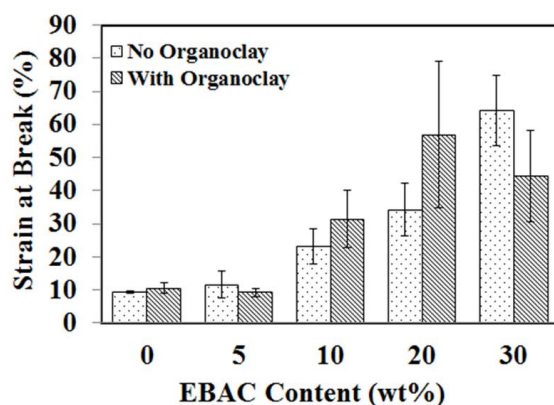
**Figure 6.** Tensile strength of PLA/EBAC blends without and with organoclay 3 phr.



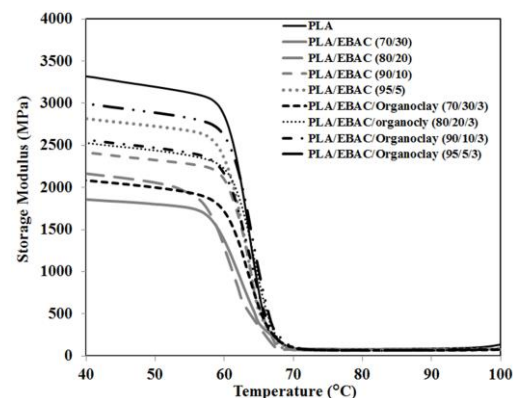
**Figure 7.** Stress at break of PLA/EBAC blends without and with organoclay 3 phr.

### 3.3. Thermomechanical Properties

The thermomechanical property of PLA/EBAC blends without and with organoclay was examined by DMA. The variation of storage modulus of PLA, PLA/EBAC blends and composites is presented in Figure 9. The storage modulus PLA/EBAC blends and PLA/EBAC/organoclay composites tended to decrease with increasing temperature. The storage modulus of pure PLA showed the highest value, and it was higher than PLA/EBAC blends and composites. The storage modulus of PLA/EBAC blends decreased with increasing EBAC content due to EBAC contain ethylene molecules which are more flexibility and an elongation than PLA.



**Figure 8.** Strain at break of PLA/EBAC blends without and with organoclay 3 phr.



**Figure 9.** Storage modulus of PLA/EBAC blends without and with organoclay 3 phr.

The behavior of the decrease of modulus was also found in the PLA/natural rubber blends [4]. The presence of organoclay increased the storage modulus of PLA/EBAC blends in every concentration. Thus, organoclay could improve the storage modulus of PLA/EBAC blends. This behavior was also observed in poly(methyl methacrylate) (PMMA)/high-density polyethylene (HDPE)/organoclay composites [15].

### 3.4. Thermal Properties

The results of thermal properties showed that the melting temperatures ( $T_m$ ) of PLA and PLA/organoclay (100/3) were 151.3°C and 153.4°C, while  $T_m$  of blends and composites was  $153.3 \pm 1.3^\circ\text{C}$ . Thus, the melting temperatures of PLA blends and composites were not significantly changed when EBAC and organoclay was incorporated in the polymer matrix. The glass transition temperatures of PLA and PLA/organoclay were 66.4 and 67.8°C, respectively. Generally, glass transition temperatures of PLA/EBAC blends were in between  $67.1 \pm 1.1^\circ\text{C}$ . Thus, addition of EBAC had no effect on the glass transition temperature of PLA. The glass transition temperature of PLA/EBAC/organoclay composites were in between  $67.7 \pm 0.4^\circ\text{C}$ . Thus, the glass transition temperatures of the PLA/EBAC blends were not significantly changed when organoclay was incorporated.

The degradation temperatures corresponding to the 10% weight loss were calculated. The degradation temperatures of PLA, EBAC and organoclay were 315.4, 412.1 and 366.2°C, respectively. This indicated the higher thermal stability of EBAC when compared with that of PLA. The result showed the incorporation of EBAC improved the degradation temperature of PLA. This indicates that an improvement in the thermal stability in the PLA/EBAC blends due to EBAC had the higher degradation temperature. The degradation temperatures of PLA/EBAC blends at 5, 10, 20 and 30 wt% of EBAC were 338.5, 339.8, 331.4 and 342.9°C respectively. While the degradation temperature of PLA blends composites was  $340.3 \pm 1.5^\circ\text{C}$ . The result showed that the addition of organoclay did not improve the degradation temperature of PLA/EBAC blends.

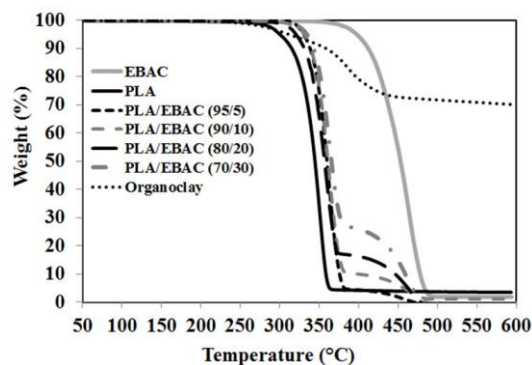
Figures 10 and 11 show the thermogravimetric curves of thermal degradation of pure PLA, EBAC, organoclay and PLA/EBAC blends and composites. It is evident that the thermal degradation of PLA, EBAC, organoclay showed only single step of weight loss, while the thermal degradation of PLA/EBAC blends and composites proceeded by two degradation steps. It was found that the first step showed a large mass loss starting at around 300°C, this main region was thermal degradation of PLA. The second step showed a small mass loss starting at around 380°C, this region was thermal degradation of EBAC. Moreover, this region showed the mass loss of PLA/EBAC blends at high EBAC content was lower than the blends at low EBAC content.



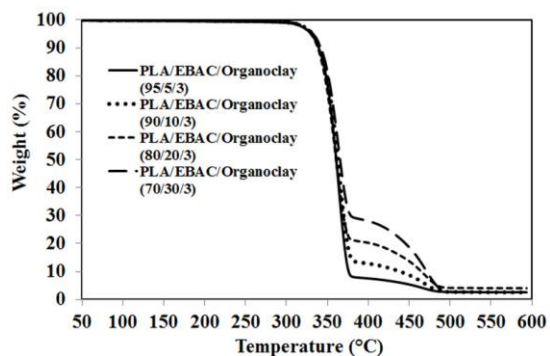
### 3.5. XRD Analysis

From the XRD results, the dispersion state of the clay platelets in the polymer/clay nanocomposites can be identified, i.e., whether the dispersed clay is intercalated or exfoliated in the polymer matrix [13]. Figure 12 show the XRD pattern of organoclay, PLA, PLA/organoclay and PLA/EBAC blends without and with organoclay. The XRD results showed that there were no peaks in XRD data of neat PLA and PLA/EBAC blends, therefore, these peaks are attributed to the presence of clay. The organoclay exhibited peak at  $2\theta$  of  $4.14^\circ$ , which corresponds to d-spacing of 2.13 nm. The clay peak in PLA/organoclay (100/3) shifted to a lower  $2\theta$  region, indicating that the d-spacing increased to 3.20 nm. This implied that the distance between the clay platelets in the PLA/organoclay was larger than that in the neat organoclay, so the dispersed clay was intercalated in polymer matrix.

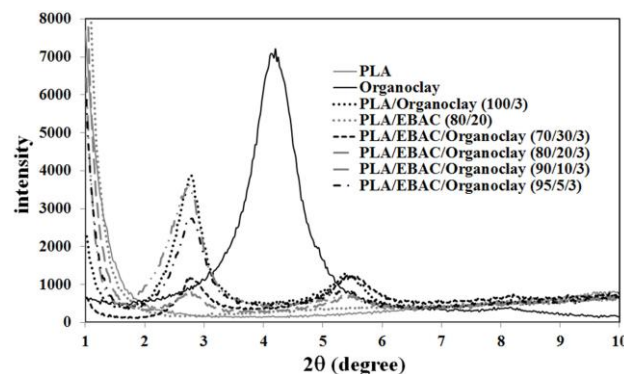
The characteristic peak of clay in PLA/EBAC blends at EBAC content 5, 10, 20 and 30 wt% with organoclay 3 phr were found at  $2\theta = 2.76^\circ$ ,  $2.72^\circ$ ,  $2.73^\circ$  and  $2.74^\circ$ , which corresponds to d-spacing of 3.20, 3.25, 3.23 and 3.22 nm, respectively. This result indicated the dispersed clay was intercalated due to the intercalation of polymer chains usually increases the d-spacing of the clay platelets [13]. However, second-order diffraction peak appeared at the higher region indicated that there was partially the conventional composite.



**Figure 10.** Thermogravimetric curves of PLA/EBAC blends.



**Figure 11.** Thermogravimetric curves of PLA/EBAC/organoclay composites.



**Figure 12.** XRD patterns of organoclay, PLA, PLA/organoclay and PLA/EBAC/organoclay composites.

#### 4. Conclusion

This paper reported the morphological, mechanical and thermal properties of PLA/EBAC blends and nanocomposites. The micrographs of PLA/EBAC blends demonstrated a two-phase separation of the dispersed phase and matrix phase, and the domain size of dispersed EBAC phase increased with increasing EBAC content. The addition of organoclay in the PLA/EBAC blend reduced the spherical domain sizes of dispersed EBAC phase significantly. The mechanical properties indicated that the strain at break and impact strength of PLA increased when added EBAC. The storage modulus increased with the addition of organoclay to the PLA/EBAC blends. The thermal properties found that the incorporation of EBAC in PLA and organoclay in PLA blends did not effect on the glass transition temperature and melting temperature of PLA. The degradation temperature of PLA was improved with the addition of EBAC. From X-ray diffraction patterns displayed the d-spacing of each PLA/organoclay and each PLA/EBAC/organoclay nanocomposites was larger than that of neat organoclay. These results imply that the spacing between clay platelets is greater in the PLA/organoclay and PLA/EBAC/organoclay nanocomposites than in the neat organoclay, this indicates the dispersed clay is intercalated in the polymer matrix.

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