

PREPARATION AND CHARACTERIZATION OF POLY-3-HYDROXYBUTYRATE/POLY (BUTYLENEADIPATE-CO-TEREPHTHALATE)/LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

YEN LENG PAK^a, MANSOR BIN AHMAD^{b*}, KAMYAR SHAMELI^{a, b}, WAN MD ZIN WAN YUNUS^c, NOR AZOWA IBRAHIM^a, NORHAZLIN ZAINUDDIN^a

^a*Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

^b*Nanotechnology and Advance Materials Department, Materials & Energy Research Center, Karaj, 31787/316, Alborz, Karaj, Iran*

^c*Faculty of Defence Science and Technology, National Defence University of Malaysia, Sungai Besi Camp, 57000 Kuala Lumpur, Malaysia*

Poly-3-hydroxybutyrate/Poly(butyleneadipate-co-terephthalate)/layered double hydroxide (PHB/PBAT/LDH) nanocomposites were prepared from PHB/PBAT blend and stearate Zn₃Al LDH via a solution casting method in this study. By using co-precipitation method, the pristine Zn₃Al LDH was prepared from nitrate salts solution at pH 7 and then modified by stearate anions through an ion exchange reaction. This modification increased the basal spacing of the LDH from 8.77 to 24.94 Å. The stearate Zn₃Al LDH infrared spectrum showed the presence of stearate ions in the synthesized Zn₃Al LDH. Mechanical properties of the nanocomposites with 2 wt% stearate Zn₃Al LDH content show 56 wt% improvements in elongation at break compared to those of the blend.

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1. Introduction

Environmental concerns and high price of crude oil have been attracting more interest on biodegradable polymers from renewable resources over the past two decades. Natural polymers, synthetic polymers and polymer from microbial fermentation such as polyhydroxybutyrate are the three groups of polymer from renewable resources.

Poly-3-hydroxybutyrate (PHB) is produced by controlled bacterial fermentation [1]. It is one of the environment friendly polymers that have been attracted widespread attention with its same physical properties to polypropylene. However, the brittleness, high cost, and poor thermal stability of PHB restrict its development and commercial application. Existence of large crystals in the form of spherulites mostly leads to brittleness of PHB. Efforts have been made by worldwide researchers to overcome those problems and to improve different properties. The most cost-effective and generally used method is blending of PHB with another kind of polymers, [2-5] such as starch, polycaprolactone (PCL), poly (vinyl acetate) (PVAc), and cellulose derivatives have been studied to modify the properties and expand its practical application [6-8].

Poly (butyleneadipate-co-terephthalate) (PBAT) is aliphatic-aromatic co-polyester that has high toughness and degrades with the assist of naturally occurring enzymes within few weeks. It has no adverse effect on the environment and its excellent physical properties give high flexibility

* Corresponding authors: mansorahmad@gmail.com

when blended with other biodegradable resins. As a result, PBAT is an excellent candidate for toughening polymers such as poly (lactic acid) and PHBV [9].

Inorganic–organic nanocomposite materials with functional organic compounds immobilized into a layered inorganic matrix have potential to offer scientific and technological advantages, since the organized two-dimensional arrays of organic species between the interlayers can result in novel functions that are different to the typical functions of the individual organic species [10–17].

An electrostatic layer-by-layer assembly technique that employs inorganic nanocomposites as building blocks is a possible means of forming a well-ordered multilayered architecture containing the arrays, because the nanocomposites have ultimate two-dimensional anisotropy with nanoscale thickness and microscale length in the plane of sheet [18]. It is known that some smectite clay minerals like montmorillonite, metal phosphates and layered oxides can be exfoliated into negatively charged nanosheets [19]. In contrast, positively charged nanosheets are a minority among exfoliated nanosheets. Recently, the exfoliation of layered double hydroxides (LDHs) has been studied as a method of preparing such positively charged nanosheets [20]. LDH nanosheets have high potential for use as building blocks to integrate negatively charged organic molecules into restricted arrays, due to their high stability and compatibility with many functional molecules [21–24].

Layered double hydroxide (LDH) is one of the attractive choices as nano-filler which have significantly improved the physicochemical properties of polymer matrix. In contrast to either neat polymer or the conventional composites, polymer nanocomposites are characterized by improved mechanical, thermal and barrier properties, reduced gas permeability, and flame retardancy [25–28]. Improvement in properties of the nanocomposites is related to their unique phase morphology that maximizes the interfacial interaction between the well-dispersed nanometer size domains and the matrices. LDH has received world-wide attention because they are useful to be incorporated in many applications, such as catalysis, stabilizer, flame retardant materials, medical materials, adsorbents, ion-exchangers, and in environmental chemistry. [29]

In this article, the preparation of PHB/PBAT/stearate- Zn_3Al LDH nanocomposites is discussed. The morphological and mechanical properties of nanocomposites have been examined. Significant improvement of elongation at break was observed when the modified LDH was incorporated into polymer blends.

2. Experimental Section

2.1 Materials

Poly [(r)-3-hydroxybutyric acid] was purchased from Sigma-aldrich, Germany, in powder form. Poly (butylenes adipate-co-terephthalate), PBAT, trade name ECOFLEX®, F BX 7011 was supplied by BASF Plastic Technologies USA. Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) was supplied by Bendosen Laboratory Chemicals, Norway. Aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$) was supplied by Hmbg Chemicals, Germany. All the chemicals were used as received without further purification process.

2.2. Synthesis of Zn_3Al LDH

The Zn_3Al LDH was synthesized via co-precipitation by adding drop wise a solution of NaOH (1M) into a 250 mL solution of 22.30 g $Zn(NO_3)_2 \cdot 6H_2O$ and 9.38 g $Al(NO_3)_3 \cdot 9H_2O$ with the mole ratio of 3:1 until pH 7 was obtained. The solution was stirred vigorously under nitrogen atmosphere in order to minimize any contamination of carbonate from the air. At 100 rpm and 70 °C, the resulting suspension was shaken for 16 hours. The slurry was filtered and washed several times with deionized water. The Zn_3Al LDH was obtained after dried at 60 °C for 24 hours.

2.3. Preparation of stearate–Zn₃Al LDH

The stearate–Zn₃Al LDH was prepared by replacing nitrate ions in the LDH layers with stearate ions using following method. One gram of dry Zn₃Al LDH was dispersed into 1 L of 0.003 M sodium stearate solution. The solution was stirred for 24 hours and aged at 70 °C in water bath. The slurry was filtered and washed several times with deionized water and dried at 60°C. The dried sample was ground and sieved into particles which were less than 100 micrometer.

2.4. Preparation of PHB/PBAT/stearate–Zn₃Al LDH Nanocomposites

The nanocomposites of PHB/PBAT blend and stearate–Zn₃Al LDH were prepared by a solution casting method. The blend composition was kept constant (PHB 90 wt% + PBAT 30 wt%) whereas the stearate–Zn₃Al LDH content was varied between 0 wt% and 5 wt%. Desired amount of stearate–Zn₃Al LDH and blend were measured and transferred into 50 mL of choloform. Both mixtures were stirred for 1 h, mixed and stirred for another 1 h. The mixture was casted in a petri dish and left in fume cupboard for few days to obtain the sample sheets.

2.5 Characterization Methods and Instruments

X-ray diffraction (XRD) measurement for LDHs and nanocomposites were carried out by using Shimadzu XRD 6000 diffracto-meter at 30 kV and 30 mA with Cu-Ka radiation of the wavelength of 1.5405 nm in 2θ range from 2 to 30°. Fourier-transform infrared (FTIR) spectra of the materials were recorded using a Perkin Elmer Spectrum 1000 series Spectrophotometer equipped with attenuated total reflectance (ATR). The infrared spectra of the samples were recorded in the range of frequency of 400–4,000 cm⁻¹. Scanning electron microscopy (SEM) images were obtained using a Philips XL30 ESEM scanning electron microscope operated at 20 kV. The samples were coated with gold by a Bio-rad coating system before viewing. Tensile test were carried out by a Universal Testing Machine, Instron 4302, according to ASTM D638-5. The samples were cut into dumbbell shape and the average of thickness and width were measured. The average of at least 5 measurements of tensile test was used in calculation.

3. Results and discussion

3.1. Characterization of Zn₃Al LDH and stearate–Zn₃Al LDH

The Fig. 1. illustrates the XRD patterns for the pristine and stearate–Zn₃Al LDH in the range of 2θ from 2 to 30°. Both LDHs are crystalline in nature with definite and distinct of layered structure.

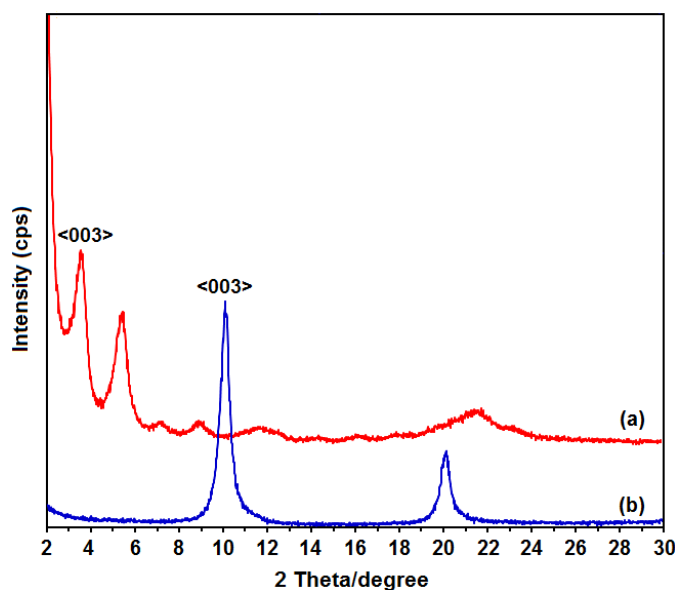


Fig. 1. XRD pattern of (a) pristine Zn₃Al LDH and (b) stearate–Zn₃Al LDH.

By using Bragg's equation, $n\lambda = 2d \times \sin\theta$, the first diffraction peak from both pristine and stearate- Zn_3Al LDH is used to calculate the basal spacing (d). The clay interlayer spacing was increased from 8.77 Å in pristine LDH (corresponding 2θ value of $\langle 003 \rangle$ peak is 10.08°) to 24.94 Å in stearate- Zn_3Al LDH ($2\theta = 3.54^\circ$) after the modification of pristine LDH with stearate ions. The increase of the basal spacing indicates that the stearate anions were intercalated into the interlayers of LDH successfully [30].

FTIR spectra of the pristine Zn_3Al LDH and stearate- Zn_3Al LDH are exposed in Fig. 2. The broad absorption peak observed was at around 3398 cm^{-1} in pristine LDH for O-H stretching of both hydroxide layers and interlayer water molecules [31]. An intense peak observed at 1340 cm^{-1} is due to the asymmetric and asymmetric vibration of the nitrate anions in the Fig. 2(a) [32]. At about 1639 cm^{-1} , the interlayer water of stretching vibration (H-OH) can be obtained. The lattice vibration bands of the M-O and O-M-O (M= Mg or Al) bonding presence at below 800 cm^{-1} region.

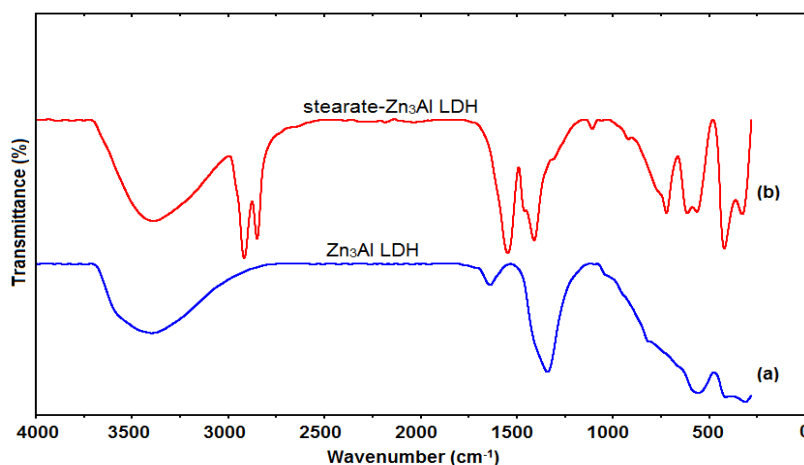


Fig. 2. FTIR spectra for (a) pristine Zn_3Al LDH and (b) stearate- Zn_3Al LDH.

At the same time, the stearate- Zn_3Al LDH spectrum [Fig. 2.(b)] shows the peak at around 2850 and 2917 cm^{-1} which exhibit the C-H stretching vibration due to appearance of the $-CH_3$ and $-CH_2$ group in the chain of stearate anions [33]. Carboxylate asymmetric and symmetric stretching is represented by two intense absorption peaks at 1546 cm^{-1} and 1409 cm^{-1} respectively [34]. It can be concluded that spectrum of the stearate- Zn_3Al LDH and pristine Zn_3Al LDH contains many similar major peaks.

Surface morphology of the pristine Zn_3Al LDH and modified stearate- Zn_3Al LDH particles are shown in Fig. 3. As shown in Fig. 3, the clay is received as porous particles in the existence of the organic anions [31].

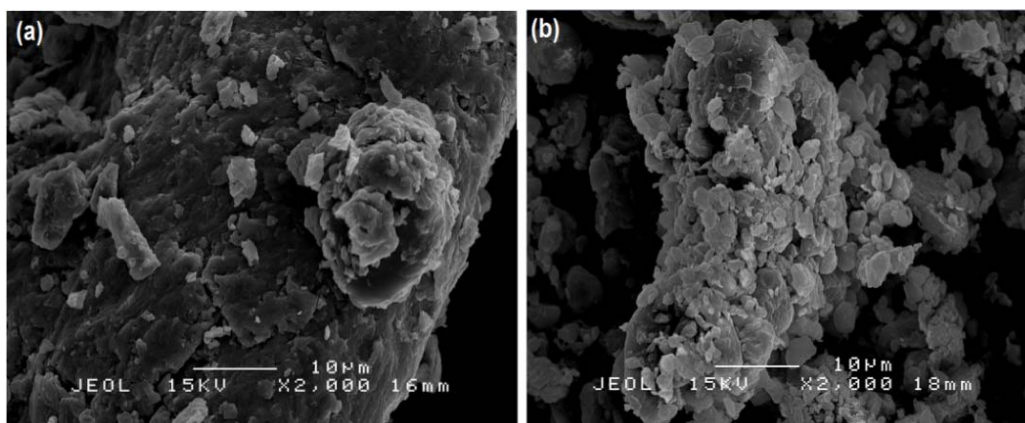


Fig. 3. Scanning electron micrographs of (a) pristine Zn_3Al LDH and (b) stearate- Zn_3Al LDH.

3.2. Characterization of PHB/PBAT/stearate-Zn₃Al LDH

XRD patterns for pure PHB, pure PBAT, PHB/PBAT blend and PHB/PBAT/LDH nanocomposites are shown in the Fig. 4. The presence of the diffraction peak in the PHB/PBAT/LDH nanocomposites with 1.0, 2.0, 3.0, 4.0 or 5.0 wt % of the LDH indicates that the stearate-Zn₃Al LDH layers are completely intercalated in the blend matrix. The interlayer spacing for 1.0, 2.0, 3.0, 4.0 or 5.0 wt % of the LDH in polymer blend were 41.25 Å, 43.70 Å, 40.87 Å, and 40.49 Å respectively.

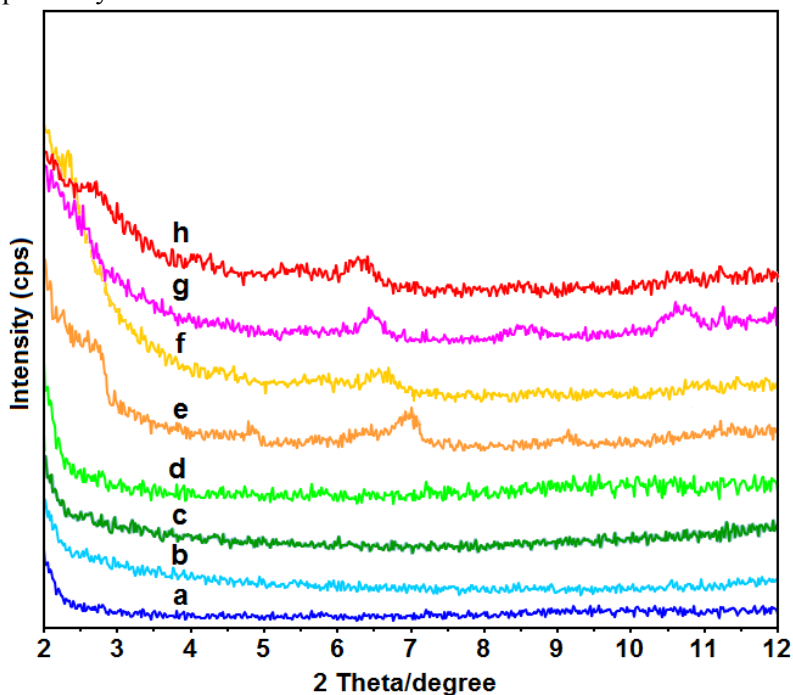


Fig. 4. XRD pattern for (a) pure PBAT, (b) pure PHB, (c) PHB/PBAT blend, and nanocomposites of 1, 2, 3, 4, and 5 wt % of stearate-Zn₃Al LDH (d-h).

The FTIR spectra of PHB, PBAT, PHB/PBAT blend and PHB/PBAT/stearate-Zn₃Al LDH nanocomposites are shown in Fig. 5. The C=O stretching bands of PHB are located at 1719 cm⁻¹, with shoulders at about 1740 cm⁻¹, which are representative of PHB crystalline and amorphous zone. Meanwhile, the major peak observed were at 1712 cm⁻¹ for C=O stretching and 1475 cm⁻¹ for aromatic C=C stretching in PBAT chains. The spectra of PHB/PBAT blend and PHB/PBAT/stearate-Zn₃Al LDH are consistent with the combination of PHB and PBAT. No major peak shifting and no new peak formation in the blend and nanocomposites spectra indicates that there is no strong interaction among PHB, PBAT and stearate-Zn₃Al LDH.

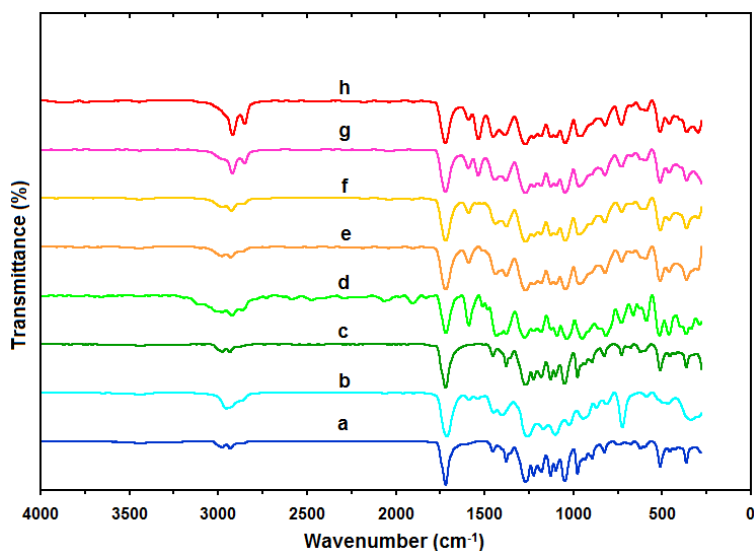


Fig. 5. FTIR spectra for (a) pure PHB, (b) pure PBAT, (c) PHB/PBAT blend and nanocomposites of PHB/PBAT with 1, 2, 3, 4, and 5 wt% of stearate- Zn_3Al LDH (d-h).

The tensile properties of PHB, PHB/PBAT blend and PHB/PBAT/LDH nanocomposites are shown in the Fig. 6 to 8. The tensile strength of neat PHB is 25.54MPa and decrease to 23.10 MPa with the addition of 10% of PBAT. The Fig. 6 shown that addition of 1 wt % of stearate- Zn_3Al LDH into PHB/PBAT blend decreases the tensile strength to 19.62 MPa. Further increase in the stearate- Zn_3Al LDH decreases gradually the tensile strength. This is maybe due to the extended aggregation of LDH layer into the blend matrix [31]. Fig. 7 shown that tensile modulus for nanocomposites also decreases as compared to the blend.

Additional of 2 wt% LDH into the polymer blend increase the elongation at break from 35.03% up to 54.58%, improvement of 56% compared to that of the unfilled PHB/PBAT blend in Fig. 8. Decreasing trend of elongation at break can be observed after further addition of 3 to 5 wt% of LDH. It may due to the presence of large agglomerates which make the nanocomposites to be more brittle, decrease of elongation at break consequently.

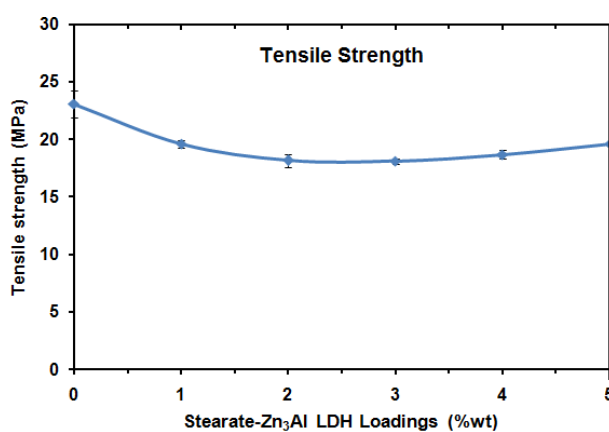


Fig. 6. Tensile strength of PHB/PBAT blends with different stearate- Zn_3Al LDH content.

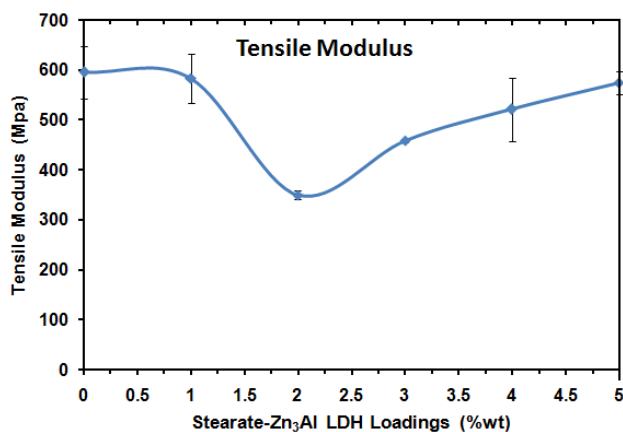


Fig. 7. Tensile modulus of PHB/PBAT blends with different stearate-Zn₃Al LDH content.

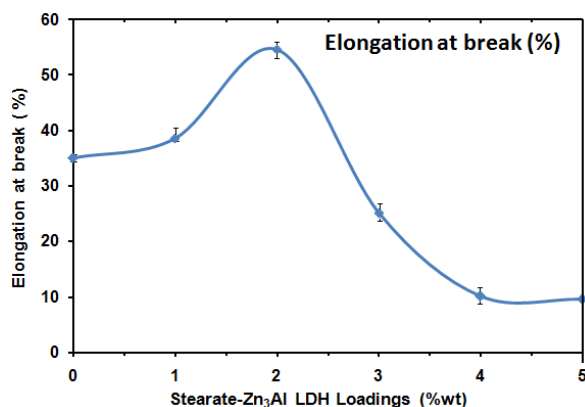


Fig. 8. Elongation at break of PHB/PBAT of different stearate-Zn₃Al LDH content.

Fig. 9 shows SEM micrographs obtained from the tensile fracture surfaces of PHB/PBAT blend and its nanocomposites containing 2.0 wt% of stearate-Zn₃Al LDH. The image of the fractured surface of the PHB/PBAT blend sample [Fig. 9(a)] shows a relatively compact solid surface indicating that the sample is brittle while the images of the 2 wt% nanocomposites [Fig. 9(b)] shows the rough and stretched surfaces which support the reduction of the rigidity of the samples.

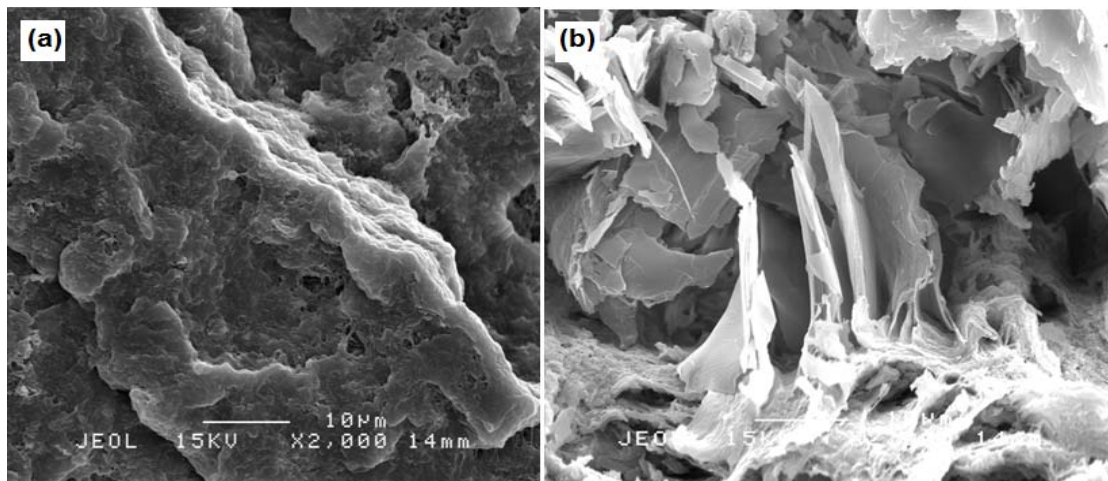


Fig. 9. Scanning electron micrograph of (a) PHB/PBAT blend and (b) 2 wt % nanocomposites.

4. Conclusion

PHB/PBAT/stearate-Zn₃Al LDH nanocomposites were synthesized successfully via solution casting. The used stearate-Zn₃Al LDH was prepared by co-precipitation and ion exchange reaction. The increased compatibility of stearate-Zn₃Al LDH with PHB/PBAT blend is found to be the key factor for the application of stearate-Zn₃Al LDH as the nano-filler. The incorporation of stearate ion into the LDH interlayer results in the larger basal spacing as compared to that of pristine Zn₃Al LDH, thus facilitating better compatibility of PHB/PBAT between the galleries of LDH. XRD analyses confirm the intercalation at lower filler loading in the PHB/PBAT matrix. Mechanical analyses of the nanocomposites showed that the presence of 2.0 wt % of the stearate modified LDH enhanced (of about 55%) its elongation at break.

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