Synthesis of Nanocomposite Materials for Biodegradable Food Packaging

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ABSTRACT

This paper concerns on synthesis of nancomposite materials, based on poly(D,Llactic acid)/poly(L-lactic acid). The Poly(L,D-lactic acid) (PDLLA) was produced from L,Dlactic acid through direct polycondensation method and poly(L-lactic acid) (PLLA) derived from L-lactide through ring-opening polymerization method. The PDLLA/PLLA films were produced through solvent casting method. The ratio of PDLLA in the PDLLA/PLLA matrix was determined by adjusting PDLLA fraction. The nanoclay used in this experiment were natural clay (Bentonite) and modified organoclay with quaternary ammonium salt (Cloisite 30B). The PLA blend nanocomposites was produced through solution intercalation with sonication. To determine the effect of amounts of nanoclay and sonication period, these two variable were varied. To analyze chemical structure of PLA, the PLA blend film were tested using Fourier Transform Infrared (FTIR). The dispersion of nanoclay on the PLA blend matrix was analyzed using X-Ray Diffraction (XRD) test. The properties of PLA blend nanocomposites film were then characterized using Universal Testing Machine (UTM), Water Vapor Permeability (WVP) test and the enzymatic biodegradability test. The fraction of PDLLA on the PLA blend was fixed 70 % wt. XRD test showed exfoliation of Cloisite 30B in the PLA matrix while the Bentonite was exfoliated as well as intercalated. The addition of nanoclay improved the tensile strength of PLA blend nanocomposites polymer to the number of 56.26 MPa and 37.65 MPa, respectively. Sonication period of PDLLA/PLLA nanocomposite affected the mechanical properties, barrier properties and polymer biodegradability. Moreover, from the WVP test, the barrier properties of the blend polymers was improved and increased twice compared to that of the pure PDLLA/PLLA.

Keywords: mechanical property, nananoclay, permeability, PLA blend nanocomposites, sonication

INTRODUCTION

The materials of conventional plastics are commonly derived from petroleum and contributes to the CO_2 emission and non-biodegradable waste which are harmful to the environment (Avérous & Pollet 2012; Simangunsong *et al.* 2018). Further, the increasing of human population contributes to the escalation of

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conventional plastics consumption. The ecosystem is considerably disturbed and damaged as a result of disposing items of non-degradable plastic materials. In order to meet the environmental issue and the food packaging demand, several number of research are intensively directed towards biodegradable food packaging development derived from natural resource and could rapidly degrade (Jayaramudu *et al*. 2013; Majeed *et al*. 2013). Polylactic acid (PLA) is one of the promising biodegradable polymer which has competitiveness due to its good properties such as mechanical, thermoplasticity, fabricability as well as biodegradability (Beeman 1994). That PLA-based polymer was made from the agricultural products and readily biodegradable becomes promising polymers in the future to replace the conventional plastic materials.

Since its approval by US Food and Drug Administration (FDA) in the 1970's, that PLA is safe polymer to have contact with biological fluid, many researchers have conducted research to improve the properties of PLA (Xiao *et al*. 2012). This is due to 100% PLA could not be used directly for food packaging, such as for packaging salads and plants (Rapa *et al*. 2016). Further, it is impossible to use PLA at higher stress levels because it has its poor mechanical properties. In order to overcome the weakness of PLA properties, several routes for PLA production have been introduced through blending, co-polymerization, and composition (Chandra & Rustgi 1998) to improve neat PLA. Furthermore, PLA nanocomposites is a promising route to enhance the mechanical and barrier properties of pure PLA (Othman 2014). In the production of packaging material such as film production, sheet casting, stretch blow molding,

and injection molding, nanocomposite becomes very promising material. Hence, improvement of the properties of PLA as a future food packaging by producing PLA blend nanocomposites is crucial to overcome the environmental problem made by commercial fossil-based plastics (Nampoothiri *et al*. 2010; Peelman *et al*. 2013; Rhim *et al*. 2013; Attaran *et al*. 2015; Iwata 2015).

As mentioned above, the blending polymer method is one of several methods to improve the properties of PLA. The fraction of two types of PLA monomer in the PLA blending, D-lactic acid and L-lactic acid, can be manipulate to generate different properties of PLA ranges from amorphous to semi or highly crystalline of polymer (Petersson *et al*. 2007). The nanoscale silicate including hectorite, saponite, sepiolite and montmorillonite are commonly used to improve the mechanical, barrier and biodegradability properties of PLA (Rhim *et al*. 2009; Raquez *et al*. 2013). Polymer-clay nanocomposites are manufactured mainly using a melt compounding, solution, and in situ polymerization.

The objective of this paper is to synthesize PDLLA/PLLA blend nanocomposites through solutionintercalation method. The PLA-blend nanocomposite films produced were analyzed using XRD analysis to show intercalation and exfoliation phenomenon in the PLA blend matrix with regard to addition of nano clay, Bentonite or Cloisite 30B. Furthermore, main properties of PLA nanocomposites as food packaging such as mechanical, water vapor barrier, and biodegradability properties were tested using Universal Testing Machine, water vapor permeability test and enzyme biodegradability test, respectively and discussed thoroughly.

MATERIALS AND METHODS

Materials

The L,D-lactic acid and L-lactide as the monomer PDLLA and PLLA were supplied from Purac Biochem. Zinc oxide (ZnO) of 99.9% purity and tin octoate [Sn(Oct)$_2$: stannous 2-ethylhexanoate] as a polymerization catalyst were supplied from Sigma-Aldrich. The solvent was used including ethyl benzene, chloroform, methanol and ethanol were all gathered from Merck. The enzyme proteinase K (lipophilic) for biodegradability test was purchased from Sigma-Aldrich. Carbonate buffer (NaHCO$_3$Na$_2$CO$_3$), pH. 8.5, bi-distilled water and sodium azide were supplied from Merck. Sodium Bentonite nanoclay was supplied by Wako Pure Chemical while the modified organoclay, Cloisite 30B, was purchased from Southern Clay Product.

Synthesis of PLLA and PDLLA

The poly(D,L-lactic acid) (PDLLA) was synthesized through direct melt-polycondensation method by converting 200 g of lactic acid using 0.1 g of ZnO as the catalyst while the poly(L-lactic acid) (PLLA) was synthesized in a 1-L four-necked flask equipped with a mechanical stirrer and a reflux condenser that was connected with a vacuum system through a vacuum pump. The reaction for synthesis PDLLA was performed under stirring condition at 180 °C for 30 hours in reduced pressure, about 50 torr. Further, the PLLA was synthesized through ring-opening polymerization by converting 755 g of L-lactide in the 2 L polymerization reactor with the addition of 0.07 g Sn-(Oct)$_2$ as a catalyst and 45 g of ethyl benzene as a solvent. Polymerization was conducted at temperature of 180 °C for 5 hours with the continuous stirring at a speed of 100 rpm. Related experimental set up and operating conditions were reported at our previous research paper (Lee *et al*. 2015).

Preparation of PDLLA/PLLA Nanocomposite Films

The film of PDLLA/PLLA was produced through solvent casting method. The production of PDLLA and PLLA resin were started with drying the film at 40 °C for 24 hours to remove the moisture contents. Then, PDLLA and PLLA were dissolved into chloroform and was continuously stirred for two hours. Solution of PLA blend were manually casted to the size of 20cm x 20cm in the glass plate to produce PLLA/PDLLA polymer blend films. The wet films were then dried at 25 °C for 24 hours. The PLA blend nanocomposites was produced through solution-intercalation method with sonication as follows. The nanoclay, Bentonite and Cloisite 30B, were firstly dried at the temperature of 60 °C for 24 hours to remove its moisture contents. The dried nanoclay were then dissolved to the 20 mL chloroform followed by continuous stirring for 1 hours at ambient temperature. The nanoclay solution was then sonicated for 1 hours in the sonication tools. In another vial, prepared 2.5 g of PDLLA/PLLA was dissolved and stirred in 30 ml of chloroform for 2 hours at ambient temperature. The nanoclay solution and PLA blend solution were then mixed and followed by sonication. The sonication process was conducted using ELMA at 29.6 kHz. The mixed solution was poured on a glass plate, pressed and followed by film drying at room temperature for 24 hours. To study the effect of the nanoclay content on the PLA blend matrix, the amount of nanoclay was varied with 0, 2.5, 5, 7.5 and 10 pph while

sonication period of mixed solution was set at 30 and 60 minutes.

Characterization

The molecular weight of synthesized polymer, PDLLA and PLLA was conducted using a capillary viscometry measurement using chloroform as solvent. Mark-Houwink equation was employed with parameters of $K(mL\ g^{-1})$ and the constants were 0.131±0.0048 and 0.777±0.0131, respectively. The chemical structures of PDLLA, PLLA, and PLA blends were analyzed using the Fourier Transform Infrared (FTIR/IR Prestige-21 Shimadzu) analysis. X-ray Diffraction (XRD/ Philips, DA107) analysis was used to calculate the distance between two silicate layers in the nanoclay as well as dispersion of nanoclay by employing Bragg's equation. The electrical voltage and electric current of XRD tools are 40 kV and 35 mA, respectively. The mechanical properties of PLA blend nanocomposites film were tested using Universal Testing Machine (UTM/TESTONE, TO-101) to calculate the stress at break, elongation at break, and Young's modulus. The size of film samples were 28mmx100mm with the cross-head speed of the UTM was 12.5 mm min^{-1} for stress at break test. The final value of mechanical properties was averaged from four measurements. The film resistance to the water vapor, Water Vapor Permeability (WVP) test were determined by placing the film horizontally over a container containing 10 grams of silica gel. The WVP value was determined by weighing container every day until the sixth day. The silica gel adsorbed the water from environment that increased container weight. The biodegradability of film was analyzed with enzymatic degradation method. The specimen samples of 20mm x 10mm were cut from film samples and then inserted into vials containing 5 mL of

buffer carbonate ($NaHCO_3$-Na_2CO_3) with pH 8.5, 0.25 mg of Proteinase K and 1 mg of sodium azide. The biodegradability test was conducted at 37 °C in a shaking incubator with the rotation speed of 140 rpm. Samples were taken periodically, washed with distilled water, and dried in an oven at room temperature for 24 hours. The dried samples were weighted and compared with its initial mass for determining percent mass loss of the film.

RESULTS AND DISCUSSION

Synthesis of PLAs and PDLLA/PLLA Blend Films

Molecular weight of PLA was measured using capillary viscometry method with chloroform as a solvent and it were calibrated using different value of molecular weight of PLA standards, 137 000, 148 000, 182 000 and 237 000 g mol^{-1}. The MW measurement of PDLLA and PLLA produced the value of 92,197 g mol^{-1} and 270 000 g mol^{-1}, respectively. PDLLA/PLLA blend film was synthesized using PDLLA as a polymer matrix and PLLA as an additive polymer and its production was conducted through solvent evaporation method using chloroform as a solvent. As a non-polar compound, chloroform could easily dissolve PLA and could rapidly evaporate at room temperature to produce a transparent film. The maximum PDLLA fraction on the PDLLA/PLLA blend film were 70% (w) and this fraction was used as polymer matrix in all production of PLA-blend nanocomposite.
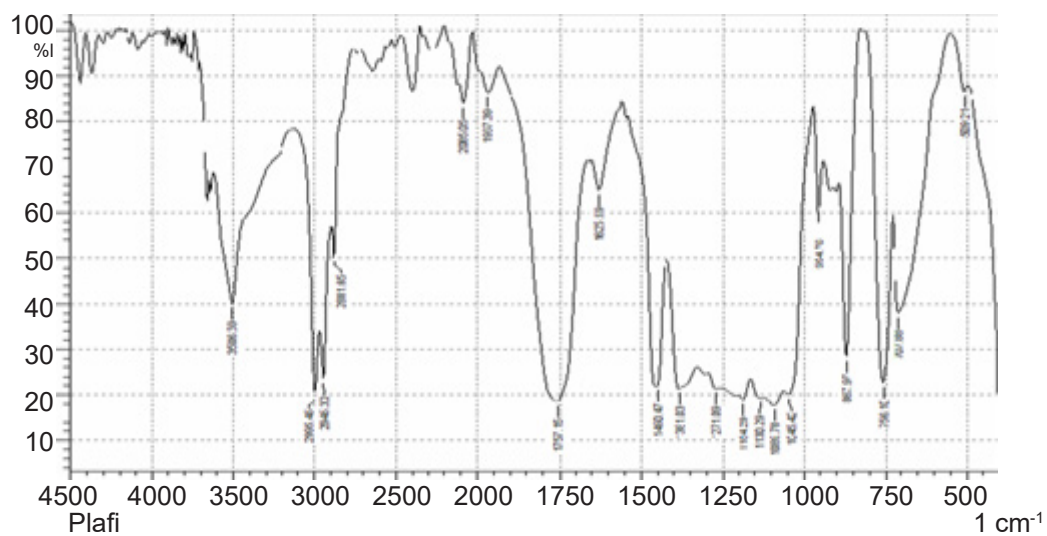
Figure 1 shows the FTIR spectra of a PDLLA, b PLLA and c blend polymer of PDLLA/PLLA 70%:30%. The functional groups existed in the PLA are methyl ($-CH_3$), ester (-C-O-R), carbonyl (C=O) and hydroxyl (-OH) groups. Further, all of functional groups of PLA existed in the PDLLA, PLLA and PDLLA/PLLA blend film
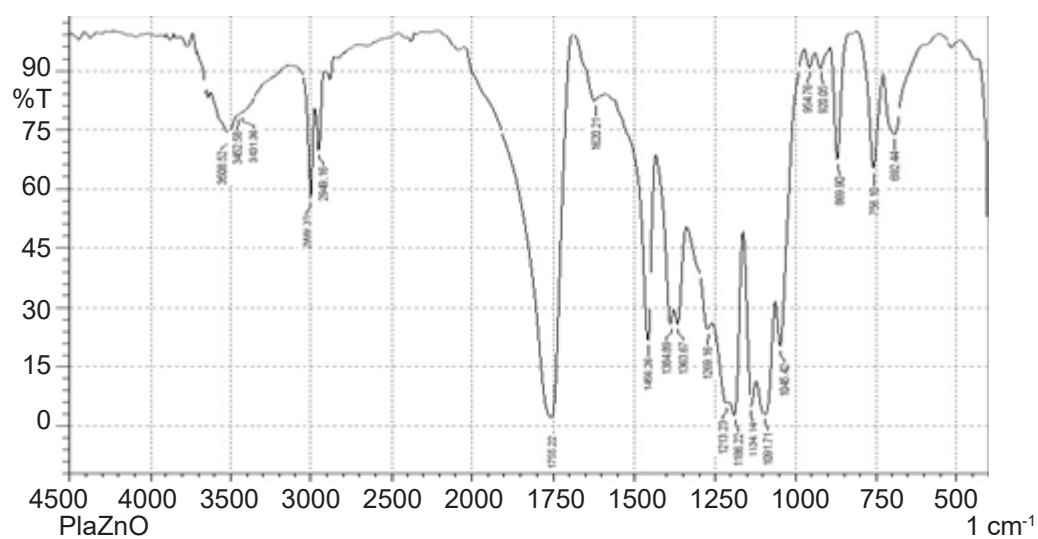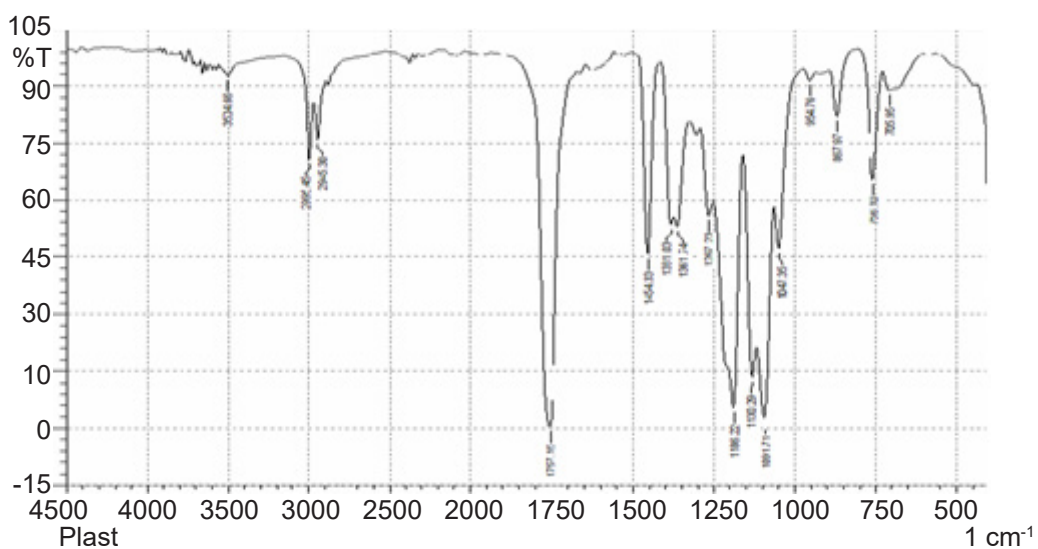
Figure 1 FTIR Spectra of a PDLLA; b PLLA; c Blend polymer of PDLLA:PLLA with ratio 70% to 30.

at the peak number of 2 995 cm^{-1}, 1 186 cm^{-1}, 1 755 cm^{-1} and 3 500 cm^{-1}, respectively. The % transmittance of hydroxyl function of PDLLA was lower than % transmittance of PLLA showing more hydroxyl function in the PLLA. It proved that the molecular weight of PDLLA was lower than PLLA as a result of shorter of polymer chains of PDLLA with more hydroxyl function. Moreover, a peak of PLA blends at 1 184 cm^{-1} indicated that there was a slight interaction between ester groups of PDLLA and PLLA in the PLA blends.

Properties of PDLLA/PLLA-Bentonite Nanocomposite Films

X-ray Diffraction Pattern

The effect of adding small amount of nanoclay into polymer blends was studied through X-ray diffraction pattern by confirming intercalation or exfoliation phenomenon of clay layers in a polymer matrix. Figure 2 shows the X-ray diffraction patterns of sodium Bentonite nanoclay and PDLLA/PLLA-Bentonite (PLA-bentonite) nanocomposite with the amount of Bentonite around 7.5 pph. The Bentonite had a characteristic peak at the 2θ value of 5.72°. By applying Bragg's equation produced distance of silicate layers in Bentonite around 1.56 nm. Moreover, the PLA-bentonite nanocomposite peak was shifted to the left at 5.41° and the distance between Bentonite layers in the polymer matrix increased to 1.7 nm. Hence, the intercalation of nanoclay lay-
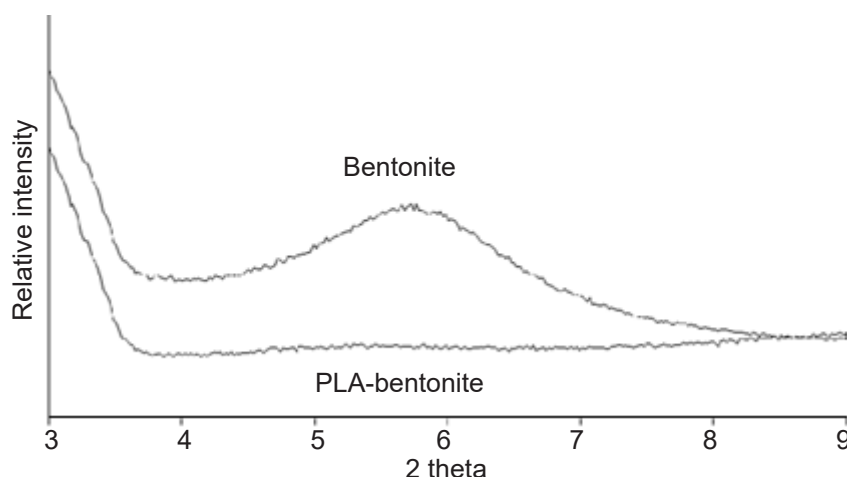

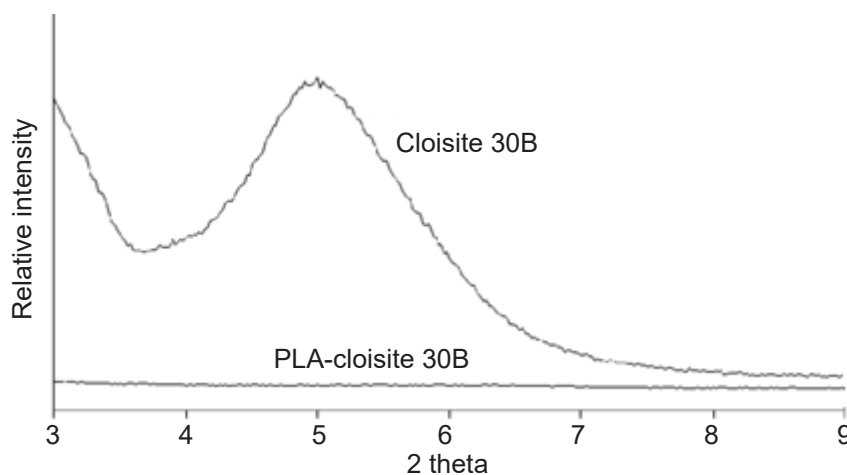Figure 2 XRD patterns of bentonite and PLA-bentonite nanocomposite.

Figure 3 XRD patterns of cloisite 30B and PLA-cloisite 30B nanocomposite.

ers was occurred in the PLA blend matrix during the mixing process of polymer solution and Bentonite through sonication treatment. Further, figure 3 shows the XRD analysis of Cloisite 30B nanoclay and PDLLA/PLLACloisite 30B (PLA-Closite 30B) nanocomposite with the amount of Cloisite 30B around 7.5 pph. The neat Cloisite 30B had a distance layer of 1.76 nm calculated from the neat Cloisite 30B peak value of 5.04° applying Bragg's equation. XRD pattern of PLA-closite 30B nanocomposite does not show any peak and this meant that exfoliation of Closite 30B nanoclay layers occurred in the PLA blend matrix. Note that the intercalation of organoclay on pure polymer might be due to different cationic modifiers present on organoclay surface. The Cloisite 30B modifier has better affinity with PLA matrix due to nature of Cloisite 30B more polar compared with the unmodified organoclay, Bentonite. It can be concluded that the structure of the nanoclay modifier is one of the important factors affecting the dispersion level of nanoclays (As'habi *et al.* 2013).

Mechanical Properties

The mechanical properties of PLA nanocomposites were tested using Universal Testing Machinge (UTM) to measure the stress at break, elongation at break and Young's modulus. The nanocomposite production was expected to improve the mechanical properties of neat PLA which is stiff and brittle, since nanoclay will act as a reinforcement agent (Jiang & Gao 2003; Noori & Ali 2014). The value of stress at break of PLA blend composites with the addition of Bentonite and Cloisite 30B based on the various amounts of nanoclay and different sonication period was shown in the figure 4. The figure 4a shows that the values of stress at break of PLA-Bentonite increased till the addition of 5 pph Bentonite and then

sharply dropped at values of stress at break. It indicates that the dispersion of Bentonite occurred well in the PLA matrix with Bentonite below 5 pph. From the XRD analysis, the addition of Bentonite in the matrix was just intercalated in the PLA matrix. The imperfect level dispersion of Bentonite in the PLA blend matrix at the higher concentration of Bentonite affected with decrease of stress at break of the polymer. Sarikanat showed that when the concentration of nanoclay increased, it reduced the concentration of polymer matrix that caused uncombined nanoclay to the polymer matrix (Sarikanat *et al.* 2011). The uncombined nanoclay then formed the clots reducing nanocomposite's structure integrity. Furthermore, the figure 4b shows that much addition of Cloisite 30B into PLA-nanocomposite led to better improvement of stress at break of PLA-Cloisite 30B. It confirmed that the dispersion of Cloisite occurred well in the PLA blend matrix and supported earlier analysis of XRD that Cloisite 30B were exfoliated in the PLA blend matrix. Furthermore, the addition of both Bentonite and Cloisite 30B showed greater values of stress at break of PLA nanocomposites with longer sonication time (60 min). It proved that the sonication time of PLA nanocomposites affected the stress at break of polymer. This may be due to better dispersion of nanoclay in the polymer matrix when the sonication time increased. The results showed that the polymer/clay nanocomposites with better mechanical strength compared to the pure polymer matrix because of the dispersed nano-sized clay particles producing high interfacial areas and ionic bonds between the nanoclay and host polymer (William *et al.* 2005; Camargo *et al.* 2009).

The value of Young's modulus of PLA nanocomposites with different amount of nanoclay and sonication period with addition of Bentonite and Cloisite 30B were
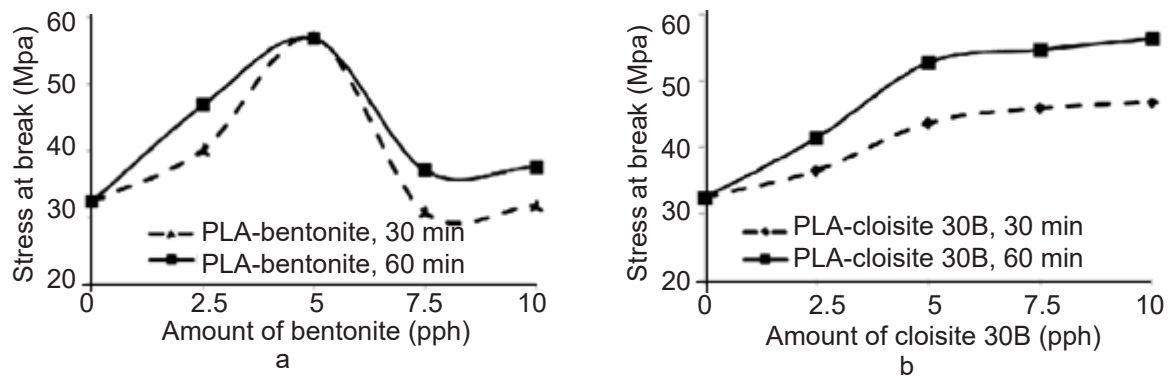
Figure 4 Values of stress at break of PLA nanocomposite films with varying amount of sonification. Times and with different nanoclays a Bentonite; b Cloisite 30B.
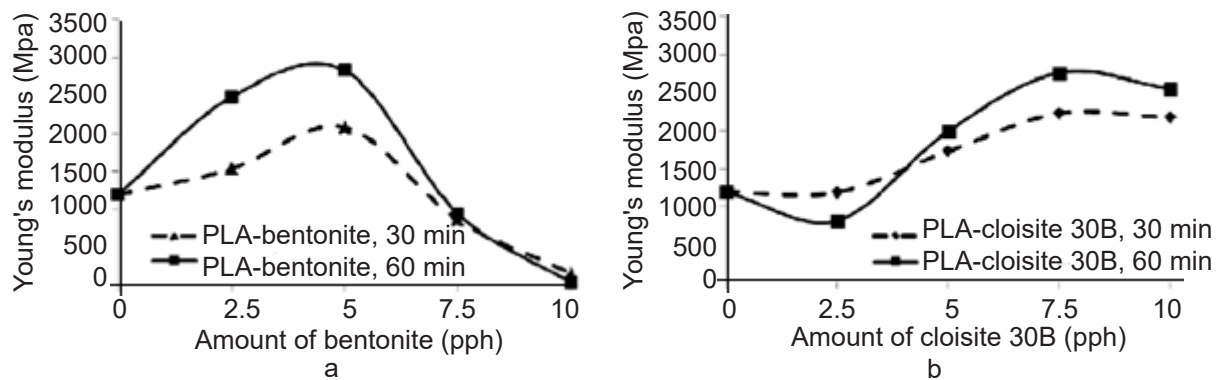

Figure 5 Values of young's modulus of PLA nanocomposite films with varying amount of sonification. Times and with different nanoclays a Bentonite; b Cloisite 30B.
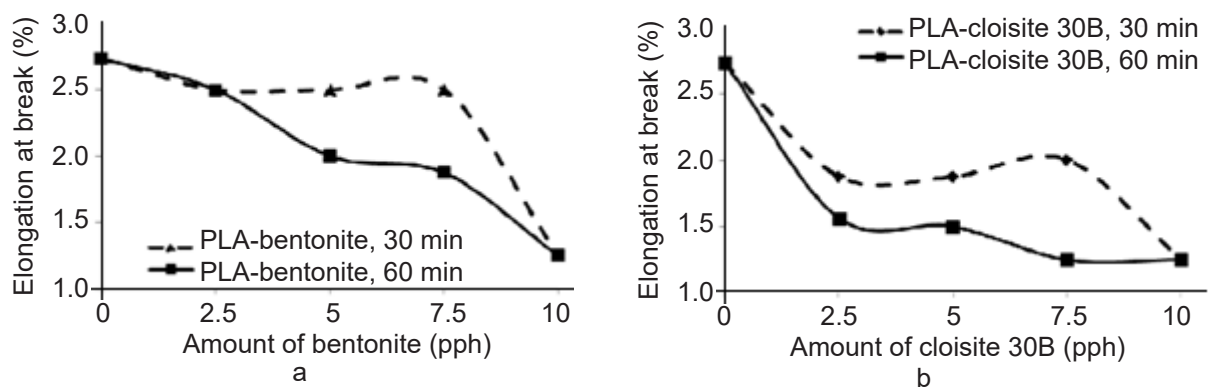

Figure 6 Values of elongation at break of PLA nanocomposite films with varying amount of sonification. Times and with different nanoclays a Bentonite; b Cloisite 30B.

shown on the figure 5, respectively. Figure 5a shows that the addition of Bentonite improved the polymer stiffness until the addition with 5 pph of Bentonite. Addition with higher amount, the Young's modulus of PLA-Bentonite nanocomposites decreased systematically. The decrease of Young's modulus proved that some Bentonite was not physically bound with the PLA matrix. Figure 5b shows the addition with higher amount of Cloisite 30B in the PLA blend matrix led to the better improvement

of polymer stiffness. This may be due to better dispersion level of Cloisite 30B in the PLA blend matrix compared with that of Bentonite which led to better polymer stiffness improvement. Cloisite 30B as a modified organoclay has better compatibility with PLA compared with Bentonite. Furthermore, according to figure 6, with longer period of sonication led to increase of Young's modulus. This result shows that the longer period of sonication allowed better dispersion of nanoclay in the PLA blend matrix. Figure 6 shows the value of elongation at break of PLA nanocomposites with different amount of nanoclay and varying period of sonication with the addition of Bentonite and Cloisite 30B, respectively. Overall, the values of elongation at break decreased with addition of more nanoclay, Bentonite or Cloisite 30B, added to the PLA matrix. Moreover, with longer sonication period for PLABentonite and PLA-Cloisite 30B, the reduction of elongation at break of PLA nanocomposites was steeper, respectively. These results show that as more well-dispersed nanoclay layers were added into the PLA matrix, it lowered the compatibility between the polymer and the organoclay fillers. The results supported other results that the addition of PEG in the PLA/PEG blend increased the free volume between polymer chains. Moreover, it induced the film elasticity as the ease of movement of polymeric chains with respect to each other is dramatically increased (Duncan 2011).

Water Vapor Permeability

For purpose of food packaging, PLA was expected to protect the food from diffusion of material surrounding the packaging. Basically, the permeability of polymer depends on several factors including po-larity and structural features of polymeric side chains, hydrogen bonding characteristic, molecular weight and polydispersity, degree of branching or cross-linking, processing methodology, method of synthesis and degree of crystallinity (Duncan 2011). The water permeability of PLA blend nanocomposites was tested via Water Vapor Permeability (WVP) test. Figure 7 shows the value of WVP of PLA blend nanocomposites with varying amount of nanoclay and sonication times with the addition of Bentonite and Cloisite 30B, respectively. The addition of Bentonite or Cloisite 30B in the PLA matrix improved the polymer permeability, hence the reduction of WVP value. The addition of nanoclay in the PLA blend matrix forced the gas to travel in the longer path in order to diffuse through film, known as *tortuous path* (Nielsen 1967). With more addition of nanoclays in the PLA matrix, it led to the improvement of polymer permeability that caused escalation of the diffusion time of water penetrating to the polymer (Ray & Okamoto 2003). WVP decreased to 45.66% with the addition of 10 pph of Bentonite while WVP reduced to 51.54% with the addition of 10 pph of Cloisite 30B. Moreover, the figure 8 shows that the addition of Cloisite 30B is more effective in reducing WVP compared with Bentonite due to more hydrophobic properties of Cloisite 30B. This experimental data also confirmed that Cloisite 30B more compatible with PLA polymer matrix compared with Bentonite. It was also discovered that longer sonication time produced better barrier properties of the nanocomposite films. Further, longer sonication time during the mixing processes of polymer solution and nanoclay created well-dispersed nanoclay layers in the PLA matrix which caused the PLA nanocomposite
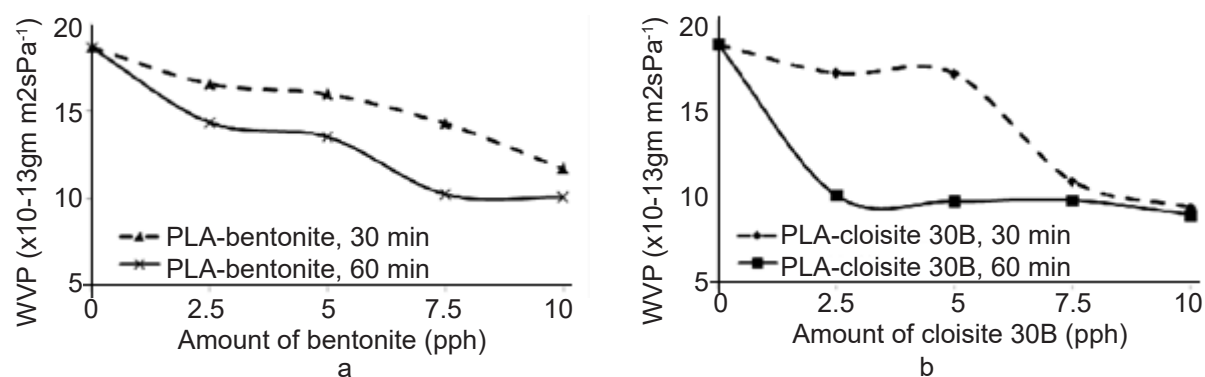
Figure 7 WVP values of PDLLA/PLLA nanocomposite films with varying amount of sonification. Times and with different nanoclays a bentonite; b Cloisite 30B.
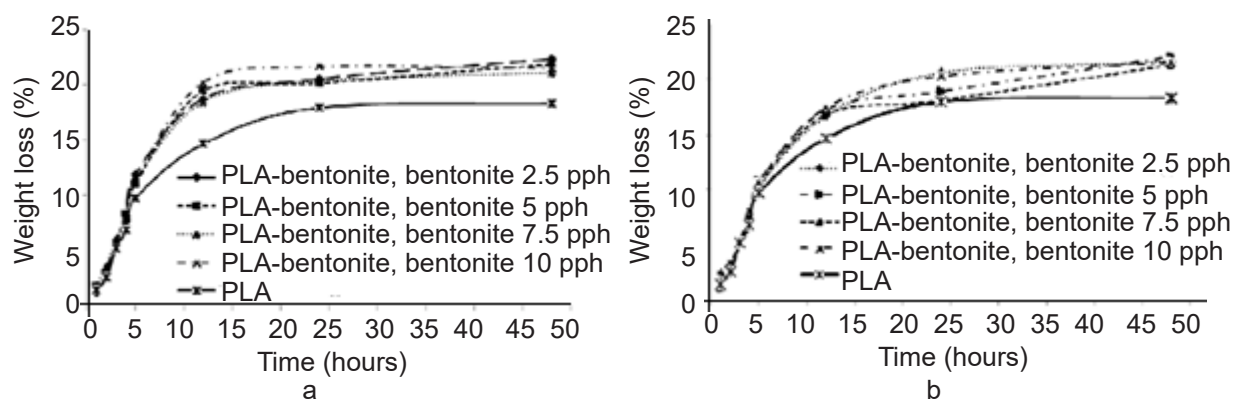

Figure 8 Percent weight loss of the synthesized PLA blend film and PLA-bentonite nanocomposite films.
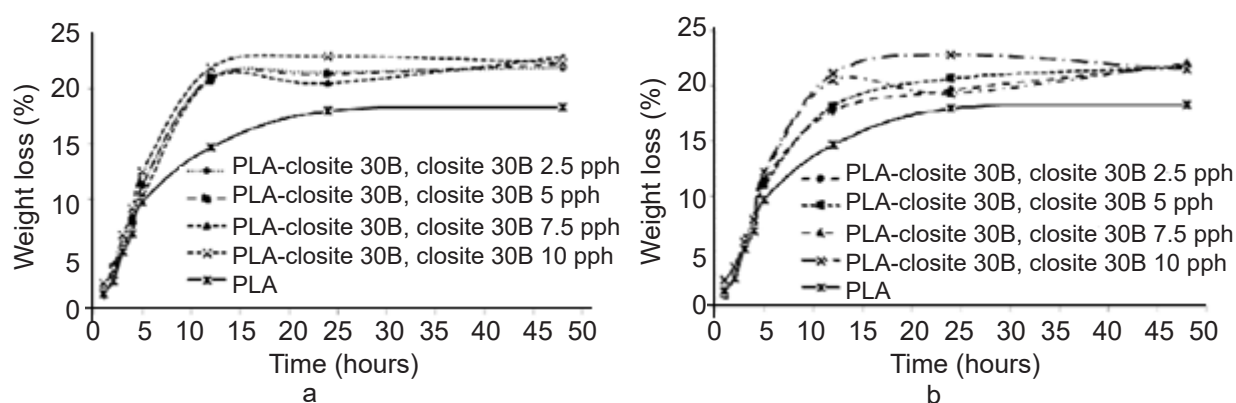

Figure 9 Percent weight loss of the synthesized PLA blend film and PLA- cloisite 30B nanocomposite films.

films to exhibit better barrier properties towards water vapor.

Biodegradability

The production of PLA blend nanocomposites was expected to enhance the bio-degradability of polymer. As stated above, the PLA biodegradability was determined using enzyme proteinase K as a catalyst. Figure 8 and 9 show the degradation rate of PLA nanocomposites with various amounts of nanoclay with the addition of

Bentonite or Cloisite 30B, respectively. Generally, the addition of nanoclay lead to biodegradability improvement of PLA blend nanocomposites. The rapid degradation rate of pure PLA and PLA blend nanocomposites were observed in the first 5 hours of biodegradability test. After 5 hours, the degradation rate decreased throughout the experiment. The effect of nanoclay type and the amount of nanoclay were clearly seen after 10 hours of degradation. The common degradation process of polymer were divided into two steps. First, the initial phases, the high-molecular-weight polymer were hydrolyzed to the lower-molecular-weight polymer. Second, the lower-molecular-weight polymer converted to CO_2, H_2O, and humus. The higher molecular weight polymer that were used in the PLA blend nanocomposites produced the slower degradation rate. Yet the molecular weight variable is out of the discussion in this paper because all of the PLA matrix that was used in the PLA blend nanocomposites production were similar. Figure 8 and 9 show that the addition of nanoclay constantly improved the biodegradability of PLA blend nanocomposites. The addition of nanoclay on the polymer matrix decreased the crystallinity of the polymer nanocomposites. Higher crystallinity of polymer made the water more easily to penetrate to the polymer matrix. Therefore, the increasing nanoclay amount on the PLA nanocomposites led to the improvement of biodegradability of polymer nanocomposites. Moreover, longer period of sonication, based on the figure 8 and 9 section a and b, led to faster biodegradability of PLA nanocomposites. It proved that the longer sonication period of nanoclay produced better nanoclay dispersion on the PLA matrix. The nanoclay

type on the PLA nanocomposites contributed to the different level of enhancement of biodegradability properties. Furthermore, the addition of Cloisite 30B generated faster biodegradability of polymer compared with Bentonite. From above XRD test, the Cloisite 30B was well dispersed and exfoliated in the polymer matrix while Bentonite was just intercalated. Therefore, the dispersion of Cloisite 30B was better than that of Bentonite resulting faster biodegradability. Furthermore, with regards to organomodified-clay, Cloisite 30B has a better relative hydrophilicity compared with Bentonite. The relative hydrophilicity of nanoclay predisposed the easiness of the water to degrade the polymer.

CONCLUSION

Nanocomposite films, PDLLA/PLLA, were successfully produced through solution-intercalation method using chloroform solution and followed with sonication. The XRD analysis showed that Bentonite was intercalated in the PLA blend matrix while Cloisite 30B was exfoliated in the PLA blend matrix. The addition of Cloisite 30B in the PLA blend matrix led to the better improvement compared to the addition of Bentonite with regards to mechanical, barrier, and biodegradability properties of PLA blend nanocomposites. Furthermore, difference sonication time during the mixing process and the different amount of nanoclay addition produced different properties of PLA blend nanocomposites. Overall, improvement of mechanical, barrier and biodegradability properties of PLA blend nanocomposites showed that PLA blend nanocomposite materials are promising materials for food packaging purpose.

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