การวิเคราะห์คุณลักษณะของพอลิแลคติกแอซิดนาโนคอมโพสิต

Characterization of Poly(lactic acid) Nanocomposites

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บทคัดย่อ

พอลิแลคติกแอซิดนาโนคอมโพสิตได้จากการผสมพอลิแลคติกแอซิดและนาโนเคลย์ (1%, 2%, 5% และ 10% โดยน้ำหนัก) ด้วยเครื่องหลอมผสมภายใน จากนั้นวัสดุที่ได้ถูกนำไปขึ้นรูปโดยกระบวนการอัดเพื่อผลิตชิ้นงานสำหรับการทดสอบ ผลกระทบของนาโนเคลย์ต่อคุณสมบัติทางกล ความหนืด การดูดซึมน้ำและการทนความร้อน จากการทดลองพบว่านาโนเคลย์กระจายตัวได้ดีในพอลิแลคติกแอซิด ทำให้ค่าโมดุลัสของพอลิแลคติกแอซิดมีค่าเพิ่มขึ้นเมื่อปริมาณนาโนเคลย์มีปริมาณ 1% และ 2% แต่โมดุลัสไม่ได้เพิ่มมากกว่านั้นเมื่อปริมาณนาโนเคลย์มากกว่า 2% ซึ่งเกิดจากนาโนเคลย์เริ่มเกาะตัวกัน นอกจากนี้การเพิ่มปริมาณนาโนเคลย์สามารถเพิ่มความหนืด การดูดซึมน้ำและการทนความร้อนของพอลิแลคติกแอซิดได้อย่างชัดเจน

คำสำคัญ: พอลิแลคติกแอซิด นาโนเคลย์ คอมโพสิต พลาสติกชีวภาพ คุณสมบัติวัสดุ

Abstract

Poly (lactic acid) (PLA) nanocomposites prepared with different nanoclay contents (1%, 2%, 5% and 10% w/w) were obtained by melt blending. The blended materials were then compression molded to produce tensile specimens. The influence of nanoclay on morphology, mechanical properties, melt flow index, water absorption and thermal stability of the PLA/nanoclay nanocomposites was investigated. Intercalation of clay with 3.2 nm basal spacing was observed in the PLA matrix leading to an increased modulus of PLA at 1% and 2% clay but it did not increase further as more clay was

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added due to the higher degree of aggregation. Increasing nanoclay content also significantly increased the melt flow index, water absorption and thermal stability of PLA.

Keyword: poly (lactic acid), nanoclay, composites, bioplastics, material properties

Introduction

Nowadays, the plastic industry occupies a predominant and growing place in our everyday life, in which most uses involve a relatively short lifetime. Disposal by incineration can contribute to pollution and burial in landfill sites is limited.[1] One solution, to at least partially solving the problem of plastic accumulation in the environment involves the use of biodegradable polymers.[2] Among these, poly(lactic acid) appears to be the most attractive because of its availability, good biodegradability, excellent physical properties and easily processed.[3, 4]

The main factors inhibiting PLA's wider industrial application are its poor thermal and mechanical resistance and limited gas barrier properties which prevent its complete access to industrial sectors such as packaging.[5] Therefore, modification of PLA through innovative technology is a formidable task for material scientists.[6] These drawbacks could be overcome by enhancing their thermomechanical properties through copolymerization, blending and filling techniques.

This new family of composite materials frequently exhibits remarkable in mechanical and material property improvement when compared with virgin polymers or conventional micro- and macro-composites. Improvements can include a high storage modulus both in solid and molten states, increased tensile and flexural properties, a decrease in gas permeability and flammability, increased heat distortion temperature and thermal stability, increase in the biodegradation rate, and so forth.[6] Indeed, the addition of nano-sized fillers would potentially have multiple benefits to PLA due to their high surface area-to-volume ratios, lower concentrations needed to achieve reinforcing effects, and the ability to potentially improve toughness along with strength and stiffness.[2] On the other hand, polymer/nanoclay nanocomposites have already shown to be a good way to improve these properties significantly. Nanoclay has layer thickness on the order of 1 nm and very high aspect ratios (e.g., 10-1000). A few weight percent of nanoclay, which is properly dispersed throughout the polymer matrix, thus creates much more surface area for polymer/filler interaction than do conventional composites.[7]

Here, nanoclay was added to PLA and the properties of nanocomposites, with different nanoclay contents, evaluated and discussed.

Experiment

Materials

Poly(L-lactide) (PLA) with an average-viscosity molecular weight of 95,000 g/mol

and a density of 1.24 g/cm^3 was synthesized by ring-opening polymerization of L-lactide in bulk under nitrogen atmosphere at 165°C for 2 h using stannous octoate (95%, Sigma) and 1-dodecanol (98%, Acros Organic) as the initiating system. The L-lactide was prepared from L-lactic acid (88%, heat stable grade, Purac, Rayong, Thailand) and was purified by re-crystallization with distilled ethyl acetate before use. The PLA has a glass transition temperature (T_g) of 60°C and a melting temperature (T_m) of 174°C, determined from differential scanning calorimeter (DSC).

Organically modified nanoclay, Closite®30B, was supplied by Southern Clay Products. The nanoclay was surface-treated by ion exchange reaction between Na^+ existing in the gallery of the nanoclay and quaternary ammonium cations.

Preparation of PLA/nanoclay nano-composites

Prior to mixing, PLA was dried in a vacuum oven at 80°C for 5 h. Nanocomposites contained 1, 2, 5 and 10% nanoclay were obtained by melt blending using an internal mixer (HAAKE Polylab OS system) with a mixing time of 4 min, 100 rpm at 170 °C. The batch was extracted from the mixing chamber manually, allowed to cool to room temperature in air and subsequently granulated. The PLA/nanoclay nano-composites were shaped into 1 mm thick tensile bars using a compression molding machine at 190°C and allowed to cool to room temperature under pressure. The ASTM D638 type IV tensile bar was used as a reference when creating the nanocomposite bars. The compression molding cycle consisted of 7 min of heating and subsequent cooling under pressure for 5 min.

Tensile Testing

Tensile test was measured on the compression molded samples following the ASTMD638-10[8] at a crosshead speed of 10 mm/min. The static tensile modulus, strength, and strain-at-break were measured at room temperature (~25 °C) and atmospheric conditions (relative humidity of ~50 ± 5%) on a universal tester (LRX PLUS, Lloyd Instrument). Results from tensile testing were reported as average value from five specimens.

X-ray Diffraction Analysis

Wide angle X-ray diffraction (XRD) analyzed the effectiveness of the clay intercalation in the composite using a Bruker / D8 Advance, Bruker BioSpin AG (Karlsruhe, Germany). XRD samples were taken from compression molded specimens and mounted on the XRD platform for analysis. A 2θ range from 2º to 40º in refraction mode was scanned at 2º/min. A computer-controlled wide angle mode goniometer coupled to a sealed tube source of Cu $K\alpha$ line was filtered electronically with a thin Ni filter. The clay interlayer distance in the PLA was calculated from the (001) lattice plane diffraction peak using Bragg's equation.[11]

Transmission Electron Microscopy Analysis

The morphologies of the PLA/nanoclay nanocomposites and the dispersion of nanoclay within the polymer matrix were

investigated using transmission electron microscopy (TEM) (JEOL JEM-1230). Specimens were cut into 50 to 70 nm slices with an ultra-microtome at room temperature.

Melt Flow Index Measurement

To evaluate the effects of nanoclay and melt compounding on the molecular structure (e.g., possible material degradation) of the PLA composites, a melt flow indexer (Tinius Olsen, Model MP1200) measured the melt flow index (MFI) of the composites. The temperature of the melt was kept at a uniform 190 °C temperature and the 2.16 kg load was applied to extrude the melt. A 100 g rod was used as a plunger. The measured values presented below were based on the mass flow rate scaled over a 10-min period.

Water uptake

The water uptake of the composites was evaluated according to ASTM D570-81.[9] The composites were preconditioned at 50 °C for 24 h and weighed (W_0). After immersing in distilled water for 24 h, the sheets were dried with paper towels to remove the excess water on the surface and weighed (W_1) [10]. The total composites weight gain was used to calculate the absorbed water. An average value from the three measurements was reported.

Thermogravimetric Analysis (TGA)

TGA used a SDT Q600 (TA Instruments) from 25 to 800 °C at a heating rate of 20 °C/min under nitrogen flows. Approximately 10 mg of each sample was used for each test. The loss of weight was recorded and normalized against the initial weight. The thermal decomposition temperatures were defined as the temperature at 5% of weight loss ($T_{5\%}$).

Results and Discussion

PLA/Nanoclay Nanocomposite Pattern and Morphologies

The structure of polymer nanocomposites has been typically studied using wide-angle XRD and TEM. Wide-angle XRD is a convenient way to determine the degree of clay intercalation by monitoring the position, shape, and intensity of the (001) diffraction peak from the dispersed nanoclays, while TEM allow direct visualization of the internal structure.[11] For the exfoliated nanocomposites, extensive delamination of the clay layers in the polymer matrix resulted in the disappearance of any XRD peak. As to the intercalated nanocomposites, an increase in the gallery spacing (d_{001}) brought on by the intercalation of the polymer molecules caused the 2θ of the (001) diffraction peak to move to a lower angle. Figure 1 shows the XRD patterns for PLA, Cloisite®30B, and PLA with 1, 2, and 10% Cloisite®30B nanocomposites. The gallery spacing (i.e., d_{001}) for Cloisite®30B measured by XRD was 1.86 nm ($2\theta \approx 4.75°$), similar to the data sheet value. For PLA/nanoclay nanocomposites, the (001) diffraction peak shift to a lower angle, ($2\theta \approx 2.75°$), (i.e., d_{001} = 3.22 nm). Moreover, as shown in Figure 1, the (001) peak intensity was stronger with higher nanoclay contents. This may be attributed to the increased of nanoclay density.[12] An increase in the gallery spacing for the nanoclays suggested that PLA molecules had intercalated into the clay galleries during the melt compounding process. This was further validated by TEM analysis -see Figure 2 where a few

aggregated clay particles at 10% content were observed. The dark entities are the cross sections and faces of the intercalated clay and the bright areas are the PLA matrices.

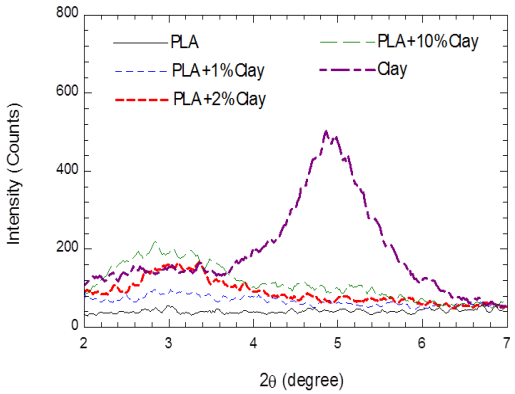
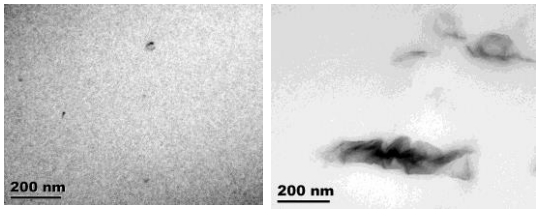


Figure 1 Wide-angle XRD patterns for PLA, nanoclay and PLA/nanoclay nanocomposites.

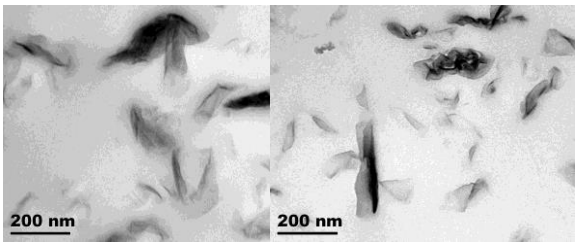
Melt Flow Rate

The pristine PLA MFI was 94 g/10 min. The MFI after melt compounding was 134 g/10 min. This suggests that PLA thermally degrades during the internal mixing process. The melt flow indices of PLA/nanoclay (Cloisite®30B) nanocomposites at various loading levels after melt compounding were also measured -see Figure 3. Adding nanoclay generally increased the viscosity of the polymer matrix and therefore reduced the MFI. This might be because an interaction may exist between PLA and the surfactants of the nanoclay, hence increasing the MFI of the nanocomposites. At higher clay loading, the MFI of PLA/nanoclay is lower.

(a) (b)



(c) (d)



(e)

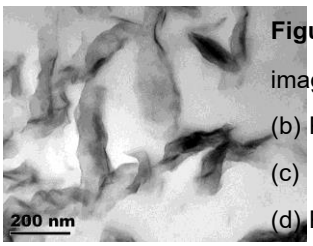


Figure 2 TEM images for (a) PLA (b) PLA/1%nanoclay (c) PLA/2%nanoclay (d) PLA/5%nanoclay (e) PLA/10%nanoclay

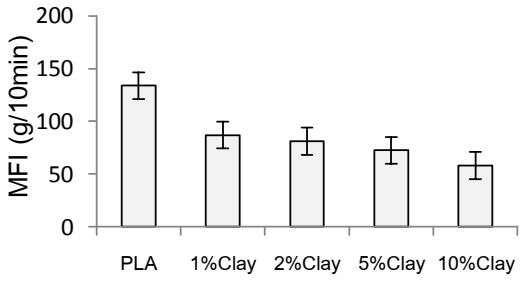


Figure 3 Melt flow indices (MFI) of PLA and PLA/nanoclay (Cloisite®30B) nanocomposites at various loading levels after melt compounding.

Tensile Properties

Figure 4 shows the results of the tensile tests (according to ASTM-D638) on the compression-molded PLA/nanoclay blend nanocomposites. Tensile strength, strain-at-break and modulus were measured. It has been reported nanocomposites display increase in properties such as strength and modulus.[1, 7, 13] Tensile properties are expected to increase when a nanoclay is well dispersed in the polymer matrix, and is mainly

attributed to adhesion between the clay and the polymer and the level of intercalation.[14]

As shown in Figure 4(a), addition of clay increased the tensile modulus of PLA by 45.5% at 2% clay loading level. An increase in Young's modulus is expected when nanoclay are introduced in a polymer matrix, due to the higher aspect ratio of the silicate layers and its large surface area.[1, 15] However, this was accompanied by a reduction in tensile strength and strain-at-break at 5% and 10% clay loading level which may be attributed to the fact that the higher degree of aggregation for Closite®30B than that at lower content.

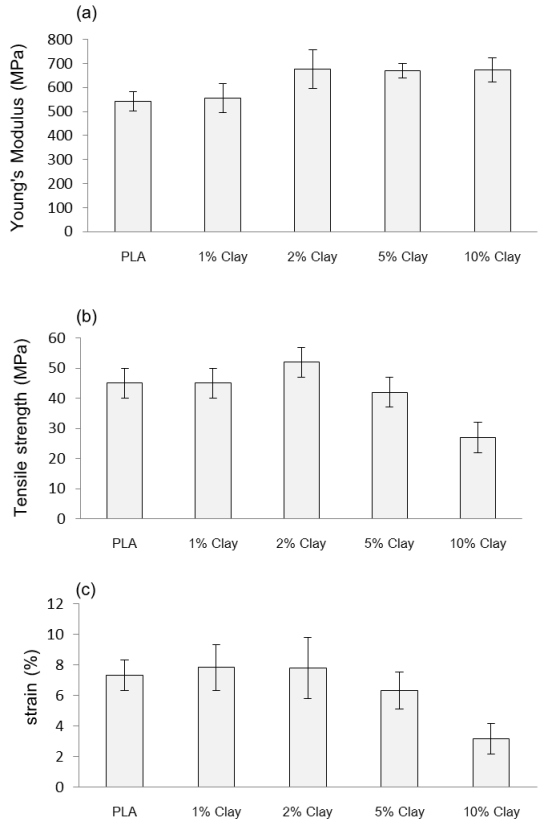


Figure 4 Mechanical properties of PLA/nanoclay nanocomposites (a) Young's modulus; (b) tensile strength (MPa); (c) strain-at-break (%).

Thermal Stability

The thermal stability of the PLA/claynanocomposite samples was examined using TGA. Figure 5 reports TGA curves for PLA nanocomposites. The thermal stability of the PLA matrix is significantly improved by the presence of clay (Table 1). This behavior is generally attributed to a barrier effect of the clay towards polymer decomposition products ablation, thus increasing onset weight loss temperature.[6]

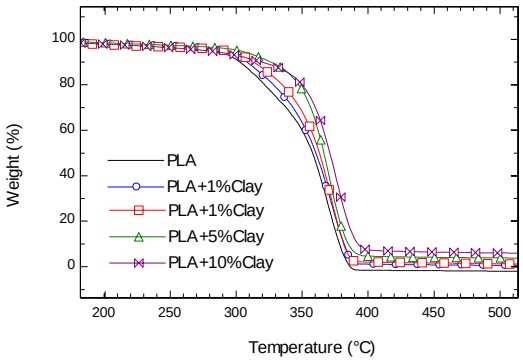


Figure 5 TGA curves for the PLA/nanoclay nanocomposite samples.

Water uptake

Figure 6 shows the water uptake of PLA/clay nanocomposites. With the introduction of nanoclay, the water uptake increased considerably which was attributed to the high relative hydrophilicity of the clay, allowing an easier permeability of water into the polymer matrix.[5] The water uptake for composites containing 10% clay was 0.77% while neat PLA had only 0.38% water absorption.

Conclusions

In this study, PLA containing intercalated nanoclay were melt compounded and then compression molded. The influence of nanoclay on mechanical properties, water absorption, and thermal stability of PLA were

investigated. When 2% clay was added, the tensile strengths increased 16% but then decreased as the clay content increased to 5% and 10%. The addition of 2% clay increased tensile modulus 25% and tensile elongation 7%. Water uptake and viscosity of the nanocomposites increased with the addition of nanoclay. The clay also improved the thermal stability of PLA.

Table 1 TGA mass loss curves for PLA nanocomposites.

Sample	$T_{5\%}$ (°C)
PLA	282
PLA+1%clay	287
PLA+2%clay	290
PLA+5%clay	302
PLA+10%clay	305

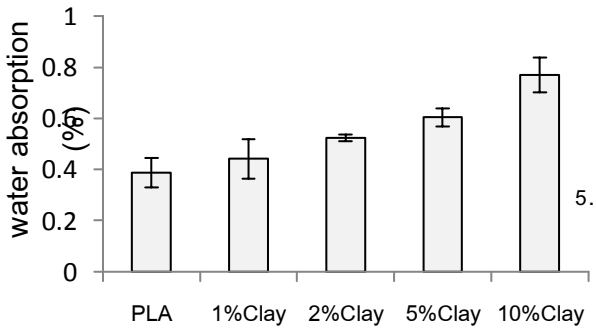


Figure 6 The water uptake of PLA/clay nanocomposites.

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