

Flexibility Improvement of Poly(lactic acid) by Stearate-Modified Layered Double Hydroxide

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ABSTRACT: Poly(lactic acid)/layered double hydroxide (PLA/LDH) nanocomposites were prepared from PLA and stearate-Mg₃Al LDH via a solution casting method. The anionic clay Mg₃Al LDH was prepared first by coprecipitation method from nitrate salts solution at pH 9 and then modified by stearate anions through an ion exchange reaction. This modification increased the basal spacing of the synthetic clay from 8.72 to 31.68 Å. The presence of stearate ions in the synthesized Mg₃Al LDH was shown by the stearate-Mg₃Al LDH infrared spectrum. When the

stearate-Mg₃Al LDH at the low concentration was dispersed in the PLA matrix, its layers were largely delaminated. The presence of 1.0 wt % of the stearate-Mg₃Al LDH in the PLA improved drastically (of around 650%) of its elongation at break but retained its tensile strength and modulus as compared to those of the pure PLA. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1077–1083, 2010

Key words: poly(lactic acid); nanocomposites; anionic clay; TEM; flexibility improvement

INTRODUCTION

Poly(lactic acid) (PLA) is one of the commercially available biodegradable polymers from the family of aliphatic polyesters, which are produced from lactic acid, a monomer that can be synthesized from many renewable resources such as corn and sugar beets.^{1,2} Although it has various good mechanical properties such as high strength, thermo-plasticity, transparency, and fabricability, its applications are limited because of its brittleness and nonflexibility.³ However, PLA may be used as a biodegradable and renewable plastic for service wares, waste-composting bags, mulch films, controlled release matrices for fertilizers, pesticides, and herbicides.⁴ Since soft and flexible polymers are required for applications such as films and textile fibers,⁵ and food packaging materials, plasticization of PLA to alter its rigidity to expand its applications in these areas is very important.

Many attempts have been made to improve the flexibility of PLA. These include copolymerization⁶ and blending with other flexible polymers such as poly(caprolactone),^{7,8} polyester-diol,⁹ poly(propylene glycol),¹⁰ and poly(ethylene glycol).^{11,12} Low-molecular weight compounds such as monomer unit of PLA, lactide, glucose monoesters, partial fatty acid esters, and citrates, have also been used as plasticiz-

ers for PLA.^{13,14} The problems of the products are that some of the plasticizers migrate rapidly to the polymer surface¹⁵ or cause phase separation in PLA matrix due to poor miscibility.⁸

However, the main drawback of most of the products is the big drop of the tensile strength and modulus due to a large amount of plasticizer agent that is needed to plasticize it.^{10,16}

The effect of plasticization of long chain fatty acids on some polymers like chitosan has been investigated.¹⁷ However, apparently there is no report of using these compounds for PLA plasticization.

Layered double hydroxides (LDHs) are anionic clays which can be represented as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/n}^{n-} \cdot mH_2O]^{x-}$, where M(II) and M(III) are divalent and trivalent cations, respectively, and A^{n-} is an exchangeable anion.¹⁸

LDHs are composed of octahedral $M^{2+}(OH)_6$ brucite-like layers which are positively charged by the partial substitution of M^{3+} for M^{2+} . Thus, anions are intercalated into the interlayers to achieve charge neutrality.¹⁹ The LDHs advantages include nontoxic materials, good sorbents for various harmful anions and room temperature preparation process.²⁰ Another advantage of LDHs is that their particle size and aspect ratio can be controlled by changing the reaction conditions,²¹ which made them useful for many applications in catalysis,²² photochemistry,²³ dye sorption,²⁴ and electrochemistry.²⁵

LDH, due to its layered structure, is an attractive choice as nanofiller considered for preparation of multifunctional polymer/layered crystal nanocomposites.²⁶ However, its use as a nanofiller are limited

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by its layers high-charge density and high content of anionic species and water molecules resulting in strong interlayer electrostatic interactions between the sheets and pronounced hydrophilic properties.²⁷ Consequently, it is difficult for a monomer or polymer to penetrate into the LDH layers or the LDH layers to be homogeneously dispersed within hydrophobic polymer matrices. To facilitate the intercalation of polymer in the layers of LDH or to achieve a good degree of the layer dispersion in polymer matrices, the interlayer space should be modified with suitable, usually organic, anions with intention of increasing both the interlayer distance and the hydrophobicity of LDH layers.

Anions are typically intercalated into LDH interlayers by three approaches.²⁸ The first approach is the coprecipitation method, which requires an addition of a solution of M^{2+} and M^{3+} ions into a base solution of the desired anions. The second technique is the direct ion exchange method, in which LDHs are stirred in a solution of the chosen anions at a suitable concentration. The last method is the rehydration method in which calcined LDH is added to a solution of desired anions.²⁹ The selection of anions for modification of LDH depends on next application of LDH. For example, Mg–Al LDHs intercalated with dodecylsulfate and dodecylbenzenesulfonate have been used to adsorb pesticides, such as triadimefon, linuron, atrazine, acephate, and diazinon, from aqueous solution.³⁰ Also LDHs containing interlayer carboxylate anions have attracted considerable attention in recent years due to interesting properties and potential applications, e.g., LDH modified with citrate, malate, and tartrate ions are able to take up hazardous organic materials and heavy metal ions from an aqueous solution.³¹

Although long chain fatty acids have been used as plasticizer for some polymers,¹⁷ they are not suitable plasticizer for PLA because of their immiscibility with PLA in their original form.

The first example of using LDHs for preparation of a nanocomposite was reported by Sugahara et al.³² They prepared an intercalated compound based on acrylonitrile and magnesium-aluminum layered double hydroxide, using the in situ polymerization method. Their work was then continued by intercalations of some polymeric anions and water soluble polymers like poly(acrylic acid), poly(vinylsulfonate) and poly(styrenesulfonate),³³ poly(oxalkylene)-amidocarboxylates,³⁴ styrene-4-sulfonate³⁵ and sulfopropyl methacrylate³⁶ either by the direct incorporating of polymeric anions into the LDH structure, or by intercalating of monomeric anions into LDH gallery, followed by in situ polymerization. The preparation of some hydrophobic polymers such as polyimide,¹⁹ linear low-density polyethylene,^{37,38} poly(methyl methacrylate),³⁹ polystyrene,⁴⁰ poly(styrene-co-methyl methacrylate),²⁷ epoxy,^{21,41} and polypropylene⁴²/LDH nanocomposites have also been reported.

In this article, the preparation of PLA/stearate-Mg₃Al LDH nanocomposites have been described. Then, the mechanical properties of the nanocomposites have been studied.

EXPERIMENTAL

Materials

Magnesium nitrate hexahydrate and aluminum nitrate nonahydrate were supplied by HmbG chemicals (Hamburg, Germany). Sodium hydroxide pellets was obtained from Merck (Darmstadt, Germany). Sodium stearate was purchased from R&M chemicals (Essex, UK) and polylactide resin 4042D was supplied by NatureWorks LLC (Minnetonka). All the above commercial chemicals were used as received.

Synthesis of Mg₃Al LDH

The Mg₃Al LDH was prepared by adding dropwise a solution of NaOH (1M) into a 250 mL solution of 19.22 g Mg(NO₃)₂·6H₂O and 9.38 g Al(NO₃)₃·9H₂O (with the mole ratio of 3–1, respectively) until pH 9 was obtained. The resulting suspension was shaken at 100 rpm and 70°C for 16 h. The slurry was filtered, washed thoroughly with deionized water, and dried at 60°C for 24 h to obtain the Mg₃Al LDH.

Preparation of stearate-Mg₃Al LDH

The stearate-Mg₃Al LDH was prepared by replacing nitrate ions in the LDH layers with stearate ions using the following procedure. One gram of the dry Mg₃Al LDH was first transferred into 750 mL of 0.003M solution of sodium stearate solution and stirred at room temperature for 24 h. The white solid obtained was then filtered, washed with deionized water three times, and dried in a vacuum desiccator at room temperature.

Preparation of PLA/stearate-Mg₃Al LDH nanocomposites

The nanocomposites of PLA with different amount of stearate-Mg₃Al LDH were prepared by a solution casting method. The desired amount of stearate-Mg₃Al LDH in 40 mL chloroform was first sonicated for 3 h, transferred into a solution of 10 g PLA in 200 mL chloroform, and refluxed for 24 h. The viscous solutions were casted in a glass Petri dish and dried in the solvent atmosphere to obtain the sample sheets.

Characterization techniques

X-ray diffraction (XRD) patterns of the LDHs and composites were recorded using a Shidmadzu XRD

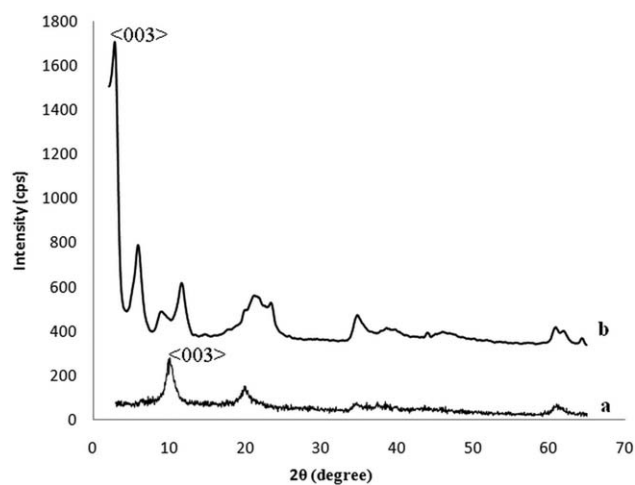


Figure 1 XRD pattern of (a) pristine Mg_3Al LDH and (b) stearate- Mg_3Al LDH.

6000 Diffractometer at 30 kV and 30 mA with $Cu-K_{\alpha}$ radiation of the wavelength of 1.5405 nm in 2θ range from 2 to 65° .

Fourier-transform infrared (FTIR) spectra of the materials were recorded on a Perkin Elmer, FTI 1650 Spectrum BX, England Spectrometer. Spectra were recorded from 400 to 4000 cm^{-1} using a KBr disc method.

Scanning electron microscopy (SEM) images were obtained using a Philips XL30 Environmental scanning electron microscope. The clean and dry samples were first coated with gold using a Bal-Tec SCD 005 sputter coater.

The transmission electron microscopy (TEM) images were obtained by employing a transmission electron microscope Hitachi, H7100 with an accelerating voltage of 200 kV. The samples were dispersed in chloroform and diluted to the right concentration. The suspension was then dropped on to the TEM sample grid and allowed it to dry. The very thin layer on the grid was observed on the microscope.

Tensile tests were performed by using a Universal Tester, Instron-4302, LEO. The samples were cut into dumbbell shape using a dumbbell cutter (Die BS

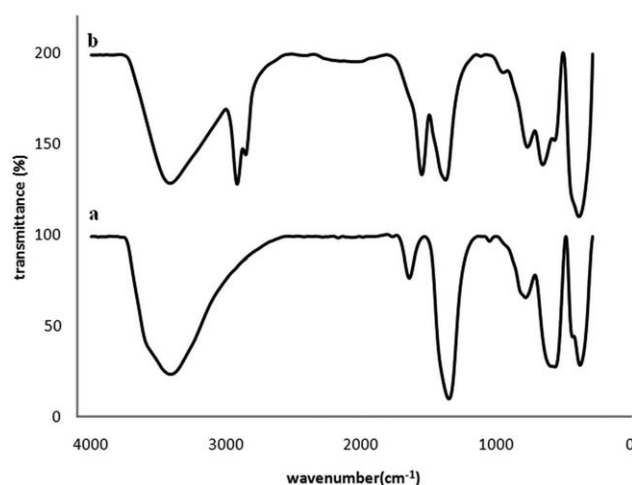


Figure 2 FTIR spectra for (a) pristine Mg_3Al LDH and (b) stearate- Mg_3Al LDH.

6476). The thicknesses of the samples were measured using a thickness gauge.

RESULTS AND DISCUSSION

Characterization of Mg_3Al LDH and stearate- Mg_3Al LDH

The XRD patterns in the range of 2θ from 2 to 65° for the pristine and modified LDH are shown in Figure 1. It is apparent that both LDH and stearate- Mg_3Al LDH are crystalline in nature with well-defined layered structure. The basal spacing (d) of the LDH or stearate-LDH is calculated from the first diffraction peak using Bragg's equation, $n\lambda = 2d\sin\theta$, where n is equal to 1 for the $\langle 003 \rangle$ peak, λ is the wave length of $Cu-K_{\alpha}$ radiation, and θ is the half of the scattering angle. The modification of LDH with stearate ions increases the clay interlayer distance from 8.72 Å in LDH (corresponding 2θ value of $\langle 003 \rangle$ peak is 10.14°) to 31.68 Å in stearate-LDH ($2\theta = 2.78^\circ$). The increase of the basal spacing indicates that the anions are successfully intercalated into the interlayers of LDH.⁴³

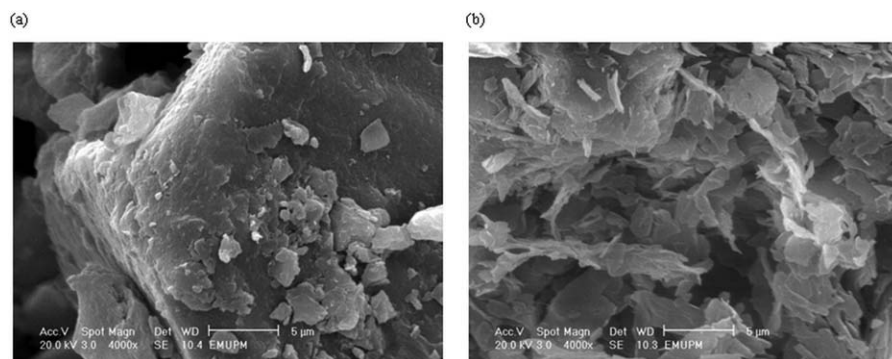


Figure 3 Scanning electron micrographs of (a) pristine Mg_3Al LDH and (b) stearate- Mg_3Al LDH.

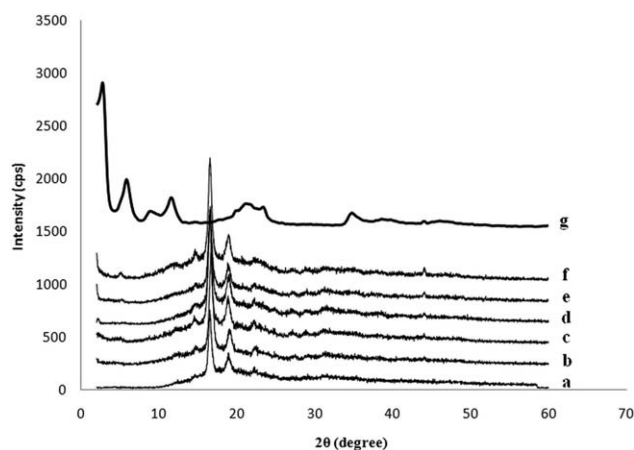


Figure 4 XRD spectra of (a) pure PLA and the nanocomposites of PLA with (b) 1, (c) 3, (d) 5, (e) 7, (f) 10 wt % stearate-Mg₃Al LDH content and (g) stearate-Mg₃Al LDH.

Figure 2 shows the FTIR spectra of the pristine Mg₃Al LDH and stearate-Mg₃Al LDH. The pristine LDH has a broad adsorption band at around 3500 cm⁻¹ due to O—H group stretching of both hydroxide layers and interlayer water molecules. The stretching vibration (H—OH) of the interlayer water

can be observed at about 1600–1650 cm⁻¹. The lattice vibration bands of the M—O and O—M—O (M = Mg or Al) bondings appear at below 800 cm⁻¹ region. The pristine LDH also shows an intense band at 1384 cm⁻¹, which can be associated with the asymmetric stretching vibration of the nitrate anions in Figure 2(a).³⁹ Meanwhile, the stearate-Mg₃Al LDH spectrum shows absorption bands at 2800–3000 cm⁻¹ [Fig. 2(b)], which are the characteristic absorptions of the C—H stretching vibration due to the presence of the —CH₃ and —CH₂ groups of long chain stearate anions.⁴⁴ It also indicates two strong absorption peaks of the carboxylate asymmetric and symmetric stretching, located at 1532 and 1398 cm⁻¹, respectively.¹⁹

Surface morphology of the pristine Mg₃Al LDH and modified stearate-Mg₃Al LDH particles are shown in Figure 3. As shown in Figure 3, the clay is obtained as porous particles in the presence of the organic anions.

Characterization of PLA/stearate-Mg₃Al LDH nanocomposites

XRD patterns of the stearate-Mg₃Al LDH, pure PLA, and PLA/LDH nanocomposites of various amounts

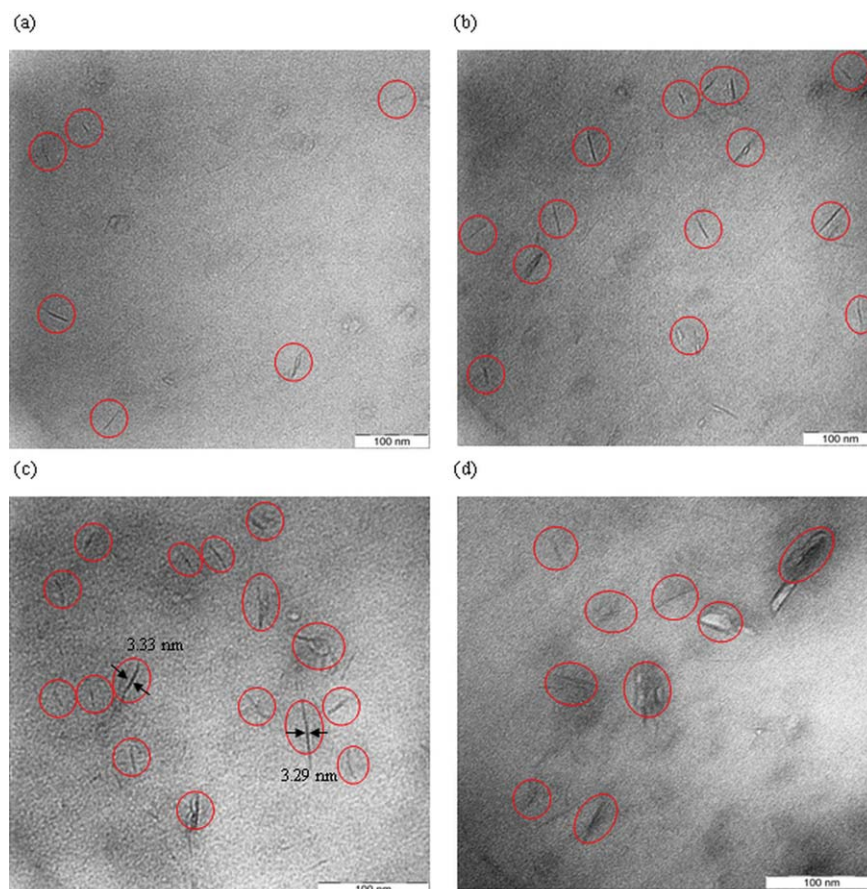


Figure 5 TEM images of PLA/stearate-Mg₃Al LDH nanocomposites with (a) 3, (b) 5, (c) 7, and (d) 10 wt % stearate-Mg₃Al LDH content. The magnification is 200,000× and the scale is 100 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

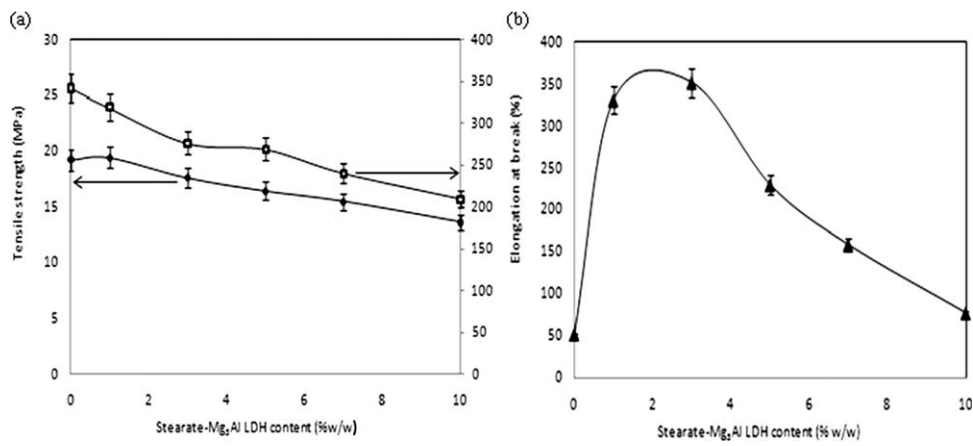


Figure 6 Tensile strength and elastic modulus (a) and elongation at break (b) of PLA with different stearate-Mg₃Al LDH content.

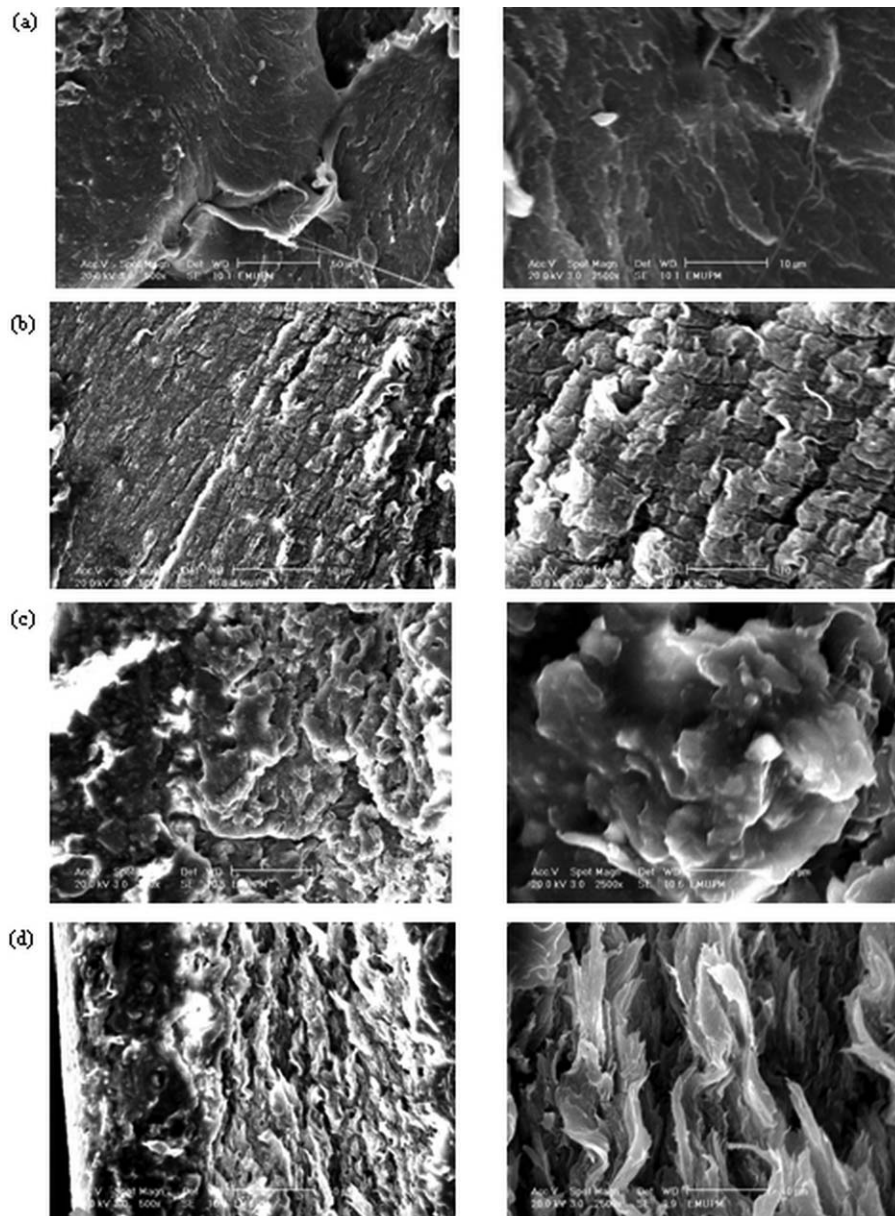


Figure 7 The fractured morphology of pure PLA (a) and PLA/stearate-Mg₃Al LDH nanocomposites with (b) 1, (c) 3, and (d) 5 wt % stearate-Mg₃Al LDH content at different magnifications, 500 and 2500 \times .

of the LDH contents are shown in Figure 4. The absence of the diffraction peak in the PLA nanocomposites with 1.0, 3.0, or 5.0 wt % of the LDH indicates that the Mg₃Al LDH layers are completely exfoliated and randomly dispersed in the PLA matrix. The presence of a very small peak at 2θ of 2.01° for the composites with 7.0 or 10.0 wt % stearate-Mg₃Al LDH content suggest that there is also a small amount of intercalated stearate-Mg₃Al LDH in the composites.¹⁹

The formation of nanocomposites can be directly observed by TEM. The TEM images of PLA/stearate-Mg₃Al LDH nanocomposites with 3.0, 5.0, 7.0, and 10.0 wt % of the modified LDH are shown in Figure 5(a–d), respectively. The dark lines represent the LDH layers in the PLA matrix. Figure 5(a,b) shows that the LDH layers are greatly exfoliated in the polymer matrix whereas Figure 5(c,d) indicates, in addition to the exfoliated, the presence of the intercalated LDH layers.

Figure 6(a,b) shows the effect of stearate-Mg₃Al LDH content on tensile strength (TS), elastic modulus (EM), and elongation at break (EB) of the PLA nanocomposites. Figure 6(a) shows the presence of 1.0 wt % of stearate-Mg₃Al LDH does not significantly change the tensile strength. However, further increase in the stearate-Mg₃Al LDH loading decreases gradually the TS. This is maybe due to the extended aggregation of stearate-Mg₃Al LDH layers in the PLA matrix. Figure 6(b) shows the effect of stearate-Mg₃Al LDH content on the elongation at break (EB) of the PLA. The EB for the PLA nanocomposites is about seven times higher compared with that of the pure PLA when the modified clay content is between 1.0 and 3.0 wt%.

In polymer industry, fatty acids have received substantial attention as plasticizers since their long hydrocarbon segments improve the matrix flexibility.⁴⁵ The considerable increase of the EB that is seen in Figure 6(b) can be linked to the presence of the long chain hydrocarbon parts of stearate anions, which are intercalated in the LDH layers.

Figure 7 shows SEM micrographs obtained from the tensile fracture surfaces of pure PLA and its nanocomposites containing 1.0, 3.0, and 5.0 wt % of stearate-Mg₃Al LDH. The image of the fractured surface of the pure PLA sample [Fig. 7(a)] shows a relatively compact solid surface indicating that the sample is brittle while the images of the nanocomposites [Fig. 7(b–d)] show the rough and stretched surfaces which support the reduction of the rigidity of the samples.

CONCLUSION

PLA/stearate-Mg₃Al LDH nanocomposites were synthesized successfully via solution casting. The

used stearate-Mg₃Al LDH was prepared by coprecipitation and ion exchange reaction. Incorporation of 5.0 wt % or less of the stearate-Mg₃Al LDH produced exfoliated PLA nanocomposites. Mechanical analyses of the nanocomposites showed that the presence of 1.0 wt % of the stearate modified LDH did not significantly change the tensile strength and modulus but drastically enhanced (of about 650%) its elongation at break.

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