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POLY (LACTIC ACID)/ORGANOCLAY BLEND NANOCOMPOSITES: STRUCTURAL, MECHANICAL AND MICROSTRUCTURAL PROPERTIES

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Poly (lactic acid)/clay nanocomposites were prepared by solution-casting and melt-blending techniques, and their morphologies and mechanical properties were studied. X-ray diffractograms revealed an intercalated–exfoliated mixed structure for the nanocomposites obtained by both techniques. TEM images show a good organoclay dispersion degree. The mechanical properties of nanocomposites from the melt-blending technique were superior to those obtained by solution-casting method. In both cases, the highest elongation at break and Young's modulus were achieved at5wt%octadecylamine-montmorillonite (ODA-MMT) content.

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1. Introduction

Poly (lactic acid), PLA, has received much attention for applications in biodegradable materials [1-3]. The polymeris produced from renewable resources, has excellent properties comparable to many petroleum-based plastics, and is readily biodegradable. Consequently, it has been proposed as a renewable and degradable plastic for use in service ware, grocery bags, waste-composting bags, films, and controlled release materials for pesticides and herbicides [4-7].

Clay has sandwich-type structures with one octahedral Al sheet and two tetrahedral Si sheets, the so called philo-silicate [8]. There are many types of philo-silicates: kaolinite, montmorillonite, hectorite, saponite, synthetic mica, etc [9, 10]. Montmorillonite, hectorite and saponite are the most commonly used layered silicates due to their small particle size and their intercalation properties. Moreover economic and environmental factors, their natural abundance and their high mechanical and chemical strength make these layered silicates useful as reinforcing particles of polymer materials [11, 12]. Although several strategies have been considered to prepare polymer/layered silicate nanocomposites, the two main techniques reported in the literature are casting and intensive mixing [13-15]. Casting produces exfoliation of the layered silicate into single layers by using a solvent in which the polymer is soluble. Layered silicates can be easily dispersed by the presence of the solvent, owing to the weak forces that stack the layers together [16]. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated, the sheets reassemble, sandwiching the polymer to form an ordered multilayer structure. This technique has been widely used with water-soluble polymers to produce intercalated nanocomposites[17, 18].

Intensive mixing involves mixing the layered silicate with the polymer matrix in the molten state. Under these conditions and, if the layer surfaces have enough compatibility with the chosen polymer, the polymer can crawl into the interlayer spacing and form either an intercalated or

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*Corresponding authors email**:** kamyarshameli@gmail.com exfoliated nanocomposite [19]. Nanocomposites are a class of composites derived from ultrafine inorganic particles with sizes in the order of nanometers that are homogeneously dispersed in a polymer matrix. Because of their nanometer sizes, nanocomposites possess properties that are superior to those of conventional composites because of the interfacial adhesion being maximized. Recently, nano-scale composites of polymers with clays or organoclays have been studied extensively [20-24].

In this study, we investigated the influence of organoclays on the properties of PLA. The properties of the hybrids in film form were studied as a function of the clay content in the matrix polymer.

2. Materials and Methods

2.1. Materials

Poly (lactic acid) was supplied by Nature Works 4060D, and was used as a matrix. Sodium Montmorillonite (Kunipia F) with a cation exchange capacity of 119 meq/100 g was obtained from Kunimine Ind. Co. Japan, and was used asnanofiller. Octadecylamine and chloroform (Merck, Germany)were used as a surfactant and solvent, respectively.

2.2. Modification of Montmorillonite (MMT)

Organoclay MMT was prepared by a cationic exchange process in an aqueous solution by vigorously stirring 20 g of Na^+-montmorillonite dispersed in 800 ml of distilled water at 80 °C with a solution of 50 mmoloctadecylamine and 50 mmol concentrated HCl in 200 ml distilled water. The precipitate was filtered, washed with hot distilled water until no chloride was detected and dried at 60 °C for 24 h. The product was labeledODA-MMT.

2.3. Preparation of PLA/ODA-MMT nanocomposites

The procedures used to obtain the nanocomposite films are shown in Figure 1a for solution casting and Figure 1b for melt blending (Figure 1b). Nanocomposites with a ODA-MMT contents of 1, 3, 5, 7, and 10 wt % were also prepared. In the solution-casting technique, films of 0.5 mm thick were obtained using chloroform as a solvent in an ultrasonic bath at room temperature for 15 min. In the melt-blending technique, films 0.8 mm thick were obtained by hot pressing.

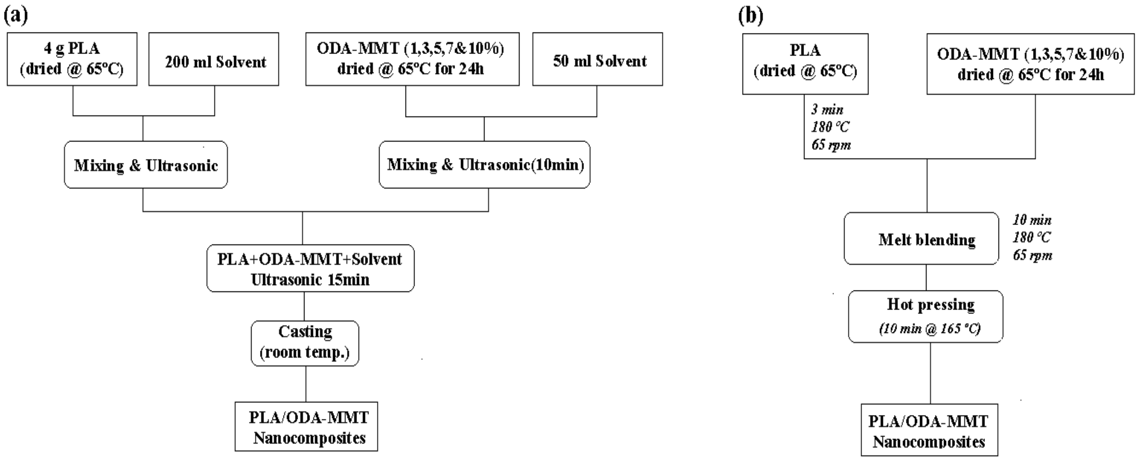

Fig. 1. Preparation of PLA/ODA-MMT nanocomposites films: (a) solution-casting and (b) melt-blending.

The nanocomposites produced were characterized by X-ray diffraction (XRD, Philips, X’pert, Cu Kα, Netherland) at a scan speed of 1°/min, and Fourier transform infrared spectroscopy (FTIR, PerkinElmer BX spectrophotometer). The tensile tests were performed in a universal testing machine Instron 4467 at a constant crosshead speed of 50 mm/min. Samples were prepared according to the ASTM D882-91 standard. Tests were carried out at room temperature. Transmission electron microscopy (TEM) was performed with a HITACHI-H 7100 machine.

3. Results and Discussion

3.1. X-ray Diffraction

The important parameter to achieve the best performance of polymer/clay composites, if clay does not produce defects, is the clay dispersion. X-ray diffractometry was used in order to identify intercalated structures. The intercalation of the polymer chains usually increases the interlayer spacing, leading to a shift in the diffraction peak towards lower angle values. The XRD results for the unmodified and modified clays are shown in the Figure 2. The measured d-spacing of Na^+-MMT is 12.16 Å (2θ=7.26º). After cation exchange with ODA, the d-spacing is 30.97 Å (2θ=2.85º). This suggests that Na^+ions are replaced by ODA in the organic modification and the ODA-MMT prepared in this work is well dispersed in water.

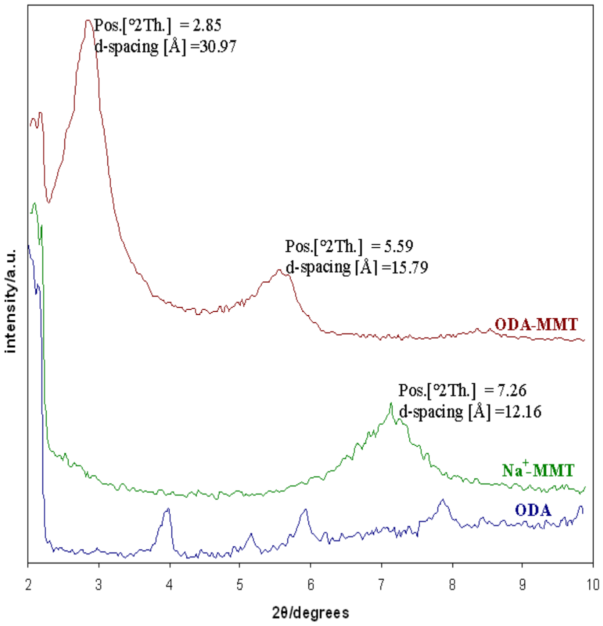

Fig. 2.XRD ODA, Na^+-MMT and ODA-MMT.

When PLA/ODA-MMT composites from melt blending and solution casting are formed, an organoclay peak in the maximum percentage of ODA-MMT in PLA at 2θ = 2.44º (d = 36.07 Aº) and an organoclay peak at 2θ = 2.49º (d = 35.42 Aº) appear in the diffraction patterns of PLA/ODA-MMT. The increase in the basal interlayer spacing implies that polymer chains are intercalated within the clay galleries [25-27]. PLA/ODA-MMT composite films showed similar diffractograms (Figure 3) when the organoclay content to PLA was increased from 1 to 10 wt %.

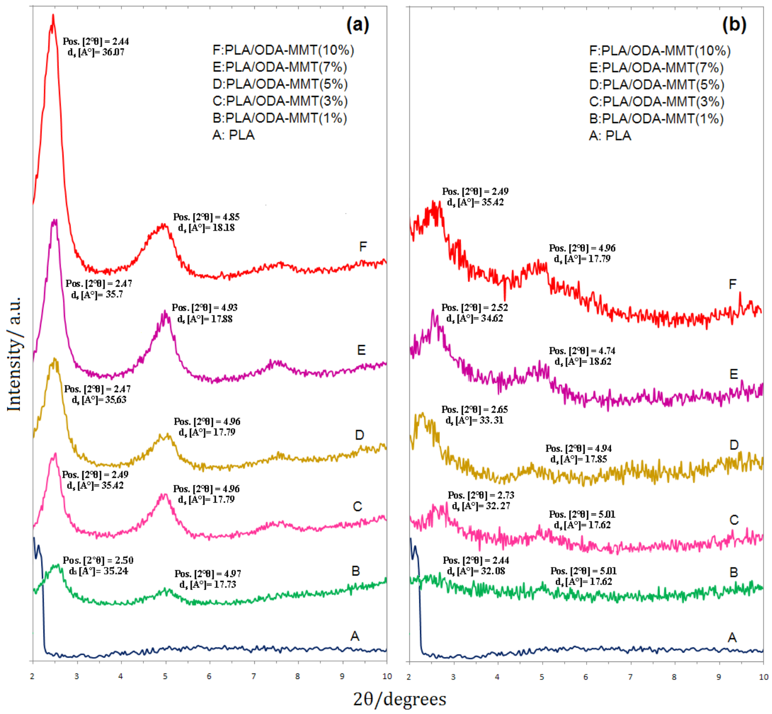

Fig. 3. XRD of PLA/ODA-MMT prepared by using melt-blending (a) and solution-casting (b).

3.2. Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was used to characterize the interfacial interaction between the modified PLA/ODA-MMT by solution-casting and melt-blending techniques (Fig. 4 (a, b)). The peaks at 1027, 2927(2850) and 3658 cm^{-1} were assigned to the C–O, C–H(double) and O–H stretching of the –CH(CH$_3$)–OH end group of PLA, respectively. The splitting of the C=O stretching at ca. 1757 cm^{-1} might be due to the presence of –NH–CO–O– group. The figure shows that neat PLA and PLA/ODA-MMT exhibit identical absorption peaks, suggesting lack of strong interactions between PLA molecules and ODA-MMT nanocomposites. In PLA/ODA-MMT, the C=O and O–H stretching peaks were shifted to lower wavenumbers (1012 and 3633 cm^{-1}, respectively). This was attributed to the strong interactions between the PLA hydroxyl end groups and the ODA-MMT platelet surfaces, and/or the ammonium groups of the surfactant in the organically modified clay [28–31].

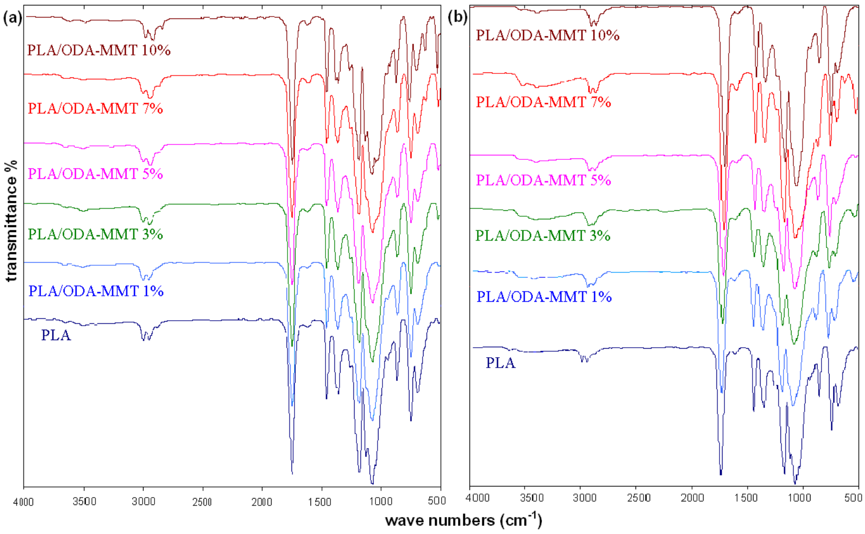

Fig. 4. FTIR spectra of PLA/ODA-MMT nanocompositesprepared
by solution casting (a) and melt blending (b).

3.3. Mechanical Properties

Fig. 5showstwo important mechanical properties, namely the elongation at break and Young's modulus, for the PLA/ODA-MMT nanocomposites prepared by using solution-casting and melt-blending techniques. The highest value for elongation at break was obtained for 5wt% organoclay content in PLA. The highest Young's modulus, the mechanical property improved by organoclay incorporation in to the polymer matrix, was also obtained for 5 wt% ODA-MMT content.

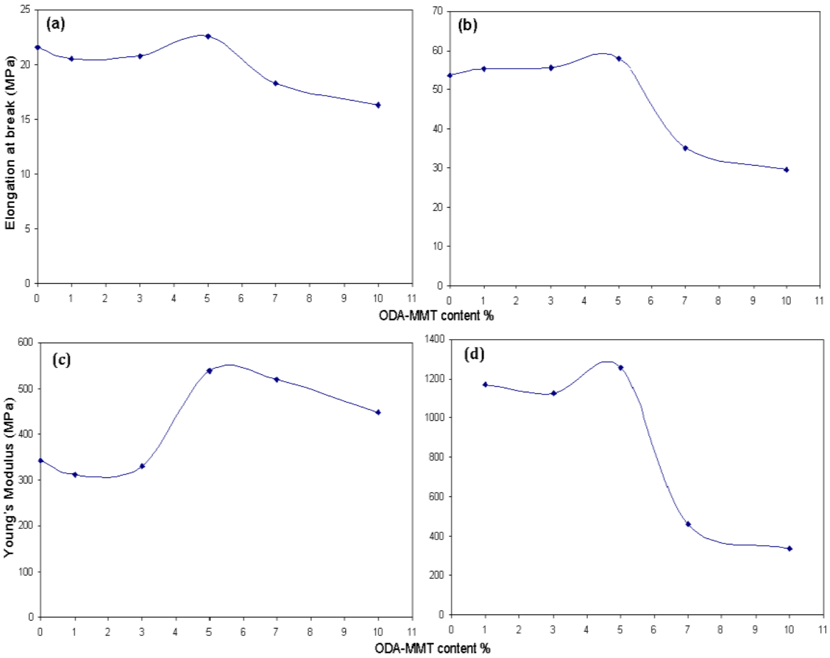

Fig. 5. Elongation at break (a, b) and Young's modulus (c, d) for PLA/ODA-MMT nanocomposites prepared by solution-casting and melt-blending techniques, respectively.

3.4. Transmission electron microscopy

To examine exactly the dispersion of the clay layers in the film-type nanocomposites, we carried out TEM studies. Typical TEM images for the nanocomposites based on 5 wt% in solution- casting and melt-blending techniques are shown in Figure 6. Each clay displayed individual clay layers that were well dispersed, exfoliated, in the PLA matrix. The density and homogeneity of the samples are similar but dispersion in samples from melt-blending(Fig. 6b) is better than that of solvent casting(Fig. 6a).

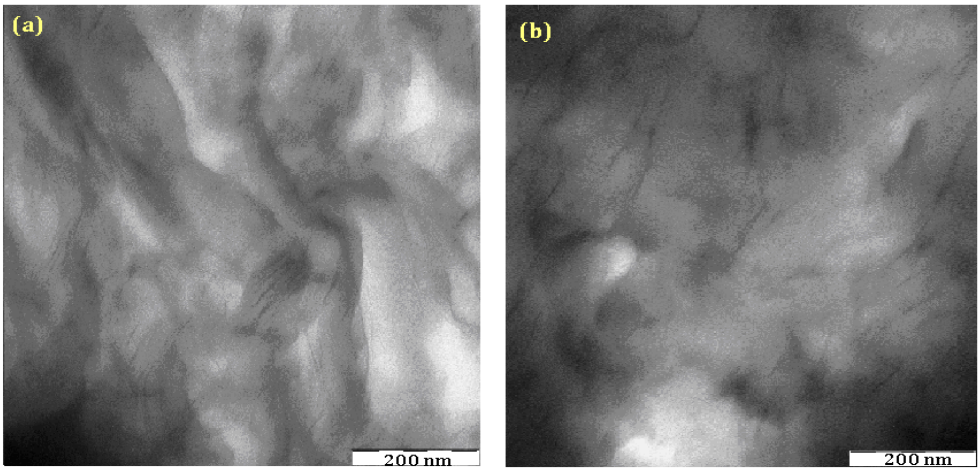

Fig. 6. TEM images of PLA/ODA-MMT nanocomposites based on 5 wt% ODA-MMT by solution casting (a) and melt blending (b) methods.

4. Conclusions

In this work, the PLA/ODA-MMT nanocomposites were prepared as an exfoliated structure by solution casting and melt blending methods. The optimum content of organoclay in both of methods was obtained at 5% because the highest elongation at break and Young's modulus were occurred in this content. Further the mechanical properties of obtained films by melt blending were superior of the films obtained by solution casting. In addition, the absence of solvents, which can produce environmental problems, is an advantage for the melt blending method.

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