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Characterization of polylactic acid ceramic composites synthesized by casting method

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Abstract

In this research, polylactic acid /SiO₂/AlO composite films were elaborated using a casting method. The morphology, microstructure, and optical properties of the PLA and composite films were investigated. The optical microscopy images show that SiO₂ and AlO were homogeneously dispersed in the PLA matrix. AFM images show in the case of pure PLA, the surface appeared smoother in comparison to the composite films, which have rough surfaces. The results of the ATR spectroscopy show, that the PLA/SiO₂ /AlO composite films contain the functional groups of Si-O-Si, Si-OH, and Al-OH due to the nucleating effect of SiO₂ and AlO particles with the PLA matrix. The XRD result shows that PLA has a semi-crystalline structure. The presence of AlO particles in the PLA matrix did not affect its semi-crystalline structure, while the addition of the SiO₂ and SiO₂/AlO particles increases the formation of the crystal phase. As a result, the crystallinity of the PLA is improved.

Keywords: Polylactic acid, AlO, SiO₂ particles, ATR, XRD characterization, cristallinity.

1. Introduction

The use of renewable resources is a high degree of attention granted polylactic acid (PLA), many properties that make it a good alternative to other synthetic polymers [1]. PLA has a lot of advantages like good biodegradability, biocompatibility and excellent mechanical properties. It is used in several areas, such as medical applications [2, 3]. Further the PLA is growing as a "green" alternative for polymers used in food packaging. PLA applications have been claimed in the field of fresh produce. The potential use of these products packaged in PLA is unlimited. Therefore, PLA applications in food packaging are ideal for maintaining the freshness of fresh produce and of products whose quality is not affected by the oxygen permeability of PLA. When selecting a polymer for an application, crystallinity plays a major role. The level of crystallinity of polymers is an important property. Because it influence on many properties of the polymer such as hardness, young's modulus, tensile strength, stiffness, gas permeability [6]. In spite of the advantages of PLA, has slow crystallization kinetics, the low cristallinity of PLA prevents its wider industrial application [4]. The degree of crystallinity controls the barrier properties of polylactic acid [5]. Crystallinity of PLA can be improved by addition of ceramic particles on the polymer matrix. However, ceramic particles are added often to PLA matrix such as, ZnO [6], TiO₂ [7], Al₂O₃ [8]. In this work, the effect of addition of SiO₂, and AlO particles on the critallinity of PLA composite films was investigated. SiO₂ and AlO particles were incorporated in PLA matrix using casting method. Different composite films were obtained; PLA, PLA/10% SiO₂, PLA/10% AlO, and PLA/5% SiO₂ /5% AlO. Morphology of the PLA and composite films was observed by optical microscopy. Interaction between PLA with SiO₂ and AlO particles was characterized using the attenuated total reflectance (ATR) spectroscopy. Structural characterizations of the PLA and composite films were analyzed using X-ray diffraction (XRD).

2. Experimental

The granulated polylactic acid (PLA) used in this work was 4043 D grade with a density of 1, 25 (g cm⁻³) supplied by NatureWorks (USA). The PLA was utilized as the matrix for all composites.

PLA-SiO₂-AlO composite films were prepared using solution casting method, PLA solution was prepared by dissolving granulated PLA 1g, in 10 ml of chloroform and stirring for 4 hours (500 rpm) using a magnetic stirrer. Different composition of PLA/ SiO₂/ AlO films were achieved by adding AlO 10 % , SiO₂ 10%, and (SiO₂ 5%/AlO 5%) 10 % by weight to PLA solution. PLA-SiO₂-AlO solutions were then stirred for 5 h (500 rpm) using a magnetic stirrer. The solutions were placed in an ultrasonic bath for 20 min to achieve a homogenised (dispersed SiO₂, AlO) solution. the solution of each blend was poured into a glass petri dish (diameter, 10 cm) and dried under room temperature for 24 h to form a thin film, followed by vacuum drying for 4 h to remove left-over solvent from the film. Finally, the films were peeled off from the petri dishes after immersing in distilled water for 10 min.

The morphology of PLA composite films was observed using an optical microscope (Nikon Eclipse LV100ND, Japan). AFM images were captured by means of atomic force microscope (AFM, ScanAsyst MultiMode 8 Bruker microscope, Karlsruhe, Germany). In order to get an optimal image, ScanAsyst mode automatically optimizes imaging parameters, including set-point, feedback gains, and scan rate. It uses a peak force tapping mode that performs a very fast force curve at every pixel in the image. At room temperature, real time scanning was performed in air with scan rates of 0.6 Hz and scan angle 0.0. The images (256 x 256) were captured and analyzed using the NanoScope Version 1.20 AFM program.

In this study, for optical characterization we used an Attenuated Total Reflectance (ATR) spectroscopy of type (Agilent CARY 360 SPECTROMETER, Germany). A minimum of 32 scans were signal-averaged a resolution of 4 cm⁻¹ was used and wave numbers from 400 to 4000 cm⁻¹.

X-ray diffraction (XRD) analyses were performed using a diffractometer Bruker D2 PHASER (Bruker AXS, Germany) equipped with a Cu K α (λ =0.154 nm) source. The generator was operated at 25 mA and 30 kV. Samples were scanned at different angles 2 theta from 10 to 80° at a scanning rate of 1°/min.

3. Results and discussion

3.1 Morphology

Figure 1 shows optical microscopy images of composite surface PLA films. A smooth surface without any specific morphological characteristic is characteristic of the neat PLA matrix (Figure 1a). However, a rough surface with a uniform distribution of SiO₂ and AlO particles is observed in the PLA/5%SiO₂/5%AlO polymer film (Figure 1c), while in the polymer films filled with a high content of SiO₂ and AlO 10% by weight, larger agglomerates (around 20 μ m) possibly, consisting of stacked platelets oriented in different directions, are visible (Figure 1b, 1d), respectively.

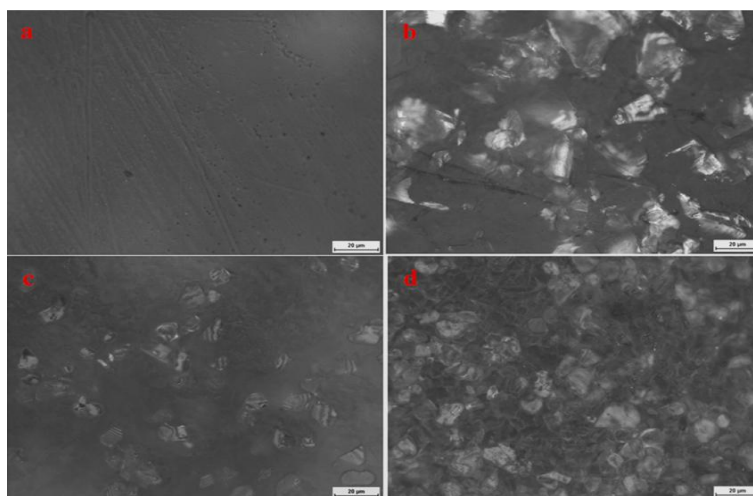


Fig. 1 Optical microscopy image of Poly(lactic acid) and its composites (x 1000): a) neat PLA , b) PLA/ 10% SiO₂, c) PLA/ 5%AlO/ 5% SiO₂ and d) PLA/10%AlO

3.2 AFM Analyses

AFM images in Figure 2 show the significant differences in the surface morphology of the PLA and composite films. The both surfaces of PLA and composite films were rather homogenous. However, in the case of pure PLA, the surface appeared smoother in comparison to the composite films which have roughness surfaces.

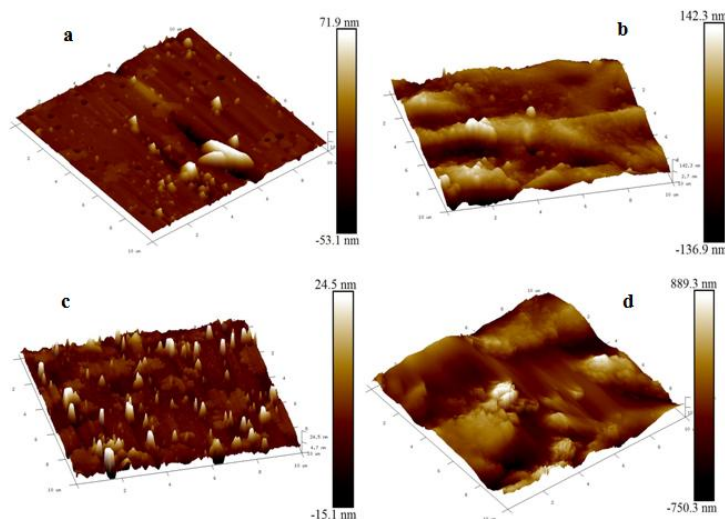


Fig. 2 AFM height images of PLA and its composites with scan size (10 µm x 10 µm): (a) neat PLA; (b) PLA/10% AlO; (c) PLA/10% SiO₂; and (d) PLA/5% SiO₂/5%AlO composites

3.3 FTIR-ATR characterization

The Attenuated Total Reflectance (ATR) spectra of pure PLA and PLA/ AlO/ SiO₂ composite films are shown in Figure 3. The absorptions bands of the asymmetric and symmetric C-H stretching vibrations of the -CH₃ group were found at 2996 cm⁻¹ and 2944 cm⁻¹ respectively [9].

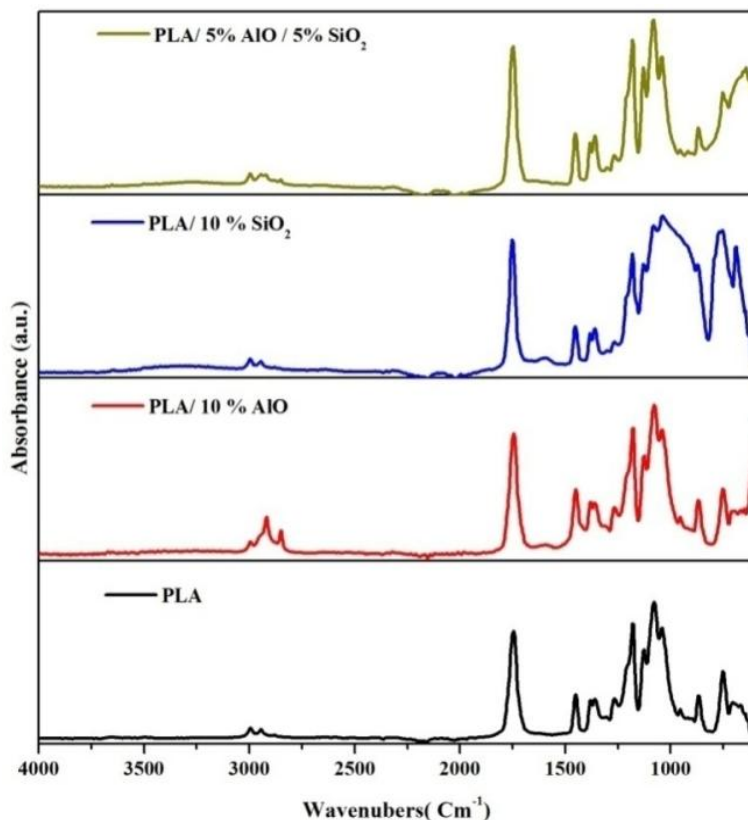


Fig. 3 The FTIR-ATR spectra of neat PLA and PLA composite films

The band located at 1748 cm^{-1} [10] is attributed to the C=O stretching of the ester group. The absorption peak for asymmetric C-O-C stretching vibration was observed at 1080 cm^{-1} . The band at 956 cm^{-1} was assigned to the characteristic vibration of the helical backbone with CH₃ rocking mode. The absorption bands at 867 and 754 cm^{-1} associated to the amorphous and crystalline phases of PLA respectively [11]. In the ATR spectrum PLA/AlO a wide absorption band appearing between 3100 and 3500 cm^{-1} attributed to stretching vibration Al-OH [12]. For the PLA/SiO₂ and PLA/ SiO₂/AlO spectra show a peak around 3400 cm^{-1} represents the stretching vibration of the Si-OH bond indicated that hydrogen-bonding interaction existed between the Si-OH and the C=O of PLA[16]. Si-O-Si and Si-O absorption peaks were identified at 1086 cm^{-1} and 693 cm^{-1} , respectively [12]. This could be explained by the nucleation effect of the particles with the PLA matrix [15,19].

3.4 XRD Analyses

In order to analyze the crystallinity of PLA and PLA composite films, X-ray diffraction analysis is a fast and effective characterization technique. Fig. 4 show XRD patterns of pure PLA and PLA composites films. The pattern of pure PLA has two peaks situated around 16.6° and 18.9° correspond to the diffraction planes (1 1 0) / (2 0 0) and 2 0 3 respectively, which characterize the crystalline phase in α form of PLA [13,17]. This phase is characterized by two anti-parallel chains in left-handed 10_3 (or deformed 10_3) helix conformation packed in orthorhombic a unit cell [14]. The addition of the AlO particles in the PLA has not changed the intensity of these peaks, so the crystalline structure is not affected.

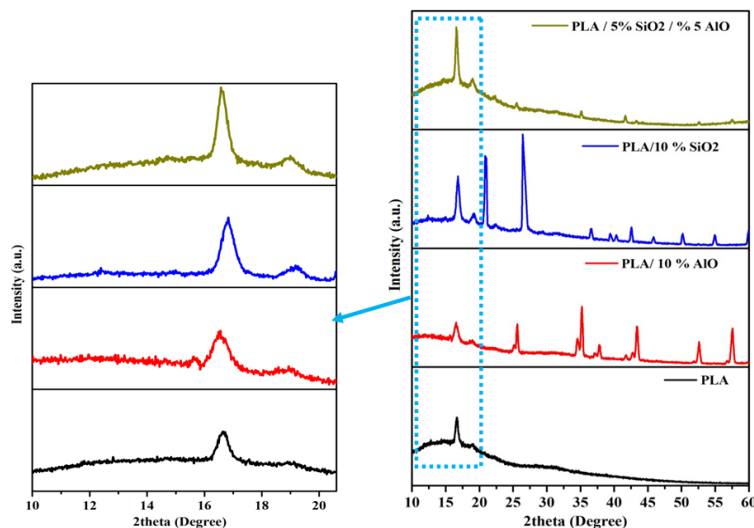


Fig.4 X-ray diffraction patterns of pure PLA and its composite films

The crystalline structure of the polymer is significantly affected by the presence of SiO_2 particles in the matrix. XRD patterns of PLA/ SiO_2 and PLA / SiO_2 /AlO composite films are characterized by intensive diffraction peak of PLA [18]. Hence, the presence of SiO_2 /AlO particles in the PLA matrix influences strongly on the crystallinity of the PLA films. This might be explain by the SiO_2 and AlO particles act as a nucleating agent so that more crystalline structures develop [15, 19], resulting in an increase of the crystallinity of the PLA [16].

4. Conclusion

In this study, we prepared Polylactic acid composites with compositions of AlO, SiO_2 and AlO / SiO_2 using a solvent casting method. The optical microscopy images indicated that SiO_2 and AlO were homogeneously dispersed in the PLA matrix, AFM images showed composite films have rough surfaces. Referencing the ATR spectra, we determined that the PLA/ SiO_2 /AlO composite films contained the functional groups of Si-O-Si, Si-OH, and Al-OH. Hence, SiO_2 and AlO particles act as a good nucleating agent to reinforce the Polylactic acid. XRD analysis shows addition of the SiO_2 and SiO_2 /AlO particles increases the formation of the crystal phase. As a result, the crystallinity of the PLA is improved.

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