RESEARCH ARTICLE

Morphological and mechanical properties of Poly (lactic Acid) / zinc oxide nanocomposite films

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ARTICLE INFO

Article History:
Received 11 March 2018
Accepted 25 April 2018
Published 01 May 2018

Keywords:
Mechanical
Morphological
Poly (Lactic Acid)/ Zinc Oxide Nanocomposite Films

ABSTRACT

Objective(s): Nowadays, tendency to use green materials can reduce environmental pollution and plastic waste. Poly (lactic Acid) PLA is one of the natural biodegradable polymers mainly used in the production of bioplastics for packaging which is made of non-toxic compounds and is easily biodegradable. In this research, the effect of 1, 3 and 5% nanocomposite zinc oxide on the morphological, mechanical properties and chemicals interaction of poly-lactic acid films was investigated.

Methods: To study morphological structure of nanocomposites, scanning electron microscope (SEM) was used. For evaluating the mechanical properties of films, tensile strength, elongation at break and young's modulus were measured by the ASTM D882 standard. Also, The Fourier-transform infrared spectroscopy (FT-IR) spectrum of films with PERKIN ELMER 1650, FT-IR spectrophotometer was recorded.

Results: Morphological shows that zinc oxide nanoparticles are well distributed in polymer matrix in all nanocomposite samples. It is clear from the result of mechanical properties that the Young's modulus was increased significantly ($p<0.05$) when the percentage of zinc oxide in the poly-lactic acid film increased from 1% to 5%. The tensile strength values of films zinc oxide nanocomposites were significantly ($p <0.05$) less than the control film. Also, elongation at break was no statistically significant. In the investigation of FTIR spectra, the percentage of created bonds between nanozinc oxide and poly lactic acid are increased by enhancing the percentage of nanozinc oxide.

Conclusions: Due to the good functional mechanical and morphological properties of PLA-nanozinc oxide films, they can be employed for various packaging.

How to cite this article
Shafiee Nasab M, Tabari M, Azizi MH. Morphological and mechanical properties of Poly (lactic Acid) /zinc oxide nanocomposite films. Nanomed Res J, 2018; 3(2): 96-101. DOI: 10.22034/nmrj.2018.02.006

INTRODUCTION

In recent years, the synthesis of biodegradable polymers has augmented due to the increased consumption of plastics and their long lifespan and also their almost non-biodegradability [1]. One of the biodegradable compounds is Poly-Lactic Acid. PLA has a great potential for replacing petroleum based polymers due to its thermoplastic nature, biodegradability, biocompatibility, mechanical strength, high elastic modulus and easy processing [2, 3]. Poly lactic acid is a linear aliphatic polyester that can be extracted 100% from renewable resources such as corn [4]. Also, it is authorized by FDA to use as a substance in contact with foodstuffs [5]. In spite of the many benefits that PLA has in comparison with other biomaterials, its utilization

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in the industry and in competition with industrial polymers faces some major challenges, such as: high water vapor and gas permeability, low glass transition (Tg) temperature, poor thermal stability and fragility which requires to improve and modify properties before use [6, 7]. To overcome these problems, some solutions can be applied like the use of plasticizers (softeners), combination with other polymers, optimization of the crystallization condition and utilization of appropriate additives to produce various nanocomposites. The use of nanoparticles and the production of nanocomposite are significantly populated to improve the properties of polymers regarding their high diversity and efficiency. A massive or bulk substance is called to a nanocomposite which generally consists of at least two separate components with complementary structure. Nanocomposite is a particular category of composites with at least one component on a nanoscale [8]. There is a better interaction between the polymer matrix and filler in polymer nanocomposites in comparison to the conventional nanocomposites. The uniform distribution of nanoparticles in the polymer matrix increase the contact surface of the matrix and nanoparticles which improves the mechanical, thermal, and preventive properties [9]. In general, the goal of employing them is to increase mechanical strength, reduce weight, enhance heat resistance, prevent better from UV, CO_2, O_2 and moisture, improve recycling capability and more protection from the product [8]. Zinc is one of the nanoparticles which is a kind of metal widely distributed in the nature and imperative for the function of many metalloproteinase. Nanoparticles of zinc oxide have some advantages over silver nanoparticles, including the low cost, white appearance and the ability to block ultraviolet radiation [10]. Nanocomposites are thought to be 21st Century materials and expected to be utilized more in the future. Industries tend to produce considerably thin films not only to reduce the material and production costs but also the environmental impacts of packaging. This result-oriented research helps the development of new active packaging based on the nanocomposite materials that prevents rancidity, change or loss of color, loss of nutrients, dehydration, gas production, creating odors and dehydration. As regards to the increment of the consumer demands and production of sustainable environmental products, nanocomposites based on the bio-polymers like Poly-Lactic Acid (PLA) have gained a peculiar attention in the field of new packaging [11, 12]. The aim of this study was to investigate the morphological, mechanical properties and chemicals interaction of poly lactic acid films with various zinc oxide nanocomposite.

MATERIALS

In this study, Poly (lactic acid) (PLA) films with 0%, 1%, 3% and 5% silicon dioxide nanocomposite were a commercial grade supplied by NatureWorks LLC, Minneapolis, USA by extrusion method which were made of (PLA (with M_n (PLA) = 88 500, index of polydispersity, M_w/M_n = 1.8, D isomer <2% and a specific gravity of 1.25 g/cm^3 (210 °C, 2.16 kg) and a melting temperature of 170 °C and the ZnO from Wacker-Chemie GmbH (Hydrophilic Wacker HDK® T40, with particle size of about 30 nm, bulk density: 280 g/L, specific surface area (BET): 25̶35 m^2/g, ZnO content ~99.5%.

Polymer Survey with Scanning Electron Microscope

First, in order to prepare the packaging cover, after placing the suspension in an acetonitrile solvent (Merck Company, Germany) in the laboratory falcons, put 3 cc of the obtained solution on the base with glue until the solvent evaporates. Then, it transfers to the spotter coater device which contains argon gas to stabilize the gold plated on the existing samples on the base. It should be noted that the gold cover is used to increase the electrical conductivity in the samples which leads to obtain more obvious images and also the argon gas causes the formation of plasma (ionized particles). Therefore, electrons are separated from positive to negative polarity based on the potential difference and then they are absorbed by detector and transmitted to the display. After 10 minutes, the prepared samples with gold cover are transferred to the compartment of the microscope device. Finally, the sample images appear on the display after adjusting the microscope on 10X magnification and related images are represented in the results section.

Mechanical Properties

The mechanical test of films was conducted in accordance with ASTM D 882 standard and by using the INSTRON Model 4465 device manufactured in the United States. Films were cut into a dumbbell shape with dimension of 10×1.5 square centimeters and placed between the two jaws of the device. The initial distance between the jaws was considered to be 50 mm and the loading speed was 50 mm / min. elongation at break, Young's modulus and tensile strength were calculated according to the film deformation and given force recorded by the software.

Investigating the interaction of FTIR chemicals

The FT-IR spectrum of films in the range of 400-4000 Cm^{-1} with PERKIN ELMER 1650, FT-IR spectrophotometer was recorded.

Statistical analysis

The software used to analyze the data are SPSS software package and Windows-based Excel spread sheet. Significant differences ($P < 0.05$) were assessed by variance analysis (ANOVA). Also, Tukey test was applied to confirm the existence of a significant difference between the means.

RESULTS AND DISCUSSION

Scanning Electron Microscope images

SEM micrographs from the surface of the films with 0, 1, 3 and 5% zinc oxide are shown in (Fig. 1). It is clear from (Fig. 1 A) that the pure PLA surface is rough. The homogeneous dispersion of the nanoparticles at the surface of the films are detected for three nanobio-composites (Figs. 1B, C and D). The micrograph shows that some dense nanoparticles of zinc oxide are distributed homogeneously on the film surface.

Mechanical Properties

The mechanical properties of the films depend on the intermolecular forces of their polymer-forming chains, the ratio of the composition of the constituents, the additives added to the film and the environmental conditions. The most important indicators for measuring the mechanical properties are tensile strength, elongation at break and the Young's modulus [13-15].

It is important to improve the mechanical properties of the biodegradable films due to the following items:

- The high mechanical strength of the film makes it harder to create mechanical damages like perforation due to the tension to the film and thus retains its deterrent to gases and moisture.
- The high flexibility of the film allows it to conform to the shape of the foodstuff without causing fracture and can be easily used as a cover.

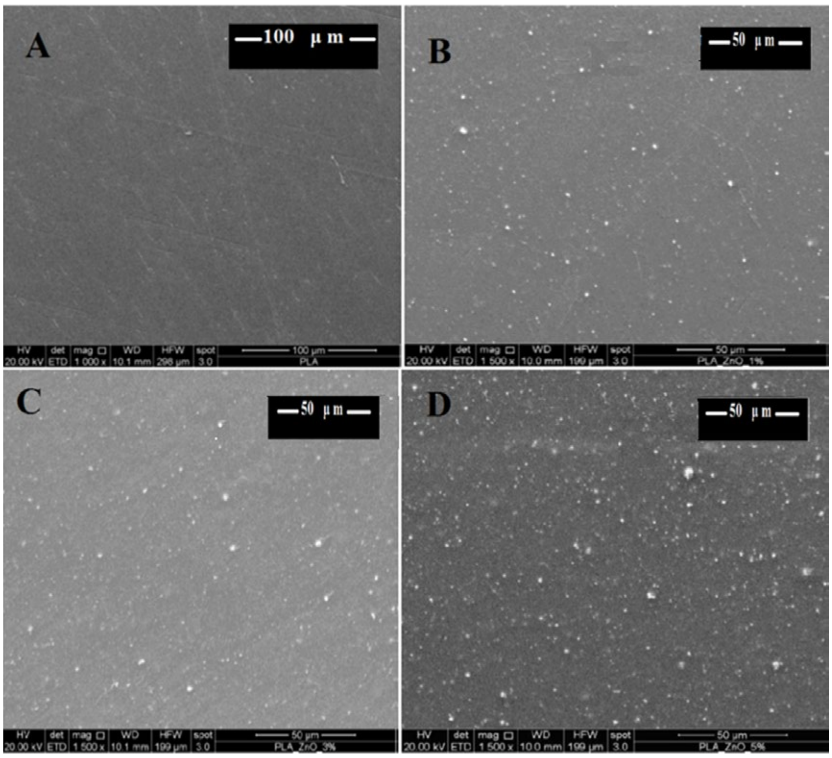

Fig. 1. Scanning electron microscopy images: A; PLA (1000 x), B; PLA/1%ZnO (1500 x), C; PLA/3%Zno (1500x), D; PLA/5% ZnO(1500x)

- The high mechanical strength of the film helps keep the foodstuff inside it from tensions during transportation.

The mechanical properties of poly-lactic acid nanocomposite zinc oxide films at three levels of 0, 1, 3 and 5% are shown in (Table 1) and (Figs. 2, 3, 4). The sample values are considered for mechanical properties including tensile strength, elongation at break and Yang's modulus. (Fig. 2) shows the amount of tensile strength. As shown in the figure, pure poly-lactic acid film has the highest value of tensile strength of 42 MPa while the lowest value is 35 MPa assigned to the poly-lactic acid films with 5% nanoparticle zinc oxide.

It can be seen from (Fig. 3) that the highest amount of elongation at break is 13.00 which is assigned to the poly-lactic acid film containing 1% zinc oxide and the pure poly-lactic acid film has the lowest value of 9.30. In fact, elongation at break for all percentages (1%, 2% and 3%) was not statistically significant.

In addition, (Fig. 4) shows that the highest value of Young's modulus is 3000 and the lowest value is 2700 that are related to the poly-lactic acid sample containing 3% zinc oxide and the pure poly-lactic acid film respectively. Poly-lactic acid containing 3% zinc oxide was statistically significant.

Table 1.Comparison of the mechanical properties of the PLA and ploy-lactic acid films containing zinc oxide

Sample (%-by weight)	E(MPa)	σ_b (MPa)	ε_b^z (%)
PLA	2700 ± 200^{a}	42 ± 3^{a}	9.3 ± 2.4^{a}
PLA/Zno 1%	2900 ± 300^{b}	41 ± 5^{ab}	13.0 ± 4.1^{b}
PLA/ZnO 3%	3000 ± 150^{c}	39 ± 3^{ab}	11.1 ± 1.5^{ba}
PLA/Zno 5%	2800 ± 100^{bc}	35 ± 3^{b}	12.8 ± 3.0^{b}

z: The gap between the jaws of device is 50mm

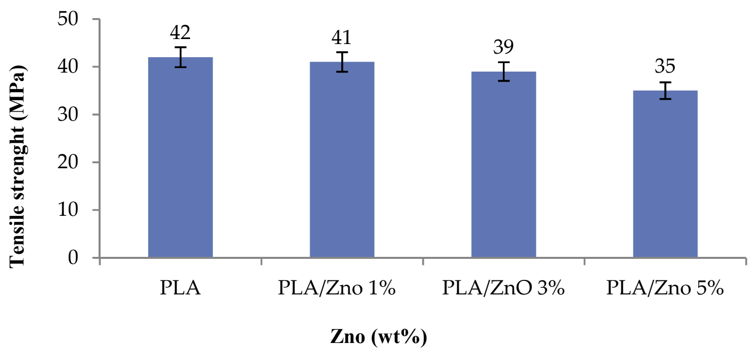

Fig. 2.Comparison of the effect of zinc oxide with different percentages on the tensile strength of the PLA film

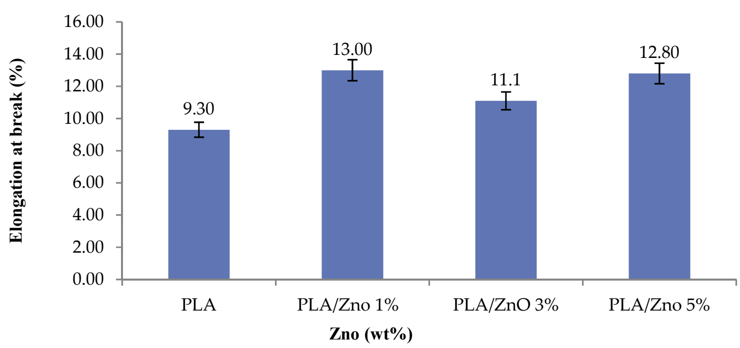

Fig. 3.Comparison of the effect of zinc oxide with different percentages in the elongation at break of the PLA film

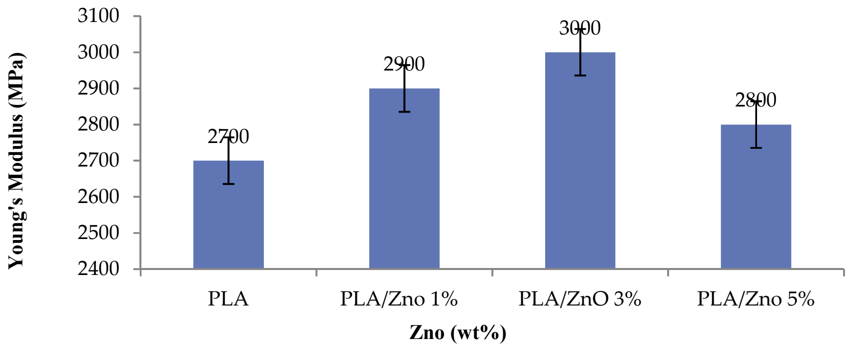

Fig. 4.Comparison of the effect of zinc oxide with different percentages on the Young's Modulus PLA Film

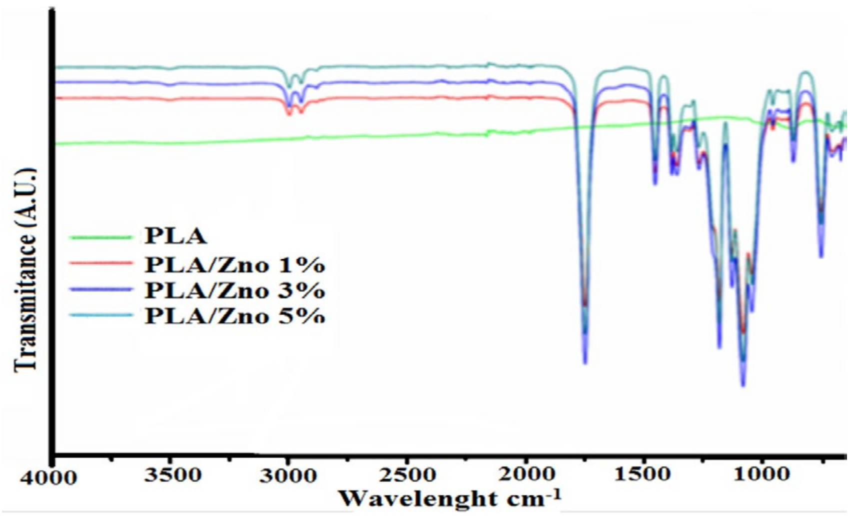

Fig. 5. FTIR spectrum for poly-lactic acid film containing zinc oxide

Investigation on Chemicals Interaction (FTIR)

The FTIR spectra of pure poly-lactic acid and poly-lactic acid films containing zinc oxide nanoparticles shows in Fig. 5. The following transmittance bands:

1454, 1384, 1362 cm^{-1} are assigned to the -CH- deformation including symmetric and asymmetric bending. 1267, 1182, 1129, 1090, 1045 cm^{-1} and 871 cm^{-1} are assigned to the stretching of C-O and C-C respectively. The transmittance band around 1750 cm^{-1}corresponds to the carbonyl carbon of the ester group of PLA.

The bands of around 2944 and 2995 cm^{-1} are assigned to the C-H stretching.

CONCLUSION

Morphological evaluation shows that the zinc oxide nanoparticles are well distributed in the polymer matrix in all the composite samples that the size of the most of the nanoparticles is 0.2 to 1.5 μm and a small number of them having the size of about 4 to 6 μm. This result seems reasonable considering the incompatible nature between the organic and mineral phases and the inherent tendency of zinc oxide nanoparticles to being dense due to their high energy levels. The results of the mechanical properties demonstrated that when the percentage of zinc oxide in the poly-lactic acid film increased from 1 to 5%, the tensile strength related to these films was reduced. The tensile strengths of zinc oxide films were significantly ($p<0.05$) less than the control film. Also, elongation at breaks were not statistically significant and enhancing the amount of zinc oxide from 1% to 5% in poly-lactic acid films led to the notable increase ($p>0.05$) of Young's modulus. In the investigation of FTIR spectra, the percentage of bonds between zinc oxide and poly lactic acid increases by enhancing the zinc oxide percentages.

ACKNOWLEDGMENTS

At the end, I am appreciated the venerable Dr. Mahsa Tabari and Dr. Mohammad Hossein Azizi for their helps in conducting this research.

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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