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PLA-ZnO nanocomposite films: Water vapor barrier properties and specific end-use characteristics

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ABSTRACT

PLA nanocomposite films with multifunctional characteristics such as mechanical, anti-UV, antibacterial, electrical, gas barrier properties are potentially of high interest as packaging biomaterials. Occasionally, desired and beneficial effects obtained by addition nanofillers come along with some drawbacks, leading to the sharp drop in the molecular weights of the polyester chains, and consequently an important loss of mechanical and thermal properties. Novel PLA-ZnO nanocomposite films were produced by melt-compounding PLA with 0.5–3% ZnO rod-like nanoparticles. The surface treatment of nanofiller by silanization (with triethoxy caprylylsilane) was necessary to obtain a better dispersion and to limit the decrease of molecular mass of PLA. The morphology, molecular, thermo-mechanical and transport properties to water vapor of PLA-ZnO films were analyzed with respect to the neat PLA. According to DSC and to XRD, the produced films were essentially amorphous. The changes in PLA permeation properties were strongly dependent on temperature and nanofiller loading. The well dispersed ZnO nanoparticles within the polyester matrix were effective in increasing the tortuosity of the diffusive path of the penetrant molecules. The activation energy remained similar for PLA and PLA-1% ZnO, but was found greater at higher loading of ZnO (3%), confirming the increased difficulty of travelling molecules to diffuse through PLA. In comparison to the neat PLA (presenting no antimicrobial efficacy), the nanocomposites were active against both Gram-positive and Gram-negative bacteria, stronger antibacterial activity being evidenced after 7 days elapsed time. By considering the multifunctional properties of PLA-ZnO nanocomposites, the films produced by extrusion can be considered a promising alternative as environmental-friendly packaging materials.

1. Introduction

The need to extend the shelf life of packaged food has brought the research to innovative solutions along with the changing needs of consumers, making the "packaging" a constantly evolving field [1–3]. The current trend is directing the research towards the development of innovative solutions both for functional packaging (active packaging and nanocomposite materials) and low environmental impact (biodegradable materials, recyclable packaging with reduced size). Most films, used to preserve food stuff, have been produced from synthetic polymers. Nevertheless, for environmental reasons, attention has lately been focused on biodegradable polymers for the preparation of food packaging films [4–6,3,7–12]. These films are usually loaded with antimicrobial agents that come into contact with food stuff, act on food-born microorganisms and inhibit their growth [13–20]. Therefore, the current research has been focused on the search for new

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bactericides that can effectively reduce the harmful effects of microorganisms. With the emergence of nanotechnology, the search for effective biocidal agents has focused on the development of nanostructure of coinage metals like silver, copper, zinc and gold [21]. However, the high cost of silver and gold metals has limited their use as antibacterial agents on industrial basis. Therefore, currently metal oxide nanoparticles, such as ZnO, have emerged out as a new class of important materials that are increasingly being developed for use in research and health-related applications, because of their low cost, easy availability, and unique chemical and physical properties. Recently, several reports have described the antimicrobial activity of ZnO nanoparticles [22–25].

Polylactide (PLA) is an environmental friendly, economical and commercially available polymer that offers great potential as disposable packaging material [26–30].

ZnO nanoparticles are well-known environmentally friendly and multifunctional inorganic additives that could be considered as nanofillers for various polymers providing properties like antibacterial effect or intensive ultraviolet absorption [31,32]. In this context, it is certainly of interest to endow PLA with antibacterial properties (and intensive ultraviolet absorption) and addition of ZnO nanoparticles to PLA could represent a relevant approach [33–35]. Unfortunately, the addition of untreated ZnO nanoparticles into PLA at melt-processing temperature leads to severe degradation of the polyester matrix, ascribed to the transesterification reactions and 'unzipping' depolymerization of PLA. By contrary, as reported elsewhere [33], ZnO adequately surface-treated by selected silanes can lead to PLA-based nanocomposites characterized by quite good preservation of PLA intrinsic molecular parameters and related physico-chemical characteristics.

In this paper we report the preparation of PLA-ZnO nanocomposites in a composition range from 0.5% to 3% nanofiller, followed by the extrusion of films. This is one of the first studies concerning the main characteristics of PLA-ZnO nanocomposite films, with a special focus on the water vapor barrier properties resulted from nanofiller incorporation. The morphology of the so-produced films and their thermal, mechanical and transport properties (sorption (S), diffusion (D), permeability (P)) to water vapor were analyzed. The investigation of transport properties was conducted at three different temperatures to evaluate also the activation energy of the diffusion phenomenon. In order to test the used ZnO as antimicrobial agent in the prepared film nanocomposites, two different types of bacteria (Gram-positive and Gram-negative) were used to evaluate the degree of inhibition of bacterial growth depending on the incubation time and filler amount.

2. Experimental

2.1. Materials

Poly(L,L-lactide) – hereafter called PLA, supplier NatureWorks LLC, was a grade designed for realization of films (4032D) with M_n = 133,000, dispersity, M_w/M_n = 1.9, whereas according to producer information the other characteristics are as follows: D isomer = 1.4%; relative viscosity = 3.94; residual monomer = 0.14%. Commercially available ZnO nanofillers (rod-like particles) were kindly supplied by Umicore Zinc Chemicals (Belgium) as Zano 20 Plus (surface coated with a silane especially suitable for the treatment of metal oxides, i.e., triethoxy caprylylsilane; ZnO content: 96.2 ± 0.5%, bulk density: 360 g/L). A thermal stabilizer, Ultranox 626A, (bis (2,4-di-t-butylphenyl) pentaerythritol diphosphite) was used at 0.3% in PLA. Throughout this contribution, all percentages are given as wt%.

2.2. Preparation of nanocomposites and films

PLA-ZnO nanocomposites were produced by melt compounding PLA with up to 3% ZnO nanofiller in a Leistritz twin-screw extruder (type ZSE 18 HP-40D, diameter of screws (D) = 18 mm, L/D = 40). The previously dried granules of PLA and additives were first mixed in a Rondol turbo-mixer (2000 rpm, 2 min) with 0.5%, 1%, 2% and 3% ZnO, followed by dosing and melt compounding in twin-screw extruder (throughput of 1.5 kg/h, speed of the screws = 100 rpm, temperature of the molten polymer ~185 °C). For the sake of comparison, unfilled PLA containing only thermal stabilizer was processed in similar conditions of melt-compounding. The granules of unfilled PLA and PLA-ZnO nanocomposites were dried (at 80 °C overnight, under vacuum) and used for the production of films by extrusion. Films with a thickness of about 150 μm were obtained using a DSM twin-screw microcompounder (batch-volume: 15 mL, speed of screws: 70 rpm, temperature of molten polymer: 185–190 °C) equipped with a flat die (width: 35 mm, die opening: 0.4 mm) and a DSM Xplore microfilm device.

2.3. Methods of characterization

Molecular weight parameters (number average molar mass, M_n, and dispersity index, M_w/M_n) of unfilled PLA and PLA-ZnO films were determined by size exclusion chromatography (SEC). Recovery of PLA from selected compositions for molecular weight parameters determination was carried out by firstly dissolving the samples in chloroform. The metallic residues were removed by liquid–liquid extraction with a 0.1 N HCl aqueous solution, step followed by intensively washing with demineralized water. Finally, PLA was recovered by precipitation in an excess of heptane. After filtration and drying, PLA solutions were prepared in chloroform (10 mg polymer/5 ml solvent). Molecular weight parameters of pristine PLA and those of PLA extracted from the studied nanocomposites were determined by SEC after a previously filtration of PLA solutions using filters of 0.45 μm.

X-ray diffraction measurements (XRD) were performed with a Bruker diffractometer (equipped with a continuous scan attachment and a proportional counter) with Ni-filtered Cu Kα radiation (λ = 1.54,050 Å).

Differential scanning calorimetry (DSC) analysis was carried out on samples with a mass ranging between 8 and 12 mg. The tests were carried out by means of a DTA Mettler Toledo (DSC 30) under nitrogen atmosphere. The