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Polylactic acid/zinc oxide biocomposite films for food packaging application

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ABSTRACT

Although PLA is much more expensive than polyolefins, such as PP and PE, there is a great interest to propose PLA based material as alternative films for food packaging being PLA derivable from natural source, compostable and biodegradable. For this purpose the research has the task to investigate and propose PLA materials with enhanced properties to be effectively and efficiently alternative to polyolefin films for food packaging application. In this contribution, biocomposite films of PLA with 1, 3 and 5 wt% of ZnO have been investigated to determine mechanical, barrier and antimicrobial (against *Escherichia coli*) properties. It is found that the biocomposite films are characterized by a good dispersion of the ZnO particles in PLA matrix, although no previous treatment was performed on ZnO particles, such as silanization, to decrease its incompatibility with the polymer. The biocomposite films have shown good mechanical properties, decrease of permeability to CO_2 and O_2, and only a slight increase to water vapour. Particularly important is that, for the biocomposite with 5 wt% of ZnO, the % Reduction for *E. Coli* test reached the value of 99.99 already after 24 h.

1. Introduction

The food market requires continuous improvement of the polymer materials properties to increase the functionality of packaging. Work is directed to improve technical features such as weld-ability, printability, mechanical and barrier properties to finally extent food shelf life providing enhanced health safety for the user. Moreover, the industries also tend to produce very thin films, in order to reduce not only the materials and production costs but also the environmental impact in the disposal of used packaging. The research is therefore oriented to develop new active packaging based on composite materials that contribute to avoid in the food development of rancidity, colour loss or change, loss of nutrients, dehydration, microbial growth, gas production, development of odours and senescence [1,2].

Composites based on biopolymers, such as polylactic acid (PLA), are currently receiving particular attention in the food packaging sector due to the increasing demands of consumers and manufactures for environmental sustainable products. Among the biopolymers, PLA has attracted great attention of many research groups because it is produced from renewable resources and it is biodegradable and compostable [3,4].

The production of PLA has numerous advantages including: (a) the production of the lactide monomer from lactic acid, which is produced by fermentation of a renewable agricultural source corn; (b) significant energy savings; (c) the ability to recycle back to lactic acid by hydrolysis or alcoholysis; (d) the capability of producing hybrid paper-plastic packaging that is compostable; (e) reduction of waste landfill volumes; (f) the improvement of the agricultural economy; and (g) the all-important ability to tailor physical properties through material modifications [4–6].

Although PLA presents significant commercial potential, some of its properties such as brittleness, low heat distortion temperature, and low melt viscosity for further processing may restrict its use for several applications. It was recently reported that the properties of PLA can be not only improved, but also tailored for specific end uses by selecting appropriate fillers and processing conditions [4].

For food packaging application, antibacterial properties, along with barrier and mechanical properties, are of particular interest. Application of nanotechnology in food packaging is considered highly promising since this technology could improve safety and quality of food while reducing the use of valuable raw materials and the generation of packaging waste [7,8].

The antibacterial activity of a polymer is usually obtained by adding metal particles, metal oxides, carbon nanotubes and organic

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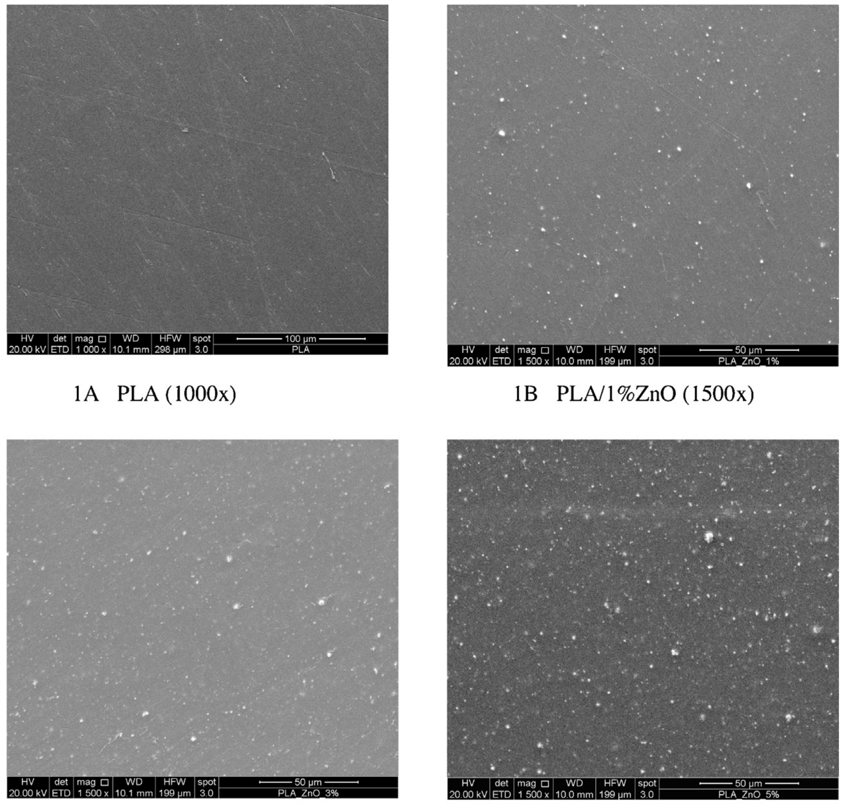

Fig. 1. Scanning electron micrographs of the surfaces of PLA and biocomposites films.

compounds. Metals and oxides particles and carbon nanotubes are the most used particles to develop antimicrobial activity [9–13]. Silver (Ag) particles are already found in many commercial products and it is reported that Ag exerts antibacterial and fungicidal against about 150 different types of bacteria [10]. Several metal oxides, such as zinc oxide (ZnO), titanium dioxide (TiO_2), magnesium oxide (MgO) and silicon dioxide (SiO_2) are known to act as antibacterial agents in addition to their ability to block UV radiation [9,11,12]. The particles of MgO and, especially, ZnO are presented as the best and safest solution for food packaging.

So particles of ZnO have been recently incorporated into a number of different polymers in order to improve the antibacterial properties of the packaging materials [9,12–16].

Recently, it was investigated the influence of a particular ZnO obtained by spray pyrolysis, with submicron dimension on the structure, morphology, thermal stability, photo stability and mechanical and antibacterial properties of iPP/ZnO biocomposites [9,17,18]. It was found that the ZnO particles impart improvements on the photodegradation resistance of iPP to ultraviolet irradiation and the biocomposites exhibit significant antibacterial activity against *E. Coli*. It was also observed that ZnO in iPP is more efficient as an antibacterial agent when the particles have micron size rather than nano size dimensions [9].

The ZnO nanoparticles have been also added to PLA, and especially its effects to barrier and antimicrobial properties were investigated [16,19]. In particular, in Ref. [16] a special ZnO with surface coated with silane, considered necessary to obtain a better distribution of the ZnO particles in the PLA matrix, was used. Among several results, it was claimed that PLA with 1, 2, and 3 wt% of ZnO had effective antibacterial activity after 7 days against *E.Coli*, whereas only the biocomposite with 3 wt% of ZnO was found functional against *S. Aureus* at the seventh day.

The aim of this study is to investigate the influence of a different ZnO on the morphology, thermal degradation stability, mechanical and barrier properties, and antibacterial property (*E. Coli*) of 3 PLA biocomposites, with 1, 3 and 5% of ZnO, respectively. The ZnO used in the work is obtained by spray pyrolysis technique which provides high purity of metal oxide composition, narrow submicron size distribution of the particle dimensions [17,18].

This particular ZnO has been already used with iPP for the production of film to be used in food packaging. It was found that ZnO particles can be well dispersed by extrusion in the polyolefin and that the films, compared to plain iPP, show better mechanical and barrier properties and, especially, excellent antimicrobial property against *E. Coli* (after 48 h the%R of the film with 5 wt% ZnO was 99.99) [9].

2. Material

Polylactic acid (PLA) in pellets, code PLA 4032D, with $d = 1.24\ g/cm^3$, was acquired from Nature Works LLC (USA). Molecular weights were determined by GPC-150C Waters Chromatography instrument (Milford, Massachusetts-USA) GPC at IPCB-CNR; they are: $Mw = 2.1 \times 105$ (g/mol), $Mn = 1.3 \times 105$(g/mol), polydispersity = 1.6 Mw/Mn. Glass transition temperature and melting temperature were also determined at IPCB-CNR by Mettler DSC 822e (Schwerzenbach, Switzerland) with a HR of 20 °C/min. The values obtained by DSC were: $Tg = 58\ °C$ and $Tm = 160\ °C$.

ZnO powder, with particles size of 100–500 nm, was supplied by Pylote SAS in Dremil-Lafage, France. ZnO particles were synthesized using a preindustrial spray scale pyrolysis platform at the Pylote SAS. This technique provides many advantages compared to other techniques of preparation: the simplicity of the process, high purity of the powders obtained, more uniform chemical composi-