Measurement 93 (2016) 442–448

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Antimicrobial food packaging prepared from poly(butylene succinate) and zinc oxide

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ARTICLE INFO

Article history:
Received 19 August 2015
Received in revised form 29 January 2016
Accepted 12 July 2016
Available online 14 July 2016

Keywords:
Biodegradable polymers
Food packaging
Mechanical properties
Antimicrobial activity

ABSTRACT

This article reports antibacterial activity, mechanical, thermal and physical properties of poly(butylene succinate) (PBS)/zinc oxide (ZnO) composite films for food packaging applications. The composite films were successfully prepared by using a blown film extruder at five ZnO levels ranging from 2 to 10 wt %. Under tension, PBS was stiffer due to the strengthening effect derived from rigid ZnO particles. However, the tear strength of the composite films was lower than the film without ZnO. Minimum ZnO content required to inhibit the *Escherichia coli* and the *Staphylococcus aureus* growths were observed at 6 wt% with the clear zone of 1.31 and 1.25 cm respectively. Thermal test results indicated the increased degree of crystallinity (X_c) and the decreased crystallization temperature (T_c) while the melting temperature (T_m) remain unchanged. Loss modulus curves informed the reduction of the glass transition temperature (T_g) of the film with ZnO at all concentrations. Release test indicated that Zn^{2+} migrated over 15 days studied while the maximum migration was observed when acetic acid was used as a food simulant.

1. Introduction

Antimicrobial food packaging is widely known to extend the shelf-life and improve the food safety [1]. Most of antimicrobial food packages were derived from petroleum based polymers. Although this kind of polymer creates high market values but the environmental awareness has shifted its interest to the biodegradable polymers [2,3].

When comparing with other biodegradable polymers, poly (butylene succinate) (PBS) can be degraded in the landfill or sea by the facilitation of bacteria and fungi [4]. It can be processed like other commodity plastics by many techniques such as blown films, fibers spinning, injection molding, thermoforming or blow molding. Moreover, PBS has some physical and mechanical properties comparable to that of polyethylene (PE) and polypropylene (PP) [4,5]. Thus, PBS seems to be a potential material to replace polyolefin in the near future [6]. However, several shortcomings such as low mechanical strength and microbiological corrosion still exists in PBS which restricted the use of PBS in many value added applications [4,7,8]. Numerous research papers have indicated that the use of inorganic filler such as ZnO could retarded the antimicrobial growth and improved the mechanical strength and in polymers. Sawai [9] reported that ZnO was the most effective antimicrobial agent for *Staphylococcus aureus* growth inhibition compared to MgO and CaO. In dental material, ZnO was found to reduce the growth of bacterial biofilms (*Streptococcus sobrinus*) by around 80% [10]. With the release of Zn^{2+}, ZnO damaged the cell membrane of *Escherichia coli* making the leakage of intracellular substances and lastly destroyed bacterial cells [11]. Mechanical strengths of polymers were improved when ZnO was added to both fossil-based and bio-based polymers. Liu et al. [4] strengthened PBS by incorporating the silane-treated ZnO. They found the increment in the flexural strength by more than 25% when ZnO was incorporated at 30 wt%. Another work by Zaman et al. [12] indicated that the addition of nano-ZnO into PP could impart notable increment in the tensile strength by more than 35%. Adding 5 wt % ZnO to poly(3-hydroxybutyrate) (PHB) increased the tensile strength of the composites from 29 to 36 MPa.

To produce PBS with antimicrobial function, Petchwattana and Naknaen [1] prepared PBS/thymol film and found its antimicrobial activity against *S. aureus* and *E. coli* at 6 and 10 wt% respectively. Another study focused on utilizing carvacrol to inhibit *S. aureus* and *E. coli* growth. The clear zones of 1.52 and 2.16 cm were

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http://dx.doi.org/10.1016/j.measurement.2016.07.048
0263-2241/

Nomenclature

ΔH_f	heat of fusion (J/g)	PHB	poly(3-hydroxybutyrate)
ΔH_m	enthalpy of melting (J/g)	PLA	poly(lactic acid)
DSC	differential scanning calorimetry	PP	polypropylene
HDPE	high density polyethylene	SEM	scanning electron microscope
LDPE	low density polyethylene	T_g	glass transition temperature (°C)
OTR	oxygen transmission rate (ml/(m^2 day))	X_c	degree of crystallinity (%)
PBS	poly(butylene succinate)	X_{PBS}	mass fraction of PBS
PE	polyethylene		

observed when carvacrol essential oil was added at 4 wt% and 10 wt% for the inhibition of *S. aureus* and *E. coli* respectively [2]. Although both essential oils exhibited good potential as antimicrobial agent in PBS film but the unpleasant odors affected the consumer acceptance. To avoid this undesired property, another antimicrobial mechanism was applied by adding ZnO to PBS. This provided PBS with good antimicrobial activity without the undesired odor from volatiles [12–14].

Thus, the current research aims to investigate the effects of ZnO particles on the thermal, physical and mechanical properties and its inhibitory action on foodborne pathogens of PBS composite films.

2. Materials and methods

2.1. Materials

PBS resin (FZ91PD) with a melting temperature and a melt flow index (MFI) of 114 °C and 6 g/10 min was used as a polymer matrix. Inorganic ZnO with an average particle size of 100 nm was supplied by U&V holdings company limited, Thailand.

2.2. Preparation of PBS/ZnO composite films

Five different compositions of PBS/ZnO were firstly prepared by dry-mixing method with various ZnO contents of 2, 4, 6, 8 and 10 wt%. The dry-blended ZnO formulations were then melt-blended by using a twin screw extruder (Labtech Engineering, LTE20-40). The extrudates were then granulized by using a blade-type pelletizer obtaining PBS/ZnO compound pellets. To remove the inherent moisture, they were kept in a desiccator for 24 h. All formulations were finally blown to obtain film of around 100 μm in thickness. They were stored again in a desiccator at room temperature for further testing and characterizations.

2.3. Microorganisms

Food pathogenic bacteria namely; *E. coli* (TISTR 780) and *S. aureus* (TISTR 1466), were obtained from the culture collection of the Thailand Institute of Scientific and Technological Research (TISTR).

2.4. Testing and characterizations

A film impact test was conducted follow the method described in ASTM D 3420 by using a film impact tester (Digital impact tester, Japan). The tensile test was determined using a Universal testing machine (Instron 5567) equipped with a 1kN load cell performed on rectangular films of 10×100 mm^2. Tear strength of the machine direction was evaluated in accord with ASTM D 1922. An oxygen transmission rate (OTR) was estimated by using an oxygen permeation tester (Mocon OX-TRAN, 2/21). The test was conducted following ASTM D 3985 with an oxygen flow rate of 40 cm^3/min at 23 °C and 0% relative humidity.

A Differential Scanning Calorimetry (DSC) (Perkin-Elmer, DSC6000) was employed to observe the thermal behavior and the degree of crystallinity (X_c) of the ZnO modified PBS films. Non-isothermal DSC measurement was tested under nitrogen atmosphere. Ten milligrams of sample were firstly cooled down to −20 °C. To remove thermal history, they were then heated up to 200 °C. After that, they were re-cooled down to −20 °C obtaining the cold crystallization curves. They were heated up to 200 °C again to obtain the second heating thermograms. The degree of crystallinity (X_c) was calculated by using Eq. (1)

$$X_c = \frac{\Delta H_m}{\Delta H_f \times X_{PBS}} \times 100 \tag{1}$$

where ΔH_m and X_{PBS} are the melting enthalpy and mass fraction of PBS respectively. ΔH_f is the heat of fusion, defined as the melting enthalpy of 100% crystalline PBS, which is 110.3 J/g [1,7].

To determine the glass transition temperature (T_g), a dynamic mechanical analyzer (NETZSCH, DMA 242) was performed on the PBS/ZnO composite films by measuring the loss modulus under tension mode. The dimension of test specimens was 3 × 40 mm. Loss modulus was recorded at a heating rate of 2 °C/min over the temperature range from −70 to 100 °C. The test frequency was set constant at 1.0 Hz. All measurements were conducted under inert nitrogen atmosphere.

The agar diffusion method was applied to evaluate the antimicrobial activity of PBS/ZnO composite films. Two different grams foodborne pathogens namely; *E. coli* (gram-negative, TISTR 780) and *S. aureus* (gram-positive, TISTR 1466) were selected as microorganisms due to their possibility of food pathogenicity. The inhibition zone was measured after the PBS/ZnO composite films were placed on the agar surface at 37 °C after 24 h incubation.

To evaluate the release of ZnO and Zn^{2+} from the PBS/ZnO composite films, deionized water, ethanol 10% and acetic acid 3% were selected as food simulants. The PBS/ZnO samples were immersed in the food simulants at 2, 6, 12, 24 h and 3, 7, 10, 12 and 15 days. After immersion, the quantity of the released Zn^{2+} was analyzed by using an atomic absorption spectroscopy (Perkin Elmer, AAnalytic 100) equipped with an air–acetylene burner. Zinc hollow cathode lamps were used as the spectral radiation sources. The wavelengths were 213.9 nm for Zn.

3. Results and discussions

3.1. Mechanical and morphological properties of PBS/ZnO composite films

Table 1 summarizes some mechanical and physical properties of the composite films with and without ZnO. Overall, the film impact strength of PBS slightly decreased with increasing ZnO