Food Control 69 (2016) 196–204

Contents lists available at ScienceDirect

Food Control

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

Thermo-mechanical, structural characterization and antibacterial performance of solvent casted polylactide/cinnamon oil composite films

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ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form
3 May 2016
Accepted 7 May 2016
Available online 10 May 2016

Keywords:
Polylactic acid
Cinnamon oil
Tensile strength
Glass transition temperature
FTIR spectroscopy
Antimicrobial packaging

ABSTRACT

Polylactic acid (PLA) based composite films were prepared by incorporating polyethylene glycol (PEG) and cinnamon oil (CIN) (25 and 50% *w/w* of PLA) via solution casting method. Morphological, structural, thermo-mechanical, spectral, and antibacterial properties of PLA/PEG/CIN films were investigated. Tensile strength (TS) and tensile modulus (TM) of the film decreased, while the elongation at break (EAB) increased by increasing CIN concentration. Using the principle of time-temperature superposition, the viscous modulus and the complex viscosity of composite films at selected temperatures and frequencies (time scales) were superimposed well in an extended frequency range. Thermal properties decreased substantially with incorporation of CIN. Significant changes in molecular organisation and intermolecular interactions between CIN and PLA/PEG matrix were observed through the FTIR spectroscopy. Scanning electron microscopic (SEM) revealed rough surfaces of the composite films. The effectiveness of composite films was tested against *Listeria monocytogenes* and *Salmonella typhimurium* inoculated in chicken samples, and it was found that the film containing 50% CIN showed an antibacterial activity during 16 days storage at refrigerated condition. The developed film has a potential for packaging of chicken samples with extended storage.

1. Introduction

Polylactide (PLA) – a linear aliphatic nature derived polyester has attracted considerable industrial attention for its biodegradability, and comparability to the mechanical properties of conventional polymer like polystyrene (Anderson, Schreck, & Hillmyer, 2008). PLA is synthesized by ring-opening polymerization of lactic acid (2-hydroxy propionic acid). In addition to biomedical applications, a significant portion of PLA has been utilized by packaging industry. Since PLA has been regarded as safe (GRAS), therefore, PLA-based packaging are currently used in many countries especially in Europe, Japan and North America for bottling water and juice, salad containers etc. (Ahmed & Varshney, 2011). The brittleness of PLA is one of the major limitations for its packaging application. Additionally, high elongation at break, flexibility and impact strength is also desired for its packaging application. To overcome those limitations, various approaches have been practiced including plasticization by incorporating low molecular weight plasticizers (e.g. polyethylene glycol, polypropylene glycol, PLA monomer) or blending with other miscible polymers for lowering the glass transition of the resultant polymers (Ahmed, Hiremath, & Jacob, 2016; Auras, Lim, Selke, & Tsuji, 2010). Furthermore, plasticized PLA exhibit increased elongation to break, which is accompanied by decreased tensile stresses at break and elastic moduli (Ljungberg, Colombini, & Wesslén, 2005).

Epidemiological studies indicate that the number of food-borne illness caused by pathogens has increased significantly (Pelissari, Grossmann, Yamashita, & Pineda, 2009). Therefore, controlling pathogens could reduce foodborne outbreaks and assure consumers a safe, wholesome, and nutritious food supply. In this regard, various naturally occurring compounds found in essential oils/spices have been demonstrated to possess antimicrobial activities and could serve as a source of antimicrobial agents to inhibit foodborne microorganisms (Deans & Ritchie, 1987; Hammer, Carson, & Riley, 1999). The area of antimicrobial packaging now becomes an active area of research in food packaging. Following the trend, numerous studies have been carried out on biodegradable polymeric antimicrobial packaging (Ahmed et al. 2016; Jamshidian

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http://dx.doi.org/10.1016/j.foodcont.2016.05.013
0956-7135/

et al., 2012; Salmieri et al., 2014; Tawakkal, Cran, Miltz, & Bigger, 2014). Nonetheless, a limited number of studies are focused on PLA/essential oil blend antibacterial packaging for food products especially for poultry products.

This paper is a continuation of a series of papers from our group on the utilization of metallic nanoparticles and essential oils as antimicrobial agents and plasticizers/toughening agents for PLA-based packaging materials. In one of our earlier works (Ahmed et al., 2016), 20% PLA was substituted by polyethylene glycol, and additionally essential oils (garlic, cinnamon, clove oil; PLA/EO = 1:1) were incorporated in the blend resulting a film with a T_g of −9 °C. The developed film was suitable only for frozen food products. To extend the application further, the objective of the present work was to improve the T_g of the packaging materials so it could be used at least refrigerated storage condition or above. Furthermore, a little information is available in the literature on thermo-mechanical properties and melt rheology of PLA/essential oil-blend film. Therefore, the objective of this study was to fabricate and characterize a composite film based on polylactide, polyethylene glycol and cinnamon oil (PLA/PEG/CIN) film. Additionally, antimicrobial effectiveness of those films was tested *in-vitro* and also in a real food system by packing chicken sample inoculated with *Listeria monocytogenes* and *Salmonella typhimurium*.

2. Materials and methods

2.1. Materials

PLA (Ingeo™ 4043D) was purchased in pellets from Nature Works LLC (Minnetonka, MN, USA), and dried overnight at 60 °C for 24 h in a vacuum oven before use. Dichloromethane (DCM) was obtained from Fisher Scientific (Loughborough, LE, UK) and used as it is. Poly ethylene glycol (PEG) (average MW = 1500 g/mol) and cinnamon oil (CIN) were procured from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Bacterial strains and media

Lyfo Disk pellets® of Gram-positive *Listeria monocytogenes* (ATCC 19114) strain was obtained from MediMark Europe (Grenoble, CEDEX, France). Culti-loops® of Gram-negative *Salmonella enterica sv thyphimurium* (ATCC 14028) strain was purchased from Remel Europe Ltd. (Dartford, Kent, UK). Brain heart infusion agar (BHIA) was procured from Conda Laboratories (Torrejón de Ardoz, MD, Spain). Tryptic soya broth (TSB) and Muller Hinton agar (MHA) were obtained from TM Media (Bhiwadi, India). Polymyxin-Acriflavin-Lithium chloride-Ceftazidime-Aesculin-Mannitol (PALCAM) agar base, PALCAM selective supplement and Xylose lysine deoxycholate agar (XLD) were purchased from Oxoid (Basingstoke, HM, UK).

2.3. Preparation of PLA based films

Solvent casting method was employed to prepare the PLA-based cinnamon oil films (PLA/PEG, PLA/PEG/CIN) (Ahmed, Varshney, Auras, & Hwang, 2010). Briefly, PLA (1.6 g) and PEG (0.4 g) were dry mixed; dissolved completely in DCM (30 mL DCM/g of PLA) by vigorous mixing at room temperature (~25 °C), and finally, appropriate quantity of CIN (25 and 50%; % w/w, PLA) were poured to the PLA/PEG solution with blending for another 15 min to ensure the oil incorporation into the film (Ahmed et al., 2016; Arfat, Benjakul, Prodpran, Sumpavapol, & Songtipya, 2014). The resultant solution was poured evenly onto glass petri-dishes with a 100 mm diameter and 15 mm depth. The solvent was allowed to evaporate at room temperature under a fume hood. The resultant films were peeled from the glass petri-dishes after 12 h, sealed in plastic pouches and stored in desiccator for 72 h.

2.4. Determination of film properties and characterization

2.4.1. Film thickness

Thickness of the films was measured using a digital hand-held micrometer (Mitutoyo, Model MCD-1″PXF, Mituyoto Corp., Kawasaki-shi, Japan) with an accuracy of 0.001 mm at 10 random locations around the film. Precision of thickness measurement was ±5%.

2.4.2. Mechanical properties

Tensile strength (TS), elongation at break (EAB) and tensile modulus (TM) of films were measured using a Texture Analyzer TA.XT plus (Stable Micro Systems, UK) with a 50 N load cell equipped with tensile grips (A/TG model) following the standard method (D882, ASTM, 2001). Grip separation was set at 50 mm and cross-head speed was 50 mm/min. TS, TM and EAB were measured in ten samples from each type of film.

2.4.3. Rheological measurements

Melt rheology of PLA/PEG/CIN films were measured using a Discovery Hybrid Rheometer HR-3 (TA Instruments, New Castle, DE, USA) attached with an electrically heated plate (EHP) at selected temperature (140, 150, 160 and 170 °C). Film samples were placed between the plates (measuring plate diameter 25 mm) in a 500-μm gap for 5 min so that the residual stresses would relax before rheological measurement. The EHP system accurately controlled the sample temperature by means of a platinum resistance thermometer positioned at the center and in contact with the opposite face of the lower plate. Frequency sweep tests (0.01–10 Hz) were carried out within a linear viscoelastic range (LVR), at a constant strain (0.03%) at selected temperatures. Effect of holding time up to 30 min on melt rheology was carried out at a constant frequency of 1 Hz and at 140 C. All rheological measurements were carried out in duplicate and rheological parameters were obtained directly from the manufacturer supplied computer software (TRIOS, TA Instruments, New Castle, DE, USA).

2.4.4. Surface color

Surface color of the films was determined using a CIE colorimeter (Hunter associates laboratory, Inc., Reston, VA, USA). Color of the film was expressed as L^* (lightness), a^* (redness/greenness) and b^* (yellowness/blueness) values. Total color difference (ΔE^*) was calculated based on the following equation (1):

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{0.5} \quad (1)$$

where ΔL^*, Δa^* and Δb^* are the differences between the corresponding color parameter of the samples and that of white standard ($L^* = 92.75$, $a^* = -0.95$, $b^* = 0.54$).

2.4.5. UV-barrier, light transmittance and transparency values

The light transmittance of films was measured at the ultraviolet and visible range (200 nm–800 nm) using a UV–visible spectrophotometer (Shimadzu UV-1800, Kyoto, Japan) following the method described by Shiku, Hamaguchi, Benjakul, Visessanguan, and Tanaka (2004). The transparency value (TV) of film was calculated using the following equation (Han & Floros, 1997):

$$TV = \frac{-\log T_{600}}{x} \quad (2)$$