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POC-4111; No. of Pages 7

ARTICLE IN PRESS

Progress in Organic Coatings xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Development of active packaging film made from poly (lactic acid) incorporated essential oil

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ARTICLE INFO

Article history:
Received 22 January 2016
Received in revised form 14 October 2016
Accepted 15 October 2016
Available online xxx

Keywords:
Polyester
Mechanical properties
Microstructures
Thermal properties
Antimicrobial properties

ABSTRACT

An active packaging film based on poly(lactic acid) (PLA) incorporated with 9 wt% bergamot, lemongrass, rosemary, or clove essential oils was developed. The influence of essential oils on the properties of the PLA/essential oil blends was studied. The mechanical and antimicrobial properties of PLA/essential oil blends were found to be superior to pure PLA. The WVP of PLA/essential oil blend films was significantly ($p < 0.05$) higher than that of pure PLA film. All FTIR spectra of PLA/essential oil blends displayed the characteristic bands of PLA-based materials. The addition of essential oils in the polymer matrix resulted in a two-step degradation process of TGA. Furthermore, essential oils led to the decrease of the glass transition temperature according to the DSC results.

1. Introduction

Currently, most materials used as disposable applications in the food packaging industry are synthetic plastic films. However, the majority of plastics are not biodegradable in nature and the growing synthetic plastic wastes have stimulated food packaging industry to develop new biodegradable packaging materials [1]. The development of bio-based antimicrobial packaging materials has generated extensive interest in the food packaging field, as it could reduce environmental impacts, meanwhile offering protection for the produce against chemical, physical, and microbiological effects [2,3].

Among the biopolymers, poly(lactic acid) (PLA) is a sustainable replacement for synthetic plastic because of its potential commercial applications. PLA is a versatile and biodegradable thermoplastic material that can be made from 100% renewable resources such as corn, sugar beet, and potato starch [4]. Furthermore, PLA is safe for the food packaging applications because it has been proven to be "Generally Recognized as Safe" (GRAS) [5]. However, its toughness, deformation at break, and thermal properties are inferior to conventional petroleum-based materials. This would limit its applications for food packaging. Considerable work has been done to improve the properties of PLA in order to enable them to compete with other commodity plastic films.

Active compounds like essential oils can be incorporated into biodegradable polymer films to improve their functional properties, such as mechanical properties and antimicrobial properties [6]. For instance, the essential oils from tea tree, bergamot, lemongrass, rosemary, and clove from medicinal plants have attracted great attention in health industry due to their potential as antioxidant and antimicrobial agents [7]. The plant essential oils are categorized as GRAS by the US Food and Drug Administration as well as the current European legislation for materials intended to be in contact with food stuff [8]. The incorporation of plant essential oil into PLA film is an interesting way to improve their industrial applications. The active antimicrobial packaging could offer the produce protection against chemical, physical, and microbiological effects [2].

However, previous reports showed that the enhancement of polymer properties not only depended on the type and concentration of essential oil, but also depended on the compatibility between polymer matrix and essential oil [9,10]. There were few reports to compare the effects of different essential oil types on the improvement of mechanical, thermal, and antimicrobial properties of PLA films. In previous works, PLA/essential oil blend films with different essential oil concentrations (0, 3 wt%, 6 wt%, 9 wt%, and 12 wt%) have been prepared. The best compromise between mechanical, barrier, thermal, and antimicrobial properties could be

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http://dx.doi.org/10.1016/j.porgcoat.2016.10.017
0300-9440/

Please cite this article in press as: Y. Qin, et al., Development of active packaging film made from poly (lactic acid) incorporated essential oil, Prog. Org. Coat. (2016), http://dx.doi.org/10.1016/j.porgcoat.2016.10.017

achieved by the addition of 9 wt% essential oil. So, 9 wt% essential oil content was selected to use in this work.

Therefore, the main objective of the present work was to prepare PLA/essential oil (bergamot, lemongrass, rosemary, and clove essential oil) blend films and investigate the effects of essential oil types on the physio-mechanical properties and antimicrobial properties of the fabricated PLA-based blend films.

2. Material and methods

2.1. Materials

Poly(L-lactic acid) (PLA) (Mw = 280 kDa, Mw/Mn = 1.98) was obtained from Natureworks LLC (Nebraska, USA). Five types of essential oils, including tea tree, bergamot, lemongrass, rosemary, and clove essential oils were purchased from doTERRA Co., ltd (New York, USA) and used as received. Chloroform, a solvent, was obtained from Chengdu kelong chemical Co., ltd (Sichuan, China).

2.2. Preparation of PLA/essential oil blend films

PLA/essential oil blend films were prepared by the solvent-casting method. Briefly, PLA (2 g) was dissolved in 50 mL of chloroform. 9 wt% essential oil was added into the PLA chloroform solution by magnetic stirring. Then, the film solution was cast onto a 20 cm × 20 cm glass plate and dried to form film. After drying, the film was peeled from the casting well and kept in a desiccator until the time of each analysis. Four types of essential oils, including bergamot, lemongrass, rosemary, and clove essential oils were incorporated into PLA matrix as 9 wt% loading. PLA/Bergamot essential oil, PLA/Lemongrass essential oil, PLA/Rosemary essential oil, and PLA/Clove essential oil blend films were named as PLA/BEO, PLA/LEO, PLA/REO, and PLA/CEO, respectively.

2.3. Thickness and mechanical properties

Thickness of the films was measured using a digital micrometer (Mitotuyo 7327, Tokyo, Japan). The mean value was taken from ten replications across each film sample. Elastic modulus (EM), tensile strength (TS), and percentage elongation at break (ε) of the films were determined using a CMT 4104 tensile testing equipment (MTS Systems Co., Ltd, Shanghai, China). Films were tested in triplicate. A 15 mm × 50 mm strip of film sample was clamped between two grips. The stretching speed was set to 50 mm/min. The main tensile parameters were obtained automatically from the computer.

2.4. Water vapor permeability

The water vapor permeability (WVP) of films was examined based on the ASTM E 96-95 standard method using a water vapor transmission measuring cup filled with the desiccant as it was described in a previous work [10]. For each film sample, 5 replications were tested, and the mean value was taken.

2.5. Film microstructure

The film samples (10 mm × 10 mm × 0.1 mm) were immersed in liquid nitrogen and cryo-fractured by hand. Scanning electron microscopy (SEM) investigations were carried out by using a SEM S-4800 (Hitachi Co., Ltd, Tokyo, Japan). SEM pictures were obtained at an accelerating voltage of 5 kV.

2.6. Transparency

The film sample was cut to the exact dimension of the side of glass cuvette and then mounted onto the inside of the cuvette. The transparency of films was recorded with a model T90 UV–vis spectrophotometer from Beijing Purkinje general instrument Co., Ltd. (Beijing, China). The transparency of films was determined from the percent transmittance of light at 600 nm. An empty cuvette was used as the blank.

2.7. Fourier transform infrared spectroscopy (FTIR)

The samples were dried in a desiccator for at least 3 weeks before analysis. A Nicolet iS10 Fourier transform infrared spectroscopy, with a spectral resolution of 1 cm^{-1} was used to recorded infrared spectra of samples. FTIR spectra were collected from 400 cm^{-1} to 4000 cm^{-1}.

2.8. Differential scanning calorimetry (DSC)

Thermal behavior of PLA/essential oil blends was determined by using DSC Q-2000 system (TA Instrument, New Castle, USA) under an inert nitrogen stream. Firstly, 10 mg of each sample was sealed in an aluminum pan. DSC scans were heated from 20 °C to 200 °C at a heating rate of 10 °C/min (5 min hold) and then cooled from 200 °C to 20 °C with a cooling rate of 10 °C/min (5 min hold). The first heating scan was used to eliminate any prior thermal history of the sample. The thermal properties were obtained from the second heating run of DSC curves. The glass transition temperature (T_g) of blends was taken at the inflection point of the thermograms in the second scan. The melting point (T_m) and cold crystallization temperature (T_c) were also recorded following standard procedures.

2.9. Thermogravimetric analysis (TGA)

The thermal stability evaluation was carried out by using Netzsch DSC-200PC analyzer (Germany). The samples were heated from 20 °C to 600 °C at the rate of 10 °C/min in nitrogen environment. Weight loss of samples was measured as a function of temperature.

2.10. Antimicrobial activity

The antimicrobial activity of the PLA/essential oil blend films was investigated against *Escherichia coli* and *Listeria monocytogenes* by the conventional liquid culture test [11]. The microorganisms were obtained from Faculty of Life Science and Technology, Kunming University of Science and Technology (Kunming, China). 0.18–0.20 g of each sample was put into a glass test tube and the tube was filled with 10 mL of broth. Then, 0.1 mL of inoculums was inoculated to the medium and the bacterial cultures concentration was adjusted to 10^6 CFU/mL [8]. The test tubes cultured with the PLA film without essential oils under the same condition were used as control. The antimicrobial activity of the PLA/essential oil blend films was determined by observing the bacterial growth. The bacterial number was converted to $\log_{10}$ colony-forming units per gram (CFU/g) prior to statistical analysis. The experiment was performed in duplicate for each sample.

2.11. Statistical analysis

The statistical analysis of the data was performed through an analysis of variance (ANOVA) using the SPSS 13.0 software package for Windows (IBM Corp., Armonk, USA). Differences between mean values were done by Duncan's multiple range tests. Data were presented as the mean ± standard deviation and the level of significance was set at $p < 0.05$.