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Preparation of poly(lactide)/poly(butylene adipate-co-terephthalate) blend films using a solvent casting method and their food packaging application

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ABSTRACT

Blend films with poly(lactide) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) were prepared using a solvent-casting method to modify the property of PLA film, and their properties were evaluated. FT-IR and DSC test results indicated that PLA is highly compatible with PBAT to form homogeneous blend films. The flexibility of PLA films increased significantly by blending small amount of PBAT without significant decrease in mechanical properties. Even the blend film with small amount of PBAT, 3.92 g of PLA with 0.08 g of PBAT ($PLA_{98}/PBAT_2$), exhibited UV screening effect without sacrificing transparency. The water vapor permeability and oxygen transfer rate of the blend films were varied depending on their blending ratio. In the packaging application for potatoes and green onion, the blend films exhibited preventing of greening of packaged potatoes and also showed antifogging effect with reduced quality changes in the packaging of green onion. The blend films have high potential for being used as UV screening or antifogging packaging films.

1. Introduction

Increased concerns on the environment and depletion of fossile fuels caused by nonbiodegradable plastic packaging materials have attracted widespresd attention on the application of biodegradable and bio-based plastic packaging materials such as poly(lactide) (PLA), poly(glycolic acid) (PGA), poly(butylene succinate) (PBS), poly(ε-caprolactone) (PCL), poly(butylene adipate-co-terephthalate) (PBAT), and polyhydroxyalkanoates (PHA) (Clarinval & Halleux, 2010; Rhim, Park, & Ha, 2013; Siracusa, Rocculi, Romani, & Rossa, 2008). Among such biodegradable plastics, PLA is one of the most promising polymers due to its versatility, superior mechanical properties, optical clarity, and low cost. Since PLA is a highly transparent and rigid plastics with high modulus (3 GPa) and strength (50–70 MPa), it has been used for fabrication of biaxially oriented films, thermoformed containers and stretch-blown bottle (Delpouve, Stoclet, Saiter, Dargent, & Marais, 2012; Dong, Zou, Yan, Ma, & Chen, 2013; Eslami & Kamal, 2013; Raquez, Habibi, Muraiu, & Dubois, 2013; Tawakkal, Cran, Miltz, & Bigger, 2014). However, PLA has some weakness for food packaging application since it has lower gas and water vapor barrier properties compared with commodity packaging films such as PE, PP, and PET. In addition, low glass transition temperature, weak thermal stability, high rigidity, and low toughness and ductility of PLA limit its applications (Harada et al., 2007).

Many research works have been performed to improve performance properties such as impact strength, flexibility, stiffness, gas barrier properties, and thermal stability, which included the addition of modifiers, blending, compatibilization and physical treatments (Jamshidian, Tehrany, Imran, Jacquot, & Desobry, 2010). Generally, blending of polymers is known to be the most effective method to obtain polymeric materials with required properties (Jain, Reddy, Mohanty, Misra, & Ghosh, 2010). Actually, blending of PLA with other polymers such as PCL, PHB, PHBV, and PBAT have been extensively studied to modify the mechanical and thermal properties, degradation rate, and permeability of gases or vapors (Jain et al., 2010; Kumar, Mohanty, Nayak, & Rahail, 2010; Rasal, Janorkar, & Hirt, 2010; Sarazin, Li, Orts, & Davis, 2007; Wu, Yuan, Laredo, Zhang, & Zhou, 2012; Yeh et al., 2010; Yokohara & Yamaguchi, 2008; Zhao, Liu, Wu, & Ren, 2010). Among the

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blending biopolymers, PBAT is interesting since it is a completely biodegradable, flexible and tough aliphatic-aromatic copolyester with high compatibility with PLA, which makes it considered as a good candidate for blending with PLA (Nofar, Maani, Sojoudi, Heuzey, & Carreau, 2015; Siyamaket al., 2012).

Yeh et al. (2010) studied the compatibility, crystallization, and tensile properties of PLA/PBAT blends in different proportions produced by melt blending and found that PBAT effectively toughened PLA. The carbonyl group of PBAT made it compatible or partially compatible with PLA during the melt-blending process (Ren, Fu, Ren, & Yuan, 2009). In addition, blending with PBAT reduced the brittleness and slowed down the crystallization of PLA (Jiang Wolcott, & Zhang et al., 2006; Ojijo, Ray, & Sadiku, 2012). Kumar et al. (2010) used glycidyl methacrylate (GMA) as a reactive compatibilizing agent for reactive extrusion of PLA with PBAT and found that the toughness of PLA/PBAT blends was improved with the addition of 3–5% of GMA. Furthermore, both PLA and PBAT are soluble in chloroform, which can be used to prepare PLA/PBAT blend using chloroform as a cosolvent (Li, Shankar, Rhim, & Oh, 2015). Most of the PLA/PBAT blends were prepared with using a melt-mixing with extrusion method, which is the preferred method for industrial production of films. To the best of our knowledge, there was no report on the preparation and characterization of PLA/PBAT blend films using a solvent casting method even though it is more convenient to prepare blend films in a lab scale to test the effect of preparation variables including blending ratio.

The main objective of the present study was to prepare PLA/PBAT blend films using a solvent casting method with different blending ratio of PLA and PBAT and to test the effect of blending on the improvement of property of PLA film by evaluating the film properties such as optical, mechanical, water vapor barrier, and thermal properties. Additonally, the applicability of the films were tested through packaging test of green onion and potato.

2. Materials and methods

2.1. Materials

Poly(lactide) (PLA, Biomer® L9000; weight-average molecular weight = 200 kDa) was obtained from Biomer Inc. (Krailling, Germany). PBAT (EnPol PBG7070; m.p. 125 °C, specific gravity of 1.20–1.25) was obtained from S-EnPol Co. Ltd. (Wonju, Korea). Both PLA and PBAT resins were dried under vacuum at 60 °C for 24 h before use. Chloroform was procured from Daejung Chemicals & Metals Co., Ltd. (Siheung, Korea). Tryptic soy broth (TSB) and agar powder were purchased from Duksan Pure Chemicals Co., Ltd (Ansan, Gyonggi-do, Korea). Fresh potatoes and green onions for packaging test were purchased from a local supermarket. Linear low density polyethylene (LLDPE) film (thickness: 10 μm, 3 M Fresh Wrap, Ilshin Chemical Co., Ltd., Ansan, Korea) was used as a control film for the packaging application test.

2.2. Preparation of films

PLA, PBAT, and their blend films were prepared using a solvent-cast method (Rhim, Mohanty, Singh, & Ng, 2006). For the preparation of neat PLA and PBAT film forming solutions, 4 g of PLA or PBAT resins were dissolved into 100 mL of chloroform with stirring using a magnetic stirrer at room temperature (23 °C) for 6 h. Additionally, PLA/PBAT film forming solutions with different mixing ratio of 3.96/0.04, 3.92/0.08, 3.6/0.2, and 3.6/0.4 g of PLA/PBAT were dissolved into 100 mL of chloroform and followed the same procedure as neat PLA or PBAT film solutions. The film forming solutions were poured onto a leveled Teflon coated glass plate (24 × 30 cm) (Cole–Parmer Instrument Co., Chicago, IL), spread evenly with a bent glass rod, and allowed to dry for about 24 h at room temperature. The resultant films were peeled intact from the casting surface. In this way, six different types of film were prepared and they were designated as PLA, $PLA_{99}/PBAT_1$, $PLA_{98}/PBAT_2$, $PLA_{95}/PBAT_5$, $PLA_{90}/PBAT_{10}$, and PBAT film based on the blending ratio of PLA and PBAT. All film samples were preconditioned in a constant temperature humidity chamber at 25 °C and 50% relative humidity (RH) for at least 48 h before further test. Film thickness was measured using a hand-held micrometer (Dial Thickness gauge 7301, Mitutoyo, Japan) with an accuracy of 0.01 mm.

2.3. Surface color and transparency of films

Surface color of the film was measured using a Chroma meter (Konica Minolta, CR-400, and Tokyo, Japan). A white standard color plate (L = 97.75, a = −0.49, and b = 1.96) was used as a background for color measurements. Hunter color (L, a, and b) values were averaged from five readings from each sample. The total color difference (ΔE) was calculated as follows:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \qquad (1)$$

where ΔL, Δa, and Δb are difference between each color values of standard color plate and film specimen, respectively.

The optical properties of the films were tested by measuring transmission spectrum in the range of 200–700 nm using a UV/visible spectrophotometer (Model 8451A, Hewlette Packard Co., and Santa Alara, CA, USA). The UV screening property and transparency of the films were evaluated by measuring percent transmittance at 280 nm (T_{280}) and 660 nm (T_{660}), respectively.

2.4. FT-IR analysis

Fourier transform infrared (FT-IR) spectra of film samples were collected using a FT-IR spectroscopy (TENSOR 37 Spectrophotometer with OPUS 6.0 software, Billerica, MA, USA) at a resolution of 4 cm^{-1} in the range of 4000–500 cm^{-1}. The film samples were placed directly on the ray exposing surface with diamond tip and 16 scans were recorded for individual sample.

2.5. Mechanical properties

Mechanical properties of the films were analyzed by measuring the tensile strength (TS), elongation at break (E), and elastic modulus (EM) according to the standard ASTM method D 882-88 using an Instron Universal Testing Machine (Model 5565, Instron Engineering Corporation, Canton, MA, USA) equipped with a 0.5 kN load cell. Rectangular strips (2.54 × 15 cm) were cut from individually prepared film using a precision double blade cutter (model LB.02/A, Metrotec, S.A., San Sebastian, Spain). Initial grip separation was set at 50 mm and cross-head speed at 50 mm/min. The TS (MPa) was determined by dividing the maximum load (N) by the initial cross sectional area (m^2) of the film sample, the E (%) was determined by dividing the extension at rupture of the film by the initial length of the film (50 mm) multiplied by 100, and the EM (GPa) was determined from the slope of the initial linear portion of the stress–strain curve obtained from the tensile test using a tangent method.