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Physical properties of nanocomposite polylactic acid films prepared with oleic acid modified titanium dioxide

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ABSTRACT

When incorporated into polymers, TiO_2 nanoparticles improve toughness, barrier properties, impart opaqueness, and have antibacterial and UV light protecting effects. However, due to low compatibility between hydrophilic TiO_2 nanoparticles and hydrophobic polymers, the added TiO_2 nanoparticles tend to agglomerate and form large clusters, reducing their effectiveness. Modification of TiO_2 surfaces with oleic acid to make them nonpolar is expected to improve compatibility between polylactic acid (PLA) and TiO_2. The objective of this study was to compare properties of nanocomopsite PLA films with oleic acid-modified TiO_2 (OT-PLA) and unmodified TiO_2 (T-PLA) with PLA films without TiO_2. OT-PLA, T-PLA and PLA films were prepared using solvent casting. Morphology, mechanical strength, UV–vis absorbance, O_2 permeability, and H_2O vapor barrier properties were determined. Scanning electron microscopy images showed aggregation of TiO_2 in T-PLA, but not in the OT-PLA films. Oxygen permeability and water vapor permeability of 1% OT-PLA were reduced by 29% and 26% compared to PLA. Flexibility of OT-PLA was higher than T-PLA, and Young's modulus of OT-PLA was lower than T-PLA or PLA. OT-PLA had higher transparency than T-PLA but provided better light blocking in UVA and UVB regions than PLA. TiO_2 modification with oleic acid improved dispersion of TiO_2 in the PLA. The OT-PLA may have a potential to be used as transparent, functional and environmentally friendly food packaging films.

1. Introduction

Biobased and biodegradable polymers for food packaging have received recent attention as environmentally-friendly alternatives to petroleum-based polymers because of their potential to reduce environmental impacts (Balakrishnan, Hassan, Imran, & Wahit, 2012; Rhim, Park, & Ha, 2013). Polylactic acid (PLA) is produced from renewable natural resources such as corn and is commercially available (Hartmann, 1998; Jamshidian, Tehrany, Imran, Jacquot, & Desobry, 2010). PLA retains good biocompatibility, rigidity, high transparency, gloss, and has good thermal processability for food packaging applications (Hartmann, 1998; Jamshidian et al., 2010). In addition, the United State Food and Drug Administration (FDA) categorizes PLA as generally regarded as safe (GRAS) for direct contact materials in food-packaging applications (Conn et al., 1995). Currently, food packaging made with PLA is used for products such as drinking cups, disposable food trays, portable containers, overwrap, lamination films, and blister packaging (Auras, Harte, & Selke, 2004; Shah, Hasan, Hameed, & Ahmed, 2008). However, brittleness and low gas and moisture barrier properties of PLA relative to non-degradable petroleum based polymers prevent PLA from being used in a wider range of food packaging applications (Balakrishnan et al., 2012; Jamshidian et al., 2010).

When nanocomposites are created by incorporation of nanomaterials into compatible polymers, they can enhance physical properties of the polymers such as mechanical strength, thermal stability, and barrier properties to oxygen and moisture as a result of reinforcement effects of nanomaterials, which have high surface area to volume ratios (Duncan, 2011; Mihindukulasuriya & Lim, 2014; Silvestre, Duraccio, & Cimmino, 2011). Besides improving physical properties, nanomaterials provide unique functions that can increase foods' shelf life in active packaging systems and can add communication functions by being fabricated into sensors and indicators for consumers, producers, and retailers in intelligent packaging systems (De Azeredo, 2009; Duncan, 2011; Mihindukulasuriya & Lim, 2014). TiO_2 is a well-known, low cost, and safe nanostructured material that has been extensively used for polymeric food packaging applications, enhancing toughness and barrier properties as well as providing brightness, antibacterial effects, and UV light protection (Gumiero et al., 2013; Llorens, Lloret, Picouet, Trbojevich, & Fernandez, 2012; Smijs & Pavel, 2011). However, TiO_2 has a high ratio of surface to volume, which limits its stable dispersion

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in a nonpolar polymer matrix due to agglomeration and entanglement of its particles (Chau et al., 2007; Luo, Li, Wang, Xu, & Wang, 2009). Particularly, low compatibility of TiO_2 nanoparticles with hydrophobic polymers such as PLA is caused by repulsive forces between TiO_2 and the PLA matrix; this has been a critical issue and tends to deteriorate physical properties, reducing transparency, barrier properties and mechanical strength (Buzarovska, 2013; Chau et al., 2007; Luo et al., 2009). Stable and homogenous dispersion of TiO_2 in a PLA matrix is important to improve performance in packaging applications (Luo et al., 2009). To overcome particle agglomeration in a PLA matrix, modification of particle surfaces to make them hydrophobic might lead to more stable and homogenous dispersions within the PLA matrix (Buzarovska, 2013; Fortunati et al., 2012). A solvent is often blended with TiO_2 nanoparticles to increase dispersibility; this helps obtain stable particle dispersions because a surface modifier that is compatible with the dispersing solvent plays a key role in producing stable colloids (Arita et al., 2010). Oleic acid may be bound to the TiO_2 surface by chelating and bridging bidenate; this may increase compatibility between TiO_2 and hydrophobic PLA solutions, and to possibly obtain stable dispersions of TiO_2 in the PLA matrix (Nakayama & Hayashi, 2007).

The objectives of our study were to determine if modifying the surface of TiO_2 using oleic acid lead to better dispersion of nanoparticles in a PLA matrix. In our study, the surface of TiO_2 nanoparticles was modified hydrophobically with oleic acid. Oleic acid is commonly used in polymers as a plasticizer and functional modifier to improve dispersion of hydrophilic nanoparticles in hydrophobic media and increase water barrier properties and flexibility (Khanzadi et al., 2015; Lai & Padua, 1998; Lim, Kim, Ko, & Park, 2015). A second objective of our work was to examine physical and barrier properties of PLA films containing modified TiO_2. Our overall hypothesis is that modification of TiO_2 nanoparticles using oleic acid can lead to better dispersion of nanoparticles in a PLA matrix and improve barrier and physicochemical properties of the polymers.

2. Materials and methods

2.1. Materials

Polylactic acid 7000D (molecular weight 210 kDa, polydispersity index 1.78) was obtained from NatureWorks LLC (Minnetonka, MN., USA). PLA was dried in a vacuum oven at 40 °C for at least 48 h prior to use to remove moisture. Titanium oxychloride ($TiOCl_2$.(HCl)x: 38–42% Ti: 15%) was purchased from Sigma Aldrich (St. Louis, MO., USA). Oleic acid (technical grade 90%) was purchased from Alfa Aesar (Wardhill, MA, USA). Ethanol (anhydrous 200 proof), chloroform (HPLC grade), and methanol (HPLC grade) were purchased from Fisher Scientific (Pittsburgh, PA., USA).

2.1.1. Preparation of TiO_2 nanoparticles and surface modification of TiO_2 with oleic acid

2.1.1.1. Synthesis of TiO_2. TiO_2 nanoparticles were prepared by a modified procedure of Nakayama and Hayashi (2007). A mixture of ethanol and water (3:2 v/v) was transferred into a three-neck, flat bottom flask. White precipitated TiO_2 was obtained by dropwise addition of a mixture of titanium oxychloride and water (1:4.5 v/v) to the ethanol and water solution with stirring for 3 h under nitrogen atmosphere at 60 °C. White TiO_2 paste was collected and washed with water and then methanol. The TiO_2 paste was dispersed in chloroform, dried at room temperature, and then in a vacuum oven at 40 °C overnight. The TiO_2 paste (0.1% w/v) was added to distilled water, methanol, chloroform or toluene to observe dispersion stability.

2.1.1.2. Surface functionalization of TiO_2 by oleic acid (OA-TiO_2). The TiO_2 paste (without drying) and oleic acid at a ratio of 1:6 (w/w) were added into a 100 mL glass bottle and capped tightly. The mixture of TiO_2 paste and oleic acid was sonicated (Model FS20, Fisher Scientific) for 10 min then vigorously stirred for 24 h at room temperature. A light yellow mixture of oleic acid and TiO_2 paste was obtained. OA-TiO_2 paste was collected and washed with methanol to remove unbound

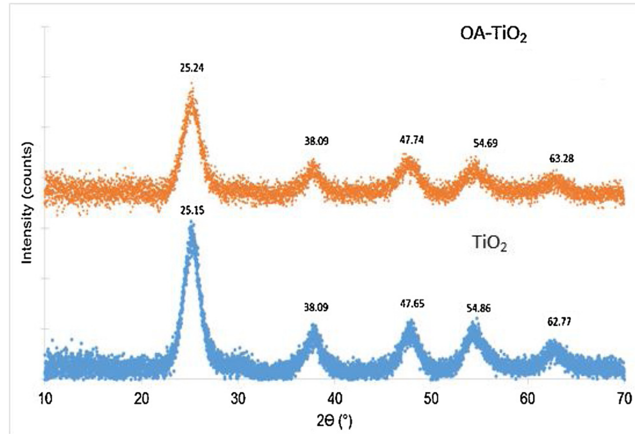

Fig. 1. X-ray diffraction powder diffraction of TiO_2 and OA-TiO_2.

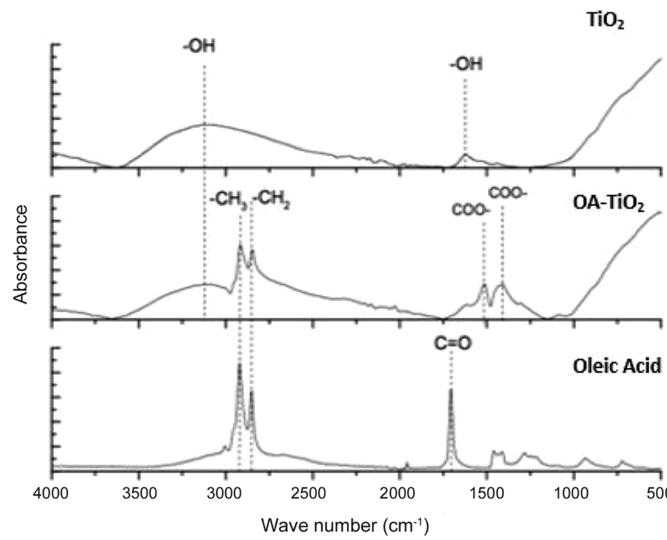

Fig. 2. The Fourier transform-infrared (FTIR) -attenuated total reflectance (ATR) of a) TiO_2, b) OA-TiO_2 and c) oleic acid.

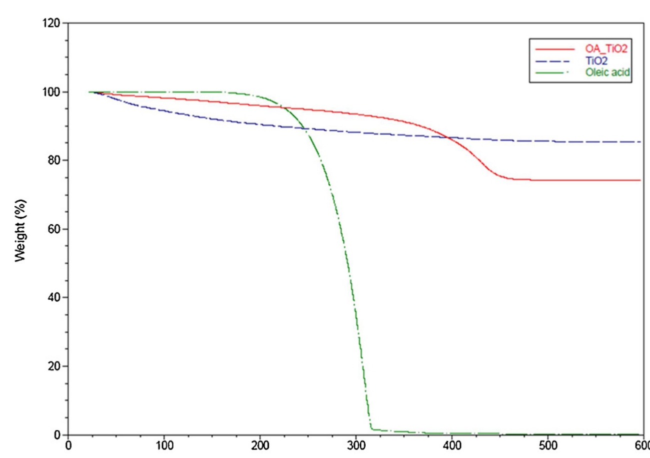

Fig. 3. Weight loss of TiO_2, OA-TiO_2 and oleic acid by elevating temperature at 600 °C.