Industrial Crops and Products 67 (2015) 11–17

Contents lists available at ScienceDirect

Industrial Crops and Products

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

Development of blend films from soy meal protein and crude glycerol-based waterborne polyurethane

Xinjie Tong, Xiaolan Luo, Yebo Li*

Department of Food, Agricultural and Biological Engineering, The Ohio State University, Ohio Agricultural Research and Development Center, 1680 Madison Ave., Wooster, OH 44691-4096, USA

ARTICLE INFO

Article history:
Received 29 August 2014
Received in revised form
29 December 2014
Accepted 30 December 2014
Available online 15 January 2015

Keywords:
Crude glycerol
Waterborne polyurethane
Soy protein
Blend film
Water resistance
Tensile strength

ABSTRACT

In the present work, crude glycerol-based waterborne polyurethane (CGWPU) was used to modify soymeal-derived protein (SMP) with improved tensile strength and water resistance. SMP–CGWPU blend films were successfully prepared by casting the aqueous dispersions of SMP and CGWPU. The effects of CGWPU content on the structure and properties of the resulting films were investigated by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile tests, and water uptake measurements. Good compatibility was observed in the blend films, which resulted from strong intermolecular interactions, such as hydrogen bonding, that existed between SMP and CGWPU. With increasing CGWPU content, SMP–CGWPU blend films had improved water resistance, thermal stability, and tensile strength, but had decreased elongation at break. The performance of SMP–CGWPU blend films was comparable to the SMP films blended with commercial oil-based Minwax urethane (MU).

1. Introduction

In recent years, there has been an increasing interest in the development of bio-based films for the packaging industry because they are renewable, biodegradable, and environmentally friendly (Kumar and Zhang, 2009; Lodha and Netravali, 2005; Lu et al., 2004, 2005; Rhim et al., 2006; Yang et al., 2009; Zhang et al., 2006). Soy protein isolate (SPI), which contains more than 90% protein, is a valuable and readily available feedstock for bio-based films (Paetau et al., 1994; Song et al., 2013; Swain et al., 2004; Tian et al., 2010). SPI films have good barrier properties in terms of lipid, oxygen, and aroma due to various interactions among amino acid monomers in soy protein (Cuq et al., 1998). However, SPI films are brittle and sensitive to moisture, which has limited their use in industrial applications (Monedero et al., 2010; Park et al., 2001; Zhang et al., 2012). Various methods have been used to modify and improve the properties of SPI films, including crosslinking (Avena-Bustillos and Krochta, 1993; Gennadios et al., 1998; Pérez-Gago et al., 1999; Pérez-Gago and Krochta, 2001; Stuchell and Krochta, 1994), plasticization (Sothornvit and Krochta, 2001; Soykeabkaew et al., 2004; Vieira et al., 2011), and blending with other polymers (Santayanon and Wootthikanokkhan, 2003; Willett and Doane, 2002).

Among these methods, blending of SPI with polymers is of great interest because of operational simplicity and a wide range of modification on films properties which can be achieved by synergistic effects between SPI and various blending polymers (Gao and Zhang, 2001). Blending of hydrophobic polymers, such as cellulose and casein with SPI, has been performed to improve the mechanical and barrier properties of SPI films. However, a co-solvent is generally needed to improve the miscibility between hydrophilic SPI and hydrophobic polymers, and the commonly used co-solvent (ionic liquid) is costly and not recyclable (Wu et al., 2009). In addition, hydrophilic polymers such as polysaccharides and pure proteins, i.e., gelatin and wheat gluten, have been used to blend with SPI in aqueous solution (Bai et al., 2012; Cao et al., 2007; Were et al., 1999; Mariniello et al., 2003). Despite good compatibility between SPI and hydrophilic polymers, the water resistance of the resulting blend films was hardly improved. Recently, waterborne polyurethane (WPU) was considered as a promising blending component for the modification of SPI films, not only because WPU can be easily mixed with SPI, but also because it has good mechanical properties and low water absorption (Kim and Kim, 2005; Lu and Larock, 2008; Santos et al., 2009; Tian et al., 2010; Zhang et al., 2012). It has been suggested that blending SPI with petroleum-based WPUs, such as polybutylene adipate-based and

* Corresponding author. Tel.: +1 330 263 3855; fax: +1 330 263 3670.
E-mail address: li.851@osu.edu (Y. Li).

http://dx.doi.org/10.1016/j.indcrop.2014.12.063
0926-6690/

polypropylene glycol-based WPUs, allowed for improvement on mechanical properties and water resistance of SPI films (Tian et al., 2010; Wang and Zhang, 2005; Zhang et al., 2012). In addition, renewable WPUs produced from vegetable oils have also been blended with SPI to obtain improved properties of the blend films (Lu and Larock, 2008, 2009, 2010).

Crude glycerol (CG), a byproduct of biodiesel production, is being generated in large quantities with the rapid expansion of the biodiesel industry. Biodiesel-derived CG contains impurities and the refining processes are costly (Kerr et al., 2007; Pagliaro et al., 2007). As a result, waste CG has become a financial and environmental liability for the biodiesel industry and it is imperative to find new applications for CG (Carmona et al., 2009; Pachauri and He, 2006; Pagliaro and Rossi, 2008). Waterborne polyurethane (WPU) coatings derived from crude glycerol have been produced with good adhesion, hardness, and elongation at break (Luo et al., 2014). However, no report has been found using crude glycerol-based waterborne polyurethane to mix with protein films for composite materials production.

In this work, soy protein was first derived from high-oleic soymeal, which is a protein rich co-product of the high-oleic soy oil extraction process, to produce soymeal-derived protein (SMP) films (Hettiarachchy and Kalapathy, 1997; PlenishTM, 2013 product benefit,). Since high-oleic soymeal is readily available in large amount due to increasing production of high-oleic soy oil in food industry, there is a research need to evaluate the conversion of high-oleic soymeal to high-value polyols and polyurethanes. The resulting SMP films were then modified by the incorporation of crude glycerol-based waterborne polyurethane (CGWPU). Blend films with different mass ratios between soymeal-derived protein (SMP) and crude glycerol-based WPU (CGWPU) were prepared by a solution-casting method. The morphology, water resistance, and mechanical and thermal properties of SMP–CGWPU blend films were investigated and compared with the blend films prepared from SMP and commercial Minwax urethane (MU).

2. Materials and methods

2.1. Materials

High-oleic soybean meal was provided by Cargill Inc., (Sidney, OH). CG was obtained from Bio100 Technologies, LLC (Mansfield, OH) and contained approximately 63.0% glycerol, 6.2% methanol, and 28.7% water. MU with a solid content of 30% was purchased from a local Sherwin-Williams' store (Wooster, OH).

Potassium hydroxide (KOH), oleic acid, glycerol, imidazole, phosphoric acid (85%), fluoroboric acid (50%), ammonium hydroxide (30%), hydrogen peroxide (50%), methyl ethyl ketone (MEK), and iodine monochloride solution (Wijs reagent) were purchased from Fisher Scientific (Pittsburgh, PA). Methanol, toluene, tetrahydrofuran (THF, high performance liquid chromatography (HPLC) grade), pyridine, and acetic acid were purchased from Pharmco-AAPER (Shelbyville, KY). Triethylamine (TEA), isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), hydrobromic acid solution (HBr, 33%), phthalic anhydride, potassium sulfate, phenolphthalein, and crystal violet indicator solution were purchased from Sigma-Aldrich (St. Louis, MO). Di-*n*-butyltin dilaurate (DBTDL) was obtained from Pfaltz & Bauer, Inc., (Waterbury, CT). All chemicals used were of reagent grade or higher purity.

2.2. Preparation of soymeal-derived protein (SMP)

Soymeal was ground (1 mm mesh screen) and oven-dried at 105 °C for 24 h before use. SMP was prepared from air-dried and ground soymeal as previously described by Margatan et al. (2013) with minor modification. The soymeal (100 g) was dispersed in 1 L of distilled water, and pH was adjusted to 10.0 with 2 M NaOH. The slurry was stirred for 1 h at 40 °C, and then centrifuged (ThermoFisher Scientific Fiberlite F12-6 × 500 LEX Rotor, CA) at 10,000 rpm (11,722 × g) for 30 min to remove the insoluble fraction. The resultant supernatant was adjusted to a pH 4.5 with 2 M HCl and stirred for 30 min at 98 °C to deactivate protein, and then placed in a refrigerator at 4 °C for 24 h to precipitate soy protein. After centrifugation and filtration, the precipitated SMP samples were dried using a freeze dryer (item No. 274449, The VIRTIS company, Inc., N.Y.) and kept in a desiccator with P_2O_5 as a desiccant prior to use. The protein content of ground soymeal and SMP were determined to be 48.6% and 88.9% (based on dry matter), respectively, using the total Kjeldahl nitrogen method (ASTM D3590-11B).

2.3. Preparation of crude glycerol-based waterborne polyurethane (CGWPU) dispersion

Crude glycerol-based multi-branched polyols were synthesized following the method previously developed in our laboratory (Luo et al., 2014). The produced polyols had an average molecular weight of 2276 g/mol (gel permeation chromatography analysis) and hydroxyl number of 186 mg KOH/g (ASTM D4272-11D).

Polyurethane was prepared by the reaction of crude glycerol-based polyols, DMPA, and IPDI with an OH/NCO molar ratio of 1:1 and an OH molar ratio of 0.8:1 between the DMPA and polyols (Lu and Larock, 2008). Specifically, crude glycerol-based polyols (6 g, 0.02 mol of hydroxyl group), DMPA (1.07 g, 0.016 mol of hydroxyl group), IPDI (4 g, 0.036 mol of NCO group), MEK (40 mL), and DBTDL (0.5 mL) were charged to a 250-mL three-neck round-bottom flask equipped with a magnetic stirrer, a condenser, a thermometer, and a nitrogen inlet. The mixture was then stirred at 80 °C under nitrogen atmosphere until the NCO peak at 2280 cm^{-1} disappeared in the Fourier-transform infrared (FT-IR) spectrum. When the reaction mixture was cooled to approximately 40 °C, TEA (0.97 g, 0.0096 mol) was added to neutralize the carboxyl groups of polyurethane, and the mixture was stirred for 30 min. Subsequently, the reaction mixture was dispersed in deionized water under high-speed stirring to produce CGWPU dispersion. The MEK was removed by a rotary evaporator at ambient temperature and the resulting CGWPU dispersion had a solids content of 20%.

2.4. Preparation of the SMP–CGWPU blend films

Alkaline SMP solution was prepared following a reported method with minor modification (Brandenburg et al., 1993). A 5% SMP solution was prepared by dispersing SMP powder in deionized water in the presence of 3% glycerol with constant stirring. The pH value of the solution was adjusted to about 10.0 with 0.5 M NaOH and monitored with a digital pH meter (Accumet AP110, Fisher Scientific, Pittsburgh, PA). The solution was heated for 30 min at 90 °C under constant stirring to denature the soy protein. The resultant SMP solution was cooled to room temperature and then stored in a refrigerator at 4 °C.

The schematic representation of blend film preparation is shown in Fig. 1. The CGWPU dispersion with a solid content of 20% was added to SMP solution to fabricate SMP–CGWPU blend films following a reported method (Zhang et al., 2012). The mixture was stirred for 1 h at room temperature, degassed, cast in Teflon plates, and then dried in an oven at 40 °C for 24 h. By changing the SMP–CGWPU dry matter ratio, i.e., 100-0, 75-25, 50-50, 25-75, and 0-100, a series of SMP–CGWPU blend films were obtained and coded as SMP, SW75-25-CG, SW50-50-CG, SW25-75-CG, and CGWPU, respectively. Blend films composed of SMP and commercial MU were also prepared at the same mass ratios (100-0, 75-25, 50-50, 25-75, 0-100) using the above mentioned method, and coded as SMP,