



The effects of thermal-acid treatment and crosslinking on the water resistance of soybean protein



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ABSTRACT

After thermal treatment at 120 °C in the presence of hydrochloric acid (thermal-acid treatment), soybean protein increased its water-insoluble network structure due to the molecular rearrangement and aggregation of unfolded protein molecules, which improved its water resistance. Modification with various crosslinkers, namely glyoxal, polyisocyanate, a glyoxal–polyisocyanate combination, water-borne epoxy latex and modified polyamide, were employed to further enhance the water resistance of the thermal-acid treated soybean protein (TSP). FTIR and DSC analyses confirmed that all of the crosslinkers could chemically react with the TSP, but the crosslinking degree varied with crosslinker species. The positive effect of crosslinker species on the water resistance and thermal stability of the TSP as evaluated by a boiling water-insoluble test and TGA analysis was in the order modified polyamide > glyoxal–polyisocyanate > polyisocyanate > epoxy latex > glyoxal. In addition, wood flour-reinforced soybean protein-based composites were successfully fabricated to investigate the possibility of manufacturing acceptable biocomposites using crosslinked and thermal-acid treated soybean protein. FTIR analysis, SEM observation and tensile property evaluation showed that all crosslinkers except glyoxal could react with wood flour to form various chemical bonds at the protein–wood interface and therefore significantly improve the water resistance and tensile strength of the obtained composites. The extent of improvement depended on the crosslinker species and crosslinking mechanism. Modified polyamide was the most preferable crosslinker for commercial applications because its modified composite had good tensile strength and the best water resistance.

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1. Introduction

Many traditional plastic composites are not biodegradable and are petroleum-derived, leading to environmental concerns when they are discarded in nature after their service life. In addition, with the increasing price and decreasing reserves of non-renewable petrochemical resources, biodegradable materials derived from natural resources, such as starch, cellulose, lignin, tannins and proteins, are being considered as prospective candidates for petroleum-based synthetic polymers due to their advantages including their easy availability, renewability, sustainability, ecological compatibility and biodegradability (Sionkowska, 2011; Reddy et al., 2013).

The soybean is a major annual agricultural crop used as a source of protein and edible oil, and it is currently cultivated widely in the USA, Brazil, Argentina and China. Soybean protein is a biodegradable and renewable biopolymer extracted from soybean meal, which is a byproduct of soybean oil production. Soybean proteins are currently used not only in traditional food applications but also in non-food applications such as wood adhesive, films, gels and emulsions (Song et al., 2011). However, use of soybean protein in novel applications such as plastics and composites is very challenging because of the structural characteristics of soybean protein.

Native soybean protein has a highly ordered, compact and collapsed globular structure, and most functional groups (such as amides, hydroxyls and carboxyls) are buried within globular particles, which leads to insufficient contact area with the solid surface (Van der Leeden et al., 2000), resulting in undesired protein–solid interface or limited reactivity sites for potential adsorption interactions and chemical reactions. In addition, soybean proteins have complicated and diverse primary, secondary, tertiary and quaternary structures, which are mainly built by weak intermolecular

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interactions including hydrogen bonds, electrostatic bonds, Van der Waals forces, disulfide bonds and hydrophobic interactions, which lead to low reactivity, low mechanical properties, high brittleness, poor water resistance, poor processability and short durability (Fahmy et al., 2010). Therefore, soybean protein is difficult to efficiently utilize in commercial biocomposite production.

Many attempts have been made to improve the reactivity and water resistance of soybean protein by altering the native coiled structure with approaches including denaturation (in the presence of alkali, urea, guanidine hydrochloride, sodium dodecyl sulfate, etc.) in mild conditions (Huang and Sun, 2000a,b; Zhang and Hua, 2007; Lin et al., 2012; Dastidar and Netravali, 2013) and hydrolysis under harsh conditions (Zhang et al., 2013). Denaturation changes the quaternary, tertiary and secondary protein structure but rarely alters the primary structure (or amino acid sequence); it is a highly effective and mild method to expose the buried reactive groups to provide more reactive sites for further covalent linkages. However, the traditionally denatured or native soybean protein solution had a low protein concentration due to the very high viscosity resulting from the high molecular weight of soybean protein, which can be up to 360,000 g/mol (Kumar et al., 2002), which in turn led to inefficient formation of composites, long molding time or increased energy required to remove water in the thin protein solution. Dry-state denaturation may be a good practical solution to this problem. Many studies have demonstrated that dry-state thermal treatment alters the native structure of soybean protein through the dissociation of subunits and unfolding of protein structure, resulting in protein aggregation and decreased solubility (Guerrero et al., 2014; Sorgentini et al., 1995; Keerati-u-rai and Corredig, 2009; Nakai, 1983; Renkema et al., 2000). Zuo et al. (2013) effectively increased the reactivity of gelatinized starch via dry-state processing, which may also be a promising solution to modify soybean protein by thermally treating it in the presence of hydrochloric acid. However, the literature review indicated that very little is known about the effects of thermal-acid combined treatment on the structures and properties of soybean protein.

Furthermore, to prolong the service life of soybean protein-based products, their water resistance or strength stability must be improved, particularly for products subjected to harsh environments (such as moist or wet conditions accompanied by the temperature fluctuations). Various methods have been used to improve the water resistance and mechanical properties of soybean protein-based products such as blending with hydrophobic resin, crosslinking modification, nano-scale clay modification and biotechnique modification. Crosslinking has proven to be effective. Formaldehyde-based resins such as phenol-formaldehyde and melamine-formaldehyde resin (Gao et al., 2012; Kuo and Stokke, 1999), glyoxal (Zhang et al., 2013), glutaraldehyde (Wang et al., 2007), methenamine, genipin (González et al., 2011), polyisocyanates (Deng et al., 2006; Zhang et al., 2013), modified polyamides (Gui et al., 2013a,b; Gu and Li, 2011), epoxy resin (Lei et al., 2014) and anhydride (Qi et al., 2013) are the most commonly used crosslinkers. Use of formaldehyde-based resins as crosslinkers decreased the environmentally friendly advantage of soybean protein due to toxic formaldehyde emission (Muttill et al., 2014). Methenamine and anhydride have low crosslinking efficiency with soybean protein. The cost of genipin is unacceptable for industrial production of traditional composites, but genipin is a good candidate for biomedical materials. The glyoxal-polyisocyanate combination was an effective crosslinker for soybean protein, and the composite could withstand 4 h in boiling water (Zhang et al., 2015). Overall, an efficient and economic crosslinker is required to extend the applications of soybean protein and its derived polymer materials.

In this study, modification of soybean protein at 120 °C in the presence of hydrochloric acid was carried out to improve the

reactivity and water resistance of soybean protein and then crosslinking by glyoxal, polyisocyanate, glyoxal-polyisocyanate combination, waterborne epoxy latex and modified polyamide were investigated to further increase the water resistance of soybean protein by improving protein-crosslinker-protein and protein-crosslinker-wood chemical linkages. The effects of thermal-acid treatment and crosslinking on the structure and properties of soybean protein and its composites were investigated. This knowledge should be useful in manufacturing a green biocomposite with low cost, good mechanical properties and acceptable water resistance using soybean protein and wood.

2. Experimental

2.1. Materials

Soybean protein isolate with a protein content of 93.4 wt% was provided by Harbin High Tech Soybean Food Co., Ltd., China. Poplar wood flour with particle size between 40 and 60 mesh was supplied by the bio-based Material Key Lab of Ministry of Education, Northeast Forestry University. The moisture content of the wood flour was approximately 8% before use. The polyisocyanate (Millionate[®] MR-200) with an isocyanate group content of 31.2 wt% or NCO functionality of 2.8 was supplied by Nippon Polyurethane Industry Co., Ltd., Japan. The waterborne epoxy latex MU-618 was purchased from Asibo Co., Ltd., Shanghai, China, with an epoxide number of 212 g/mol. Modified polyamide was supplied by the Xinquan Paper-making Additives Plant, Shangdong, China, with solid content of 12.5%, pH value of 4.9 and viscosity of 68 mPa.s (25 °C). The other chemicals used in this study such as glyoxal and hydrochloric acid were reagent grade and purchased from local chemical companies.

2.2. Thermal-acid treatment of soybean protein

In a high-speed mixer with rotating speed of 800 rpm, 120 g of SPI was blended with 24 g of 0.5 mol/L HCl solution. The mixture was wrapped with aluminum foil and kept at 120 °C in a preheated oven for 30 min. After that, the foil was removed and the treated protein was kept at 50 °C in a blast oven for 24 h to dry protein and remove HCl. Finally, the thermal-acid treated protein was ground into powder and passed through a 100-mesh sieve before use. The control was prepared by mixing 120 g of native soybean protein with 24 g of water.

2.3. Composite compounding

TSP was blended with the crosslinker (30% glyoxal, 30% polyisocyanate, 15% glyoxal + 15% polyisocyanate, 30% epoxy latex or 30% modified polyamide, on the basis of solid soybean protein) in a high-speed mixer (1500 rpm) until evenly mixed. The obtained mixture was further blended with wood flour until evenly mixed (solid mass ratio of 35:65). The final mixture was transferred into a fluoride-plating metal mold with dimensions of 25 × 35 mm followed by compression molding at 120 °C and 7–8 MPA for 320 s to form composite sheets with a thickness of approximately 3.5 mm. The biocomposites prepared with TSP were labeled C-TSP-GO, C-TSP-PMDI, C-TSP-GO-PMDI, C-TSP-WE and C-TSP-MPA, according to the crosslinker used, respectively. They were labeled C-SPI-GO, C-SPI-PMDI, C-SPI-GO-PMDI, C-SPI-WE and C-SPI-MPA if soybean protein isolate was used. Two control composites were fabricated with wood flour and protein without crosslinkers and labeled C-TSP and C-SPI.

The composites were moisture conditioned at 23 °C and 60% RH chamber for three weeks prior to the determination of their properties.

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