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Grafting soyprotein isolates with various methacrylates for thermoplastic applications

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ABSTRACT

Soyprotein isolates were grafted with four different methacrylates and compression molded into films with good dry and wet tensile properties. Soyprotein isolates are obtained as coproducts during soybean processing, have unique properties and have been widely studied for various industrial applications. Although films with properties suitable for various applications have been developed from soyproteins by solution casting, attempts to obtain thermoplastics from soyproteins with high strength and stability under aqueous environments have not been successful. In this research, soyproteins were grafted with methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA) and hexyl methacrylate (HMA) and the grafting conditions were optimized. Influence of grafting conditions on % monomer conversion, % grafting efficiency and % homopolymers were studied. Grafted samples were analyzed for their thermal behavior using thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) and grafting was confirmed using nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR). Grafted samples were compression molded into films and the influence of % homopolymers on tensile properties was investigated. It was found that increasing length of alkyl chains decreased grafting efficiency but improved the thermal behavior and provided films with better properties. At high humidity (90%), HMA grafted soyprotein films containing 25% homopolymers retained about 73% of their dry strength, had elongation of 16.5%, better than thermoplastic films previously developed from soyprotein isolates.

1. Introduction

Biodegradable thermoplastic films have been developed from both natural and synthetic polymers for various applications in an effort to replace the films made from the non-renewable synthetic polymers. Natural polymers including carbohydrates such as starch and cellulose, proteins such as corn zein, wheat gluten, soyproteins and also chicken feathers have been made into thermoplastic films (Reddy et al., 2013; Reddy and Yang, 2013). Some of the synthetic polymers used to develop biodegradable films include poly(lactic acid) (PLA) and polycaprolactone (PCL) (Tian et al., 2012). Although natural polymers, especially proteins, have some unique properties that make them preferable for films used for food packing and other applications, biothermoplastic films made from natural polymers generally have inferior properties compared to films made from synthetic polymers (Song et al., 2011). Films made from natural polymers lack the strength, are considerably brittle and also do not have adequate stability under aqueous conditions. Attempts have been made to improve the properties of natural polymer films by crosslinking, chemical modifications and by blending with synthetic polymers.

Soyproteins are obtained as coproducts of soybean processing, have some unique properties and have been extensively studied for various non-food applications including films, as resins for composites, adhesives, fibers and micro and nanoparticles. Films have been developed from soyproteins using the solution casting and compression molding approaches (Kumar et al., 2002; Song et al., 2011). Since soyproteins do not dissolve in common solvents, solution

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cast films have been developed from soyproteins by hydrolyzing the proteins using alkali solutions. However, solution cast films are much weaker than compression molding due to the hydrolysis of the proteins during dissolution. Approaches such as addition of plasticizers, crosslinking agents and blending with other polymers have been used to obtain solution cast soyprotein films with improved properties.

Thermoplastic films have also been developed from soyproteins using various physical and chemical modifications (Reddy et al., 2013). Treating soyproteins at different pHs, steaming, addition of plasticizers and crosslinking agents are some of the approaches used to prepare thermoplastics from soyproteins (Reddy et al., 2013; Song et al., 2011). Similarly, soyproteins have also been acetylated and made into thermoplastic films with strength of 1.8–2.5 MPa, elongation of 73–113% without the need for any plasticizers (Foulk & Bunn, 2001). Glycerol and ε-polycaprolactone were used as plasticizers and plastic sheets with improved tensile strength, elongation and water resistance were obtained by injection and compression molding (Chen et al., 2008). Although various physical and chemical modifications have been done to develop thermoplastics from soyproteins, the products obtained are considerably weaker and also do not have the stability under aqueous environments necessary for industrial applications.

Grafting of synthetic polymers is a common approach used to make biopolymers thermoplastic. Carbohydrates such as starch and cellulose, proteins such as poultry feathers have been grafted with various synthetic polymers to produce thermoplastics with acceptable properties (Jin et al., 2011). Studies have also been done on grafting soyproteins with synthetic polymers. Styrene was grafted onto soyprotein isolate in an 8 mol/L urea solution using ammonium cerrous nitrate and potassium persulfate as initiators (Xi et al., 2005). Grafted soyprotein exhibited a melting curve at about 120 °C and a grafting efficiency of 61% was obtained. No thermoplastics were developed in this research (Xi et al., 2005). Soyprotein isolates were grafted with gum acacia and the effect of ultrasonic treatment on the grafting reaction and physiochemical properties of the conjugates were studied in an effort to improve their emulsion stability (Mu et al., 2010). Protein–saccharide graft reactions were used to improve the emulsifying, antioxidant and antimicrobial effects of soyproteins for food applications (Guan et al., 2011). A novel biodegradable copolymer poly(1,4-dooxan-2-one) was grafted onto soyprotein isolates by ring opening polymerization (Li et al., 2008). PPDO grafts with length as high as 14 were achieved which determined the thermal properties and crystallization behavior (Li et al., 2008).

Vinyl monomers such as methyl, ethyl, butyl acrylates and methacrylates have been grafted onto biopolymers to improve the thermoplasticity and water resistance. Chicken feathers, soyproteins and corn zein have been grafted with acrylates (Jin et al., 2011). We have recently demonstrated that grafted feathers can be compression molded into films with good mechanical properties and water stability and with the biocompatibility required for medical applications (Reddy and Yang, 2013). Coproducts obtained during ethanol production containing carbohydrates and proteins were also grafted with methacrylates and made into thermoplastic films (Reddy et al., 2012). A study on graft copolymerization of methyl methacrylate (MMA) onto soyproteins reported that MMA was successfully grafted onto soyproteins and grafting decreased the water absorption but no thermoplastics were developed (Lu et al., 2011). Ethyl methacrylate (EMA) was grafted onto soyprotein concentrate using ascorbic acid/potassium persulphate as redox initiator (Kaith et al., 2011). Grafted copolymers showed higher moisture resistance and increased chemical and thermal stability but no thermoplastics were developed.

In this study, we have grafted soyprotein isolates with methyl, ethyl, butyl and hexyl methacrylates. Influence of grafting conditions on grafting efficiency, % grafting, % homopolymers were studied and the grafted soyproteins were compression molded into films. Properties of the grafted soyprotein films and the influence of % homopolymers on the tensile properties and water stability have been reported.

2. Materials and methods

2.1. Materials

Soyprotein isolate (SPI) (Profam 646) with 90% protein content was obtained from Archer Daniels Company, Decatur, IL. Methyl, ethyl, butyl, hexyl methacrylates, sodium bisulfite, potassium persulfate, acetone and other chemicals required for grafting were reagent grade and used as received.

2.2. Grafting

SPI was first dispersed in water in a four necked flask. Later, the required amount of monomers, initiator and reducing agents were added and the flask was deoxygenated by passing nitrogen. Grafting was performed under nitrogen atmosphere. The grafting reaction was continued for 1 h at temperature of 40–80 °C and various amounts of monomers were added to obtain the desired level of grafting. After completion of the reaction by adding 2% paradioxybenzene, the grafted soyproteins were collected and first washed with water to remove any unreacted monomers and inorganic salts. Later, the grafted sample was weighed and used to determine the grafting parameters including % grafting, grafting efficiency, % homopolymers and molar grafting ratio as described in our previous research (Jin et al., 2011).

2.3. Homopolymers

During the grafting reaction, some of the monomers react with themselves and form homopolymers which affect the properties of the grafted soyproteins and the films developed. For instance, the soyproteins grafted with MMA and BMA may have the same grafting ratio but the amount of homopolymers may be different depending on the grafting efficiency. To understand the effect of homopolymers, the grafted soyproteins were soxhlet extracted in acetone for 48 h to completely remove the homopolymers. Later, the homopolymers were collected by evaporating the acetone. During compression molding of the films, a known amount of homopolymers was added to study the effect of homopolymers on tensile properties.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR was used to confirm grafting of the methacrylates onto soyproteins. A thermo electron (Model iS 10) spectrophotometer with a diamond cell operating in the total attenuated reflectance mode was used for the study. Spectrums were collected from 500 to 4000 cm^{-1} and each sample was scanned 32 times at a resolution of 8 cm^{-1}. At least three spectrums were collected for each sample and the average of the three measurements was used to plot the spectrums.

2.5. Thermal analysis

Thermal behavior of the soyprotein samples before and after grafting of the acrylates was analyzed using thermogravimetric analysis (TGA) and also by differential scanning calorimetry (DSC). TGA studies were done on a Sigma T300 analyzer using about 5–8 mg of samples that were heated up to about 600 °C under nitrogen atmosphere. Three samples were analyzed for each grafted