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Physicochemical properties of soy protein adhesives modified by 2-octen-1-ylsuccinic anhydride

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ABSTRACT

Soy protein adhesives (SPA) with high solid content display great potential as alternatives to petroleum-based adhesives. This study investigated the adhesive properties of SPA as modified by 2-octen-1-ylsuccinic anhydride (OSA) at different concentrations. Physicochemical properties including electrophoresis profile and turbidity and thermal and rheological properties also were characterized in detail. OSA was grafted to some soy protein molecules through a reaction between amine, hydroxyl groups of protein, and anhydride groups as confirmed by Fourier transform infrared spectroscopy (FTIR). The conformation of OSA-modified SPA was unfolded as indicated by the absence of high molecular weight protein bands in reducing sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) and by the decrease in thermal stability detected by Differential Scanning Calorimetry (DSC). The turbidity of OSA-modified SPA decreased at pH basic to isoelectrical point (IP) but increased at pH acidic to IP. The wet strength of SPA applied on two ply plywood increased to 3.2 MPa at 3.5% OSA concentration compared to 1.8 MPa for the control; then the strength leveled off as OSA concentration increased further. SPA modified with 3.5% OSA worked better on maple wood veneer than yellow poplar wood veneer when three ply plywood was made. Wood cohesive failure (WCF) was observed for both soaked maple and yellow poplar plywood specimens: 60% WCF for the former and 5% WCF for the latter. The oily nature and hydrophobic long alkyl chains are the main reasons to improve the adhesion performance of SPA.

1. Introduction

As bio-based resources, soybean proteins have shown great potential as adhesives in the wood composite, packaging, and labeling industries (Zhong et al., 2002; Qi and Sun, 2010). The dominant storage proteins in soybean are globulins (50–90%), which comprise glycinin (11S) and β-conglycinin globulins (7S). The two components are composed of a combination of 20 different amino acids (Peng et al., 1984). Each amino acid is known to have functional groups attached to the side polypeptide chains of the protein molecule. These functional groups, including OH, COOH, NH_3, are available for various chemical modifications, such as succinylation, alkylation, acetylation, and esterfication that could alter the microstructure of soybean protein and affect its functionalities (chemical and mechanical properties) to a large extent (Kim and Kinsella, 1986; Howell, 1996; Zhu, 2006). For the last few decades, substantial research has been conducted to improve the water resistance of soy protein through chemical modification (Huang and Sun, 2000; Rogers et al., 2004; Wang et al., 2005, 2007; Huang, 2007; Zhong et al., 2007; Qi and Sun, 2011).

Succinic anhydride is the most frequently used chemical agent for protein derivatization. It is used primarily to improve functional properties of protein in various food products by increasing protein solubility and emulsification properties and a lower isoelectric point (Franzen and Kinsella, 1976; Achouri and Zhang, 2001; Lawal and Adebowale, 2004). The principle reaction mainly involves N-acylation: succinic anhydride reacts with the ε-amino group of lysine in protein, converting it to a negatively charged residue (Beuchat, 1977). Little information is available about the effects of anhydride on adhesion performance of soy protein adhesives. Zhu (2006) utilized solid succinic anhydride to modify soy protein isolate through succinylation reaction and reported a decrease in adhesion strength due to hydrophilic carboxyl groups. Liu and Li (2007) also found maleic anhydride to have negative effects on adhesion performance of soy protein. In this research, liquid 2-octen-1-ylsuccinic anhydride (OSA), which had an oily nature and possessed long hydrophobic alkyl chains, was used to modify soy protein adhesives. We assumed that the oily nature and long alkyl chain introduced to soy protein accompanied by the succinylation reaction would improve protein adhesion strength. The proposed

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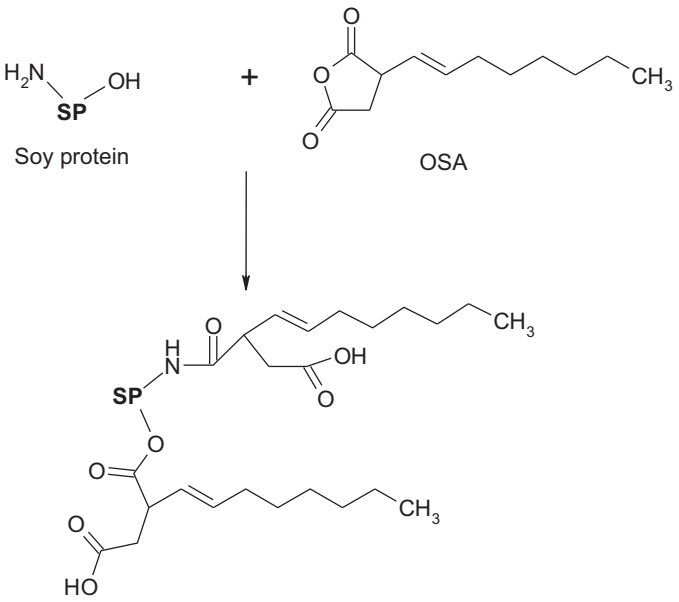

Fig. 1. Schematic illustration of reaction mechanism involved in SPA and OSA, where the functional groups of amine-anhydride and hydroxyl-anhydride are illustrated. (Schematic illustration of reaction mechanism involved in soy protein and OSA, where the functional groups of amine-anhydride and hydroxyl-anhydride are illustrated.)

scheme of reactions between soy protein and OSA is described in Fig. 1.

Our preliminary studies successfully exploited a new viscous cohesive soy protein adhesive modified by sodium bisulfide (SPA), with high solid content of 27%, good flowability, long shelf life, and good water resistance (Qi et al., 2012). The objective of this research was to study the adhesive properties of SPA as modified by OSA at various concentrations, and to characterize physicochemical properties of OSA-modified SPA, such as turbidity, thermal, rheological, and morphological properties.

2. Materials and methods

2.1. Materials

Defatted soy flour (Cargill, Cedar Rapids, IA) was used as the starting material. The soy flour contained about 50% protein and 10% moisture with a dispersion index of 90. Sodium bisulfite ($NaHSO_3$) was obtained from Fisher Scientific (Fair Lawn, NJ). OSA was purchased from Sigma Aldrich (St. Louis, MO). Cherry wood veneers with dimensions of 50 × 127 × 5 mm (width × length × thickness) were provided by Veneer One (Oceanside, NY). Yellow poplar veneer and maple wood veneer with dimensions of 300 × 300 × 3.5 mm (width × length × thickness) were provided by Ashland Company (Covington, KY).

2.2. Adhesive preparation and modification

SPA was prepared based on previous research (Qi et al., 2012). The aqueous protein extract was prepared by mixing defatted soy flour in water at 6.25% solid content at pH 9.5. $NaHSO_3$ was added to the slurry at 6 g/L on the basis of water volume, and the slurry was stirred for 2 h at room temperature. Then the carbohydrate was removed from soy protein by centrifuging at 12,000 × *g*. The pH of the supernatant was adjusted to 5.6 with 2 N HCl, centrifuged at 12,000 × *g*, and the precipitation with 27% solid content was used as the control SPA. The product yield was approximately 45% (wet protein/soy flour), and soy protein was predominantly glycinin. OSA was added to SPA at concentrations of 2%, 3.5%, 5%, and 6.5% (dry weight basis), then stirred for 2 h before use as an adhesive.

2.3. Infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopic data were collected in the region of 800–4000 cm^{-1} using a PerkinElmer Spectrum 100 FTIR spectrometer (Waltham, MA). OSA-modified SPA samples were freeze-dried and ground for FTIR analysis. Then the samples were made into a disk under the constant force of 30 units. Each disk was scanned 16 times at a resolution of 2 cm^{-1} and transmission spectra were recorded.

2.4. Sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE)

Reducing SDS-PAGE was performed on a 4% stacking gel and 12% separating gel with a discontinuous buffer system according to the method described by Laemmli (1970). OSA-modified SPA samples were mixed with a sample buffer containing 5% 2-mercaptoethonal, 2% SDS, 25% glycerol, and 0.01% bromphenol blue. A total of 8 μg of protein was applied to sample slots. Molecular weight standards were run with the samples. Electrophoresis was performed at 40 mA and 150 V for 120 min. The gel was stained in 0.25% Coomassie brilliant blue R-250 and destained in a solution containing 10% acetic acid and 40% methanol.

2.5. Rheology properties

Apparent viscosity measurements of OSA-modified SPA samples were performed using a Bohlin CVOR 150 rheometer (Malvern Instruments, Southborough, MA) with a parallel plate (PP20, 20 mm plate diameter and 500 um gap). The shear rate dependence of apparent viscosity measurements were tested in the shear rate range of 0.1 to 50 s^{-1}. The testing temperature was 23 °C. A thin layer of silicone oil was spread over the circumference of the sample to prevent sample dehydration during the test.

2.6. Differential Scanning Calorimetry (DSC)

Thermal denaturation properties of OSA-modified SPA samples were evaluated by a differential scanning calorimeter (DSC) (Q200, TA instrument, Schaumburg, IL) calibrated with indium and zinc. Modified soy protein samples (20 mg) were hermetically sealed in Tzero aluminum hermetic pans. Each sample was held at 20 °C for 1 min then scanned from 20 °C to 130 °C at a heating rate of 10 °C/min. Peak temperatures and denaturation enthalpies were calculated from thermograms by Universal Analysis 2000 software.

2.7. Turbidity

The turbidity of OSA-modified SPA samples was determined by spectrometer (UV-1650PC, Shimadzu Scientific Instruments, Columbia, MD). Samples were diluted to 0.1% with deionized water and the solution was adjusted to various pH values. The absorbance of protein solutions was measured at 600 nm after 30 min stirring. All measurements were done in duplicate and the average was reported.

2.8. Scanning electron microscopy (SEM)

A Hitachi S-3500 N (Hitachi Science System, Ibaraki, Japan) SEM was used to observe the microstructure of OSA-modified SPA samples. The freeze-dried samples were ground into fine powder, then affixed to an aluminum stub with two-sided adhesive tape and coated with an alloy of 60% gold and 40% palladium with a sputter