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Properties of a soybean meal-based plywood adhesive modified by a commercial epoxy resin

Jing Luo [a,1], Xiaona Li [a], Haoxiang Zhang [b], Qiang Gao [a,*], Jianzhang Li [a,*]

[a] MOE Key Laboratory of Wooden Material Science and Application, MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy, Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing 100083, China
[b] Engineering Management, Faculty of Engineering, University of Ottawa, Ottawa, Canada, K1N6N5

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ABSTRACT

In this study, soybean meal flour, polyacrylamide (PAM), sodium dodecyl sulfate (SDS), and a commercial epoxy resin (EP) was used to develop different adhesive formulations. The solid content and viscosity of the adhesives were measured. Three-ply plywood was fabricated to measure the water resistance of the different adhesives. The crystallinity and infrared spectra of the cured adhesives were investigated. The results indicated that PAM and SDS acted as denature and retention agents, respectively, to improve the water resistance of the resulting adhesive by 38.7%. EP reacted with active groups on protein molecules to form a cross-linking network to decrease the crystallinity of the cured adhesive and improve its water resistance. Incorporating 5 wt% EP improved the water resistance of the adhesive by 236.7% and the wet shear strength of the resulting plywood to 1.12 MPa, which met interior use requirement. Adding EP also increased the adhesive solid content to 32.85 wt% and decreased the adhesive viscosity to 20,415 mPa s, which would be beneficial to soybean meal-based adhesive industrial applications.

1. Introduction

Formaldehyde-based resins, such as urea-, phenol-, and melamine-formaldehyde resins, play predominant roles in the plywood manufacturing industry [1]. However, these resins derive from non-renewable fossil resources of which reserves are limited, and their resulting products have formaldehyde emission issues [2]. Therefore, there is an urgent need to develop formaldehyde-free adhesives from renewable bio-resources.

Soy protein-based adhesives have become of major interest since the soybean is an abundant and low-cost raw material. However, this type of adhesive has exhibited a major weakness i.e. poor water resistance for bonding plywood [3]. Therefore, much work has been carried out to improve the water resistance of soy protein-based adhesives. Major chemical modification approaches designed to enhance water resistance can be classified into three categories. The first category is protein denaturing agent modification. Researchers have used alkali [4], urea [5], and sodium dodecyl sulfate (SDS) [6] to denature protein and improve the water resistance of soy protein-based adhesives. These denaturing agents break the structure of soy protein molecules and expose the inside non-polar groups of soy protein. These exposed non-polar groups prevent moisture intrusion into the cured adhesive thus improving its water resistance. However, this improvement is limited since soy protein also possesses many non-polar groups, such as $-NH_2$, –COOH, and –OH. In addition, the resulting plywood does not meet interior use requirements. The second category is soy protein molecular modification, such as graft modification, acetylated modification, protein enzyme modification, and biomimetic modification. Soy protein molecular modification mainly focuses on grafting high activity groups onto soy protein molecules. These groups react with the non-polar groups in the soy protein molecule and form a cross-linked network in the soy protein-based adhesive after curing [7]. This process effectively improves the water resistance of the adhesive, but the process itself is complex and costly, making it impractical for plywood fabrication. The third category is mixing with reactive cross-linkers and resins. Researchers have used glycidyl methacrylate [8], maleic anhydride [9], polyethylene glycol diacrylate [10], and polyacrylic acid solution [11] as cross-linkers to improve the water resistance of soy protein-based adhesives. These cross-linkers react with the $-NH_2$, –COOH and other exposed groups to increase the cross-linking density of the adhesive during the hot press process. However, the water resistance of panels bonded with the modified soy protein-based adhesives do not usually meet requirements for interior use. Other researchers have mixed

* Corresponding authors.
E-mail addresses: luojing.rowe@gmail.com (J. Luo), gao200482@163.com (Q. Gao), lijianzhang126@126.com (J. Li).
[1] Contact information: MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Beijing 100083, China.

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soy protein products with synthetic resins such as phenol-formaldehyde [12,13], melamine-urea-formaldehyde [5], and polyamidoamine-epichlorohydrin (PAE) resins [14], to improve water resistance. Such resins have been shown to react with soy protein molecules to form solid, interpenetrating networks which minimize moisture intrusion [15]. This process improves the water resistance of the adhesive so that the resulting plywood meets the requirements for interior use. However, soybean meal-based adhesives enhanced with formaldehyde-based resins still contain free formaldehyde. The PAE reinforced soybean protein-based adhesives are formaldehyde free, but the low solid content of the PAE solution (12.5%) increases transportation cost, which limits its application.

Epoxy resins are widely used as matrices for advanced composites because of their many useful properties such as their outstanding mechanical performance, good chemical resistance, and superior dimensional stability [16]. Commercial epoxy resins could be used to modify soy protein-based adhesives due to their high epoxide equivalent and solid content. Therefore, using an epoxy resin could be a practical way to enhance a soy protein-based adhesive. To our knowledge, this approach to soybean modification has not been extensively studied.

Most researchers have used soy protein isolates (SPI) as a raw material in the development of soy protein-based adhesives. These adhesives are relatively expensive and have a low solid content. As a product of soy protein, soybean meal is abundant, low cost, and has suitable protein content [11]. The protein content of industrial grade soybean meal ranges from about 45–55% depending on the source. Therefore, it can be a feasible raw material for the preparation of wood adhesives because of these advantages.

In this study, a commercial epoxy resin (M85) from the Tianjin Synthetic Materials Institute, polyacrylamide (PAM), and sodium dodecyl sulfate (SDS) were used to develop different soybean meal-based adhesive formulations. Effects of components on the developed adhesive properties were investigated. Structures and properties of resulting adhesives were characterized by torque rheometer, Fourier transform infrared spectroscopy (FTIR), and X-Ray diffraction (XRD). Three-ply plywood specimens were fabricated with the resulting adhesives and their wet shear strength tested according to the Chinese National Standards (GB/T 17657-1999).

2. Materials and methods

2.1. Materials

Soybean meal (SM) was obtained from Xiangchi Grain and Oil Company in Shangdong Province, China. Prior to use the soybean meal was milled into flour ($\geq$ 200 mesh) (43–48% soy protein, 30–34% polysaccharide, 8–10% moisture, 3–5% fiber, 5–7% ash, and 0.2–0.8% fat). Polyacrylamide (PAM) and sodium dodecyl sulfate (SDS) were obtained from Tianjin Chemical Reagent Co, China. Poplar veneer ($40 \times 40 \times 1.5$ cm, 8% moisture content) was provided from Wen'an, Hebei Province, China. A commercial epoxy resin (M85, without curing agent) was obtained from the Tianjin Synthetic Materials Institute, having a weight per epoxide (WPE) of 85–89, an epoxy value of 0.86, with three active groups and viscosity ranging from 2300 to 3200 mPa s.

2.2. Adhesive preparation

For the SM adhesive, soybean meal flour (28 g) was added to tap water (72 g) and mixed for 20 min at room temperature. For the SM/PAM adhesive, soybean meal flour (28 g) was added into the polyacrylamide (PAM) solution (72 g, 0.01%) and mixed for 20 min at room temperature. For the SM/PAM/SDS adhesive, sodium dodecyl sulfate (SDS) (1 g) was added into the SM/PAM adhesive and further mixed for 20 min at room temperature. For the SM/PAM/SDS/EP adhesive, various amounts of M85 epoxy were added into the SM/PAM/SDS adhesive and further mixed for 20 min at ambient temperature. The addition amounts of M85 were 5 g, 10 g, 15 g and 20 g.

2.3. Solid content measurement

The solid content of the adhesive was determined using an oven-drying method. Approximately 3 g (weight α) of the adhesive was placed into an oven with the temperature set to 105 °C for drying until a constant weight (weight β) was obtained. The value of the solid content was calculated using Eq. (1). The average value of the solid content was calculated from three parallel samples.

$$\text{Solid Content } (\%) = \frac{\beta\,(g)}{\alpha\,(g)} \times 100\% \quad (1)$$

2.4. Preparation of plywood samples

Three-ply plywood samples were made under the following conditions: 180 g/m^2 adhesive coverage for each surface, 1 min/mm hot pressing time at 120 °C pressing temperature, and 1.0 MPa pressure [17]. After hot pressing, the plywood samples were stored under ambient conditions for at least 8 h before testing.

2.5. Water resistance measurement

The water resistance of the interior use plywood (Type II plywood) was determined using a wet shear strength test in accordance with China National Standards (GB/T 17657-1999). Twelve plywood specimens (2.5 cm $\times$ 10 cm) cut from two plywood panels were submerged in water at 63 ± 2 °C for 3 h, and then dried at the room temperature for 10 min before tension testing. The bonding strength was calculated from Eq. (2).

$$\text{Bonding strength (MPa)} = \frac{\text{Tension Force (N)}}{\text{Gluing area (m}^2\text{)}} \quad (2)$$

2.6. Dynamic viscoelastic measurement

The apparent viscosity of the different adhesives was determined using a rheometer with a parallel plate fixture (20 mm diameter). The distance was set to 1 mm for all of the measurements. The experiments were conducted under a steady shear flow at 25 °C. The shear rates ranged from 0.1 to 100 s^{-1} in 10 s^{-1} increments. All of the measurements were conducted in triplicate, and the initial average value was reported.

2.7. Fourier transform infrared (FTIR) spectroscopy

The adhesive was cured in an oven at 120 ± 2 °C until a constant weight was obtained and ground into a powder. FTIR spectra of different cured adhesives were recorded on a Nicolet 7600 spectrometer (Nicolet Instrument Corporation, Madison, WI) from 500 to 4000 cm^{-1} with a 4 cm^{-1} resolution using 32 scans.

2.8. X-ray diffraction (XRD)

The adhesive was cured in an oven at 120 ± 2 °C until a constant weight was obtained and ground into a powder. X-ray diffraction (XRD) patterns were recorded on an XRD diffractometer (XRD-6000, Shimadzu, Kyoto, Japan) using a cobalt source and a 0.2 theta scan ranging from 5° to 80° at 45 kV and 30 mA, the