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Camelina protein adhesives enhanced by polyelectrolyte interaction for plywood applications

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ABSTRACT

Camelina protein is a major by-product created after oil extraction from camelina seeds; it has drawn research attention as an economical material for bio-industrial implications. The present study investigates the influence of polyelectrolyte interaction on camelina protein structure and effects on wood bonding performance when used as a bio-adhesive. Infrared spectroscopy (IR) and transmission electron microscopy (TEM) images revealed that after interacting with polymeric amine epichlorohydrin (PAE), a cationic polyelectrolyte, camelina protein is partly unfolded with more flexible chain structures. PAE works as a bridge among different protein molecules primarily through electrostatic and hydrophobic interactions. Separation by size exclusion chromatography showed that soluble PAE modified proteins are smaller in molecular size. Polymeric amine epichlorohydrin modified proteins had reduced solubility, possibly indicating increased hydrophobicity. The PAE treatment of camelina protein greatly improved both dry and wet adhesion strength when used as an adhesive. Dry bond strength increased from 2.39 ± 0.52 MPa to 5.39 ± 0.50 MPa with 100% wood failure and wet bond strength was dramatically increased from 0.37 ± 0.22 to 2.35 ± 0.17 MPa on two layer cherry wood tests. Two aliphatic structures with hydrophobic chains were introduced into the PAE modified protein system to further improve water resistance and get wet bond strength increase from 0 to 1.30 ± 0.23 MPa on three layer yellow pine wood tests. This study demonstrates the possibility of camelina as a green resource for the adhesive industry.

1. Introduction

Camelina is a native flowering plant found in the Mediterranean region of Europe and Asia. Camelina is known as an oilseed crop, which is planted in many areas including Austria, China, Finland, Germany, Ukraine, and the United States. Camelina seed contains about 39% oil of which 90% is made up of polyunsaturated fatty acids (Putnam et al., 1993). Current research has focused on the utilization of camelina oil as bioenergy, for example, as jet fuel and biodiesel, as well as use as a biolubricant and in animal feed. Camelina based fuel has an 80% reduction in net carbon emissions and the fuel has been used in commercial airlines and military planes in North America (Johnson, 2011). The successful industrial utilization of camelina oil may stimulate increased planting of more camelina and at the same time increase the need to exploit byproducts from the oil extraction process.

Defatted camelina meal contains roughly 40% protein, 12% fiber and small amount of gum and vitamins (Sampath, 2009). According to a recent study, there are three main protein fractions including albumins, globulins, and glutelins in camelina protein with varied solubility and structure (Li and Qi, 2014). Camelina protein is currently mainly used as animal feed additive. Based on the similarity of amino acid composition between soy protein and camelina proteins, camelina proteins would be useful new resources to replace soy protein in biomaterials. Modified camelina meals have improved physicochemical properties when used as thermal plastics, composite sheets, and wood adhesives (Kim, 2012; Reddy et al., 2012). However, the mechanical strength of native camelina protein based adhesive is too weak for industrial application. To improve the use of camelina proteins as adhesives, modifications to the native protein structure and properties need to be made. Disrupting native compact, globular protein structures and producing, more open, flexible and interwoven polypeptide chains can improve protein attachment to solid surfaces and distribute the concentration of stresses generated at the interface into the bulk solid (Van Der Leeden et al., 2000). Polyelectrolyte chemicals bear electrolyte groups containing either cations or anions with different chain lengths and other functional groups in the main chain. Protein-

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polyelectrolyte interactions arise from interactions between a three-dimensional fixed and heterogeneously charged protein with a flexible charged chain strand of the polyelectrolyte. Strong bonding is formed through electrostatic interactions among charged groups and hydrophobic interactions among hydrophobic segments of the polyelectrolyte and hydrophobic patches of proteins (Chodankar et al., 2008; Fan et al., 2014). Therefore, the three-dimensional network of protein may be strengthened. Based on previous work, aliphatic chains can be introduced into the protein-polyelectrolyte system to further increase the water resistance of protein based adhesives. (Liu et al., 2015, 2017). Thus, a chemical crosslinker, Tetrakis(hydroxymethyl)phosphonium chloride (T), was also introduced to modify camelina protein and further improve adhesive performance. T is an economical, amine-reactive, aqueous cross-linker for protein based molecules. The T-amine reaction mechanism was studied using primary and secondary amino acids (Chung et al., 2012). The high reactivity and water solubility of T is essential to work with camelina protein.

The goals of the present study were to investigate ways to improve the use of camelina protein as a bio-adhesive through the interactions between cationic amine-epichlorohydrin and camelina protein. Specific objectives of this study were to 1) reveal the mechanism of how polyelectrolyte, chemical cross-linker, and aliphatic chains could influence the structure of camelina protein; 2) characterize the plywood bonding strength, rheology, and other physiochemical properties of camelina protein based adhesives.

2. Material and methods

2.1. Materials

Camelina meal was purchased from Field Brothers Inc (Pendroy, MT, US) and contained 15% lipids (db), 32.4% crude protein (db), and 11.0% moisture (db). Polymeric amine epichlorohydrin (PAE) was provided by Wuhu Hangchen Trading Co. Ltd (WuHu, China). PAE is in aqueous solution at a 12.7% solid content and pH 3.9. Undecylenic acid (99%, UA) was purchased from Sigma–Aldrich (St. Louis, MO). Tetrakis (hydroxymethyl)phosphonium chloride (T, 80% water solution), hydrochloric acid (HCl), sodium hydroxide (NaOH), and hexane were purchased from Fisher scientific (Waltham, MA). The water borne polyurethane was made from BiOH® polyols according to our previous studied methods (11). Cherry wood veneers with dimensions of 50 mm × 127 mm × 5 mm (width × length × thickness) were provided by Veneer One (Oceanside, NY). Yellow pine veneers with dimension of 300 × 300 × 3.5 mm were purchased from Ashland Company (Covington, KY).

2.2. Preparation of Camelina protein

Camelina protein was extracted according to previous method with slight modifications (Li and Qi, 2014). Camelina meal was defatted using hexane at a ratio of 1:10 (w/v) for two hours with three repeated cycles. The defatted camelina meal (DCM) was then spread into thin layers (under 2 mm) to allow hexane to evaporate in a fume hood for 48 h. The DCM was suspended into water at a ratio of 1:30 (w/v) and stirred for two hours, then the DCM slurry was centrifuged to remove the water soluble gum and other impurities. The insoluble fraction was then dispersed into water at ratio of 1:30 (w/v) and the pH was adjusted to 12 using 3 Mol/L NaOH with continuous stirring for two hours to dissolve protein and then centrifuge. The supernatant was adjusted to pH 4.5 using 3 Mol/L HCl to precipitate protein. To remove the salts, protein was washed with distilled water twice and then redissloved at pH7 for freeze drying. The final protein isolate had about 83% protein as measured by Elemental Analyzer (Perkin Elmer 2400 SeriesII CHNS/O, Waltham, MA) using a 6.5 nitrogen to protein conversion factor.

2.3. Preparation of modified camelina protein based adhesives

Camelina protein was dispersed into water at a 10% solid content at different pH values and allowed to stabilize at the pH for 30 min. Varied amounts of PAE (3.8%, 6.4%, 12.7%, 19.0%, weight ratio to camelina protein) solution were then add to the protein slurry. The pH of the slurry was maintained using sodium hydroxide. Camelina protein slurry was stirred under the same conditions without PAE to use as control.

The adhesive formulation was further improved by introducing a cross-linker and hydrophobic aliphatic chains. The protein was first dispersed in water and then different amount of T, UA, or WPU was added to the slurry. The pH of the slurry was maintained at 8 for UA and WPU, 4.5 and 8 for T, using NaOH and HCl and the mixture was stirred for two hours. Next, 10% of PAE (volume ratio to the mixture) was added to the CT/CU/CW mixture and the pH was maintained at 4.5 or 8. The CTP/CUP/CWP adhesives were further stirred for another four hours. All the preparation procedures were done at room temperature (23 °C).

2.4. Wood bonding performance tests

2.4.1. Two-layer wood specimen

Cherry or yellow pine wood pieces were preconditioned at 23 °C and 50% RH in a chamber (Electro Tech Systems, Inc., Glenside, PA) for at least one week prior to use. According to previous studies, the camelina protein adhesives were brushed on wood at 2.36 mg/cm^2. The wood pieces were rested for 15 min before assembling together. To avoid the influence of hot press condition on adhesion strength, a relative higher temperature of 170 °C and a longer time of 10 min were used at a pressure of 1.4 MPa. The wood assemblies were cooled at room temperature and conditioned at the chamber at 23 °C and 50% RH for one day before cutting.

Each wood assembly was cut into five small pieces at a dimension of 50 mm × 20 mm (length × width). Two of the small wood pieces were further conditioned and used for dry strength testing. Three of the small wood specimen were soaked in water at room temperature for 48 h. Wet strength was tested immediately after soaking. Adhesion strength was expressed as the stress at maximum load. ASTM D906-98 method was followed with modification for wood testing (ASTM, 2004). Wood failure was evaluated in accordance to the standard for estimating the percentage of wood failure in adhesive-bonded joints (ASTM, 2002a). Wood specimens were tested with an Instron tester (Model 4465, Canton, MA) based on ASTM Standard Method D2339-98 at a crosshead speed of 1.6 mm/min (ASTM, 2002b). Water resistance of the two-layer wood specimen was measured based on ASTM Standard Methods D1183-96 and D1151-00 (ASTM, 2002c). Dry strength data were the average of four replicates and wet strength data were the average of six replicates.

2.4.2. Three-layer wood specimen

The 300 × 300 × 3.5 mm dimension yellow pine veneers were preconditioned in a 27 °C, 30% RH chamber at least one week before wood adhesion test. The three veneers were layered up in a way that grain lines of the middle panel were perpendicular to the grain lines of the top and bottom panels. Approximately 20–22 g/ft^2 (wet basis) adhesive was brushed on the two faces of the middle veneer panel only. The assembled wood specimen was standing for 15 min before hot press. The hot press conditions were 150 °C, 10 min at 1.03 MPa.

The bonded three layer wood specimen were conditioned in a chamber at 23 °C and 50% RH for two days and then cut into ten small pieces (82.6 × 25.6 mm) and four large wood pieces (50 × 127 mm) based on the ASTM standard method D906-98 (ASTM, 2004). Four of the small wood pieces were used to test dry adhesion strength. Water resistance was evaluated in terms of wet shear adhesion strength and three cycle soaking test (ANSI/HPVA, 2004). Six of the small wood pieces were soaked in water for 24 h at 23 °C and then wet adhesion was