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Synthesis of bio-adhesives from soybean flour and furfural: Relationship between furfural level and sodium hydroxide concentration

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ABSTRACT

Soybean–furfural (SoyFu) adhesives were synthesized through cross-linking soybean flour with furfural under alkaline conditions and the performance of the resulting bio-adhesives was evaluated by manufacturing plywood panels. A total of 30 different bio-adhesive formulations were studied (5 levels of furfural content and 6 levels of sodium hydroxide or pH). Thirty 2-ply plywood panels prepared with these adhesives were pressed at 140 °C for 4 min. Shear tests were performed on the panels according to ASTM D2339-1998 (2004). The statistical analysis indicated that an interaction existed between furfural (crosslinker) and sodium hydroxide (pH) levels. The best quality panels were produced using adhesives containing high levels of sodium hydroxide (12, 20 and 28 g/100 g soy flour) and high levels of furfural (50 and 100 g/100 g soy flour). ^{13}C nuclear magnetic resonance analyses were also performed on a selected formulation. The spectra analysis, however, did not prove that furfural was involved in covalent or ionic bonds with soybean flour.

1. Introduction

A majority of the polymers that one comes across every day are derived from petrochemical sources, like polyesters, that are used to make clothes or polyvinyl acetate (PVA), the white glue that is used to make furniture. All of these polymers are from non-renewable sources which take about 100–120 million years to form. Estimates indicate that oil and natural gas reserves will last for another 53 and 55 years respectively, while reserves for coal should last for another 113 years. These estimates were based on 2013 production levels for the rest of the time horizon [1] (shale gas is, however, not included in these statistics). Even if these reserves are underestimated, they will be more difficult and less ecofriendly to use, thereby increasing operating costs and making them less attractive.

Soybean and furfural are both materials from renewable sources and can be used as replacements for petrochemical sourced polymers. Soybean has very high protein content and these proteins can be used to create natural adhesives, as was the case before World War II [2]. The many functionalities of soy proteins, the entanglement of these proteins and the peptide bonds between amino acids produce strong adhesives [3]. Furfural is an aldehyde that can be obtained from any plant containing pentosans, a type of sugar [4]. It is the base of a whole family of chemicals called furans [5]. Furfural can, like formaldehyde, react with phenol or urea but is less volatile, and thus less harmful to lungs and skin. It is known to create polymers with increased heat tolerance as compared to formaldehyde [6]. It can also react with proteins and crosslink them to improve the structural strength of the adhesive [7,8].

In the present case, soybean flour and furfural were used to prepare replacement adhesives for bonding two-ply plywood panels instead of using phenoplast resins like phenol–formaldehyde or phenol–urea–formaldehyde. Soybean flour is an inexpensive product compared to soy protein isolate, but is considered to be less moisture resistant. The carbohydrates present in the soybean flour do not participate directly to the entanglement effect, but they are known to

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react with proteins through Maillard reaction [9]. However, before they can be used as adhesives, soybean proteins contained in soy flour have to undergo a denaturation treatment in order to open their tertiary structure and expose the hydrophobic amino acids residues [10,11,8]. Denaturation can be carried out using heat under high or low pH, a urea solution, or cationic agents to treat the soybeans. While exposing the hydrophobic amino acids and becoming more reactive, the proteins also undergo an entanglement process that creates an insoluble system. Using a high pH to treat the proteins will not only lead to the unfolding of the tertiary structure of the proteins but also hydrolyze and undo the second and first structures which, according to the literature, are not desirable because of the reduced entanglement effect [12].

Proteins cannot only be denatured or hydrolyzed, but can also be crosslinked with different types of molecules such as ketones, aldehydes or alcohols [13–17]. This allows the creation of an even more entangled three-dimensional network. The hydrolysis of the proteins, on their side, lowers the entanglement effect, but allows the exposure of more reactive sites for aldehydes, like furfural, due to the addition of new amine functions coming from the cleavage of peptide bonds. Thus, contrary to uncrosslinked soy proteins, hydrolysis could increase adhesion strength by allowing more furfural molecules to react with proteins.

The main objective of this work was to find the optimal alkaline pH and furfural quantity to use with soybean flour for synthesizing wood adhesives with good performance. To achieve this, six quantities of sodium hydroxide and five quantities of furfural (the crosslinker) were used to prepare 30 bio-adhesives used to manufacture plywood panels.

2. Material and methods

2.1. Materials

Analytical grade furfural was purchased from Sigma-Aldrich with a purity of at least 99%. Whole soy flour was obtained from Moulin Abénakis located in Sainte-Claire, Canada. Per 100 g, this soy flour was composed of 40 g of proteins, 33.3 g of carbohydrates, 13.3 g of lipids, 5.6 g of water and 7.8 g of minerals. Demineralized water was used for the production of all adhesive mixtures. Sodium hydroxide was in the form of pellets purchased from EMD and was then dissolved in water at a concentration of 50% (1:1 ratio). Yellow birch (*Betula alleghaniensis* Britton) sliced veneers were used to prepare 2-ply plywood panels.

2.2. Bioresin synthesis

Soybean–furfural (SoyFu) resins were all synthesized using the same method: water, soybean flour and furfural were first mixed together in a professional Waring mixer for 2 min. Subsequently, sodium hydroxide was added drop by drop to the mixture over a period of 10–12 min in order to ensure the homogeneity of the bioresin. Finally, the resins were poured into a 1 l reactor and stirred and heated at 65 °C for 1 h. The resins were then cooled down to 25 °C for 10 min and characterized. A total of 30 different bio-adhesive formulations were studied (5 levels of furfural content and 6 levels of sodium hydroxide or pH).

2.3. Bioresin characterization

Viscosity, pH and solid content of the resulting resins were measured. The pH was measured with an electronic pH meter from Fisher Scientific, model Accumet AB-15. The resin was poured into a 600 ml beaker and stirred with a magnetic stirrer; the measurement was taken when the reading stabilized for 1 min. Viscosity was measured with a Brookfield viscometer, model DV-I+, using RV spindles at 25 °C. Solid content was evaluated based on the mass of the resin sample before and after 24 h of oven drying at 103 °C. About 1 g of the wet resin was put in an aluminum plate and weighted. The plate containing the resin was put in an oven for 24 h and weighed again. The solid content was calculated according to the following equation: Solid content (%)= 100*Mass of oven-dried resin sample/Mass of wet resin sample.

2.4. Veneer making and testing

Two-ply plywood panels ($315 \times 169 \times 1.4$ mm^3) were prepared using an electrically-heated press with the dimensions of 340×360 mm^2. 81 g/m^2 of resin on a solid basis was applied to the veneers through a single glue line. The panels were pressed at 140 °C for 4 min with a press closing time of 15 s and an opening time of 30 s. The pressure applied on the panel was 1380 kPa. One panel was manufactured per bioresin formulation.

After pressing, the resulting plywood panels were cut into shear test specimens with a laser cutting tool according to ASTM D2339-98 [18]. Test specimen dimensions were 2.54×8.26 cm^2 with a glued area of 2.54×2.54 cm^2 as shown in Fig. 1. The specimens were then conditioned at 20 °C and 40% relative humidity for 1 week prior to testing. Five replicate specimens were tested per panel and the shear test results were subject to a two-factor analysis of variance (ANOVA) using the least significant difference (LSD) method.

2.5. ^{13}C Nuclear magnetic resonance analysis

Two samples of the 4.5 SoyFu resin were prepared for ^{13}C nuclear magnetic resonance (NMR) analysis. One was lyophilized for 48 h while the other was heated in an oven at 103 °C for 24 h. Both samples were ground into powders using a mortar and pestle. Carbon cross-polarization magic angle spinning (CPMAS) spectra were recorded on a Bruker Avance solid state NMR at a frequency of 75 MHz. Samples were packed in 7 mm zirconia rotors and spun at 4 kHz at the magic angle. Cross-polarization contact time was set to 1 ms and high power two-pulse phase-modulated (TPPM) decoupling was applied during the ^{13}C signal acquisition for typically 2000 scans.

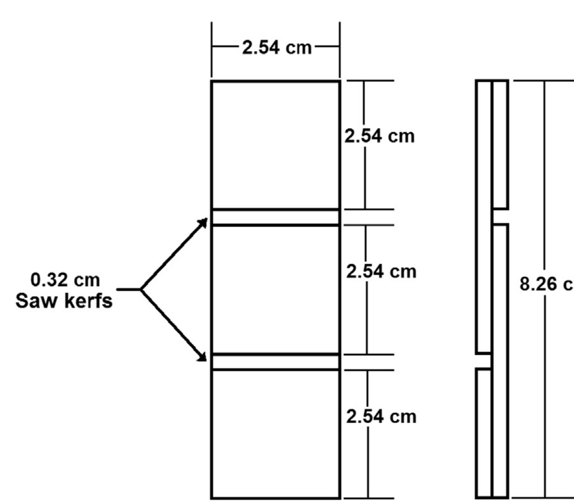

Fig. 1. The configuration of shear specimen prepared according to ASTM D2339-98.