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Preparation and development of a chemically modified bio-adhesive derived from soybean flour protein

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ABSTRACT

In this study, the potential of chemically modified soybean flour (SF) to be used as a strong and water resistant adhesive for bonding plywood composites was investigated. SF, sodium hydroxide (NaOH), acetic anhydride (AA), and polyethylenimine (PEI) were used to prepare adhesive formulations. Solid content and viscosity of adhesives were measured. Formulations were characterized using FTIR and UV absorption spectra to evaluate chemical changes of adhesives during modification. Water resistance and shear strength of plywood samples were measured, as well. FTIR analysis indicated that NaOH denatures SF; therefore amino groups buried inside the compact protein structure become available. In an SF/acetic anhydride adhesive (ASF), reaction with AA converted amine and hydroxyl groups to less polar components i.e. amides and esters, respectively. Using PEI for adhesives resulted in improved bond strength and water resistance. In this case, FTIR analysis showed that primary and secondary amines in ASF/PEI/NaOH formulations had disappeared. This could be due to a reduction in amine concentration and the formation of amides resulting in the occurrence of cross linking reactions. Absorption spectra of PEI, SF/PEI, and acetylated formulations with PEI showed a shift of λ_{max} to a shorter wavelength due to the modifications. Comparing the water resistance and the shear strength of plywood samples containing the above mentioned formulations, with ones based on phenol formaldehyde (PF), revealed that SF with NaOH, AA, and PEI had the best adhesion performance.

1. Introduction

Recently, synthetic formaldehyde based adhesives such as phenol formaldehyde (PF), urea formaldehyde (UF), and melamine formaldehyde (MF) have played a significant role in the wood composite industry. However, regarding the emission issue of formaldehyde and dependency of these conventional adhesives on fossil fuels, more attempts should be undertaken to develop new formulations from renewable resources [1–3]. Thus, the wood composite industry should seek environmentally friendly wood adhesives obtainable from renewable materials [1,2,4]. Considering the environmental issues manifested in legally restricted usage of the finite non-renewable materials, researchers are increasingly interested in biomaterials, including bark, starch, lignin, and protein [5].

Soybean flour (SF) is one form of soy protein which is abundant, low priced and sustainable with easy handling [1,6]. The industrial grade of soybean protein usually has a uniform protein content in the range of 44 to 55 percent [7]. SF has been used as a wood bio-adhesive since 1923 [8]. However, compared to synthetic resins such as UF and PF, SF also has its own disadvantages, such as lower water resistance, lower shear strength, and higher viscosity that limit its applications. In order to increase the water resistance and strengths of the soybean-based adhesives, many studies have focused on chemical modification. Mussel adhesive protein has been used as a model to show effective ways of converting soy protein to an excellent wood adhesive [9,10]. In addition, a polyamidoamine-epichlorohydrin (PAE) resin was used as an excellent curing agent for a soybean protein adhesive [11]. The influence of sodium dodecyl sulfate (SDS) and a modified polyacrylic acid solution (MPA) on soybean meal adhesive were studied by Gao et al. [12]. The results showed that plywood samples bonded by a soybean meal/SDS/MPA adhesive met interior plywood requirements.

In this study, several formulations of chemically modified SF adhesive were prepared. The resulting adhesives were evaluated

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as an ingredient in a three-ply plywood composite with a view to developing a strong and water resistant formulation. The SF was modified with NaOH, acetic anhydride (AA) and polyethylenimine (PEI), step by step to provide an excellent adhesive. Although the aforementioned materials have been used alone or in combination with other substances in the literature, the combination and formulation presented in current research has not been investigated till now, with this study demonstrating the development of a new formulation that can improve plywood properties. The different adhesive formulations studied here were analyzed by Fourier transform infrared (FTIR) spectroscopy and UV absorption spectroscopy to evaluate the functional groups and changes in the structure of soy protein after chemical modification. Apparent viscosity, solid content of the adhesives, water resistance and shear strength of beech three plywood samples were also evaluated.

Table 1
pH of adhesive formulations.

Components				pH
PEI	NaOH	AA	SF	
N	N	N	Y	6.47
N	Y	N	Y	10.36
N	N	Y[a]	Y	4.81
N	N	Y[b]	Y	4.29
N	N	Y[c]	Y	3.87
Y	Y	N	Y	10.53
Y	Y	Y[a]	Y	10.28
Y	Y	Y[b]	Y	10.27
Y	Y	Y[c]	Y	10.31

Y represents that the component was present in the formulation N represents that the component was not present in the formulation.

[a] Acetylated SF for 0.5 h.
[b] Acetylated SF for 1 h.
[c] Acetylated SF for 1.5 h.

2. Materials and methods

2.1. Materials

SF (8 wt% moisture content) was provided by Top Soy Co (khoy, Iran); Anhydride acetic and sodium hydroxide (NaOH) were purchased from Merck Co (Germany). A 50 wt% aqueous branched PEI solution (M_w=750,000) was supplied by Sigma-Aldrich (Milwaukee, WI, USA). Phenol formaldehyde resin (with a solid content of 59%) was obtained from Rezitan Co (Iran). Beech veneers (300 × 300 mm) were provided by a local plywood mill.

2.2. Methods

2.2.1. Preparation of different adhesive formulations

SF was modified by adding chemicals, step by step. Five different adhesive formulations were obtained as follows:

1) SF adhesive: SF (20 wt%) was added into water and was stirred for 30 min at 25 °C to obtain the soybean flour adhesive.
2) SF/NaOH adhesive: 1 N NaOH solution was added to soybean flour adhesive (formulation 1) to adjust pH to 10 and the resulting mixture was stirred for 30 min at 50 °C.
3) SF/ acetic anhydride adhesives (ASF): SF and acetic anhydride (with ratio of 6:10) were stirred at 50 °C for 0.5, 1 and 1.5 h. To remove excess unreacted acetic anhydride, the resulting mixtures were filtered with distilled water three times then dried using a freeze drying method.
4) SF/PEI adhesive: A 50 wt% PEI solution and distilled water were mixed with SF to make a 20 wt% water solution (dry weight ratio of ASF to PEI was 6:1). NaOH solution (1 N) was then added to the mixture in sufficient quantity to achieve a pH of 10.
5) ASF/PEI adhesives: A 50 wt% PEI solution and distilled water were mixed with an ASF formulation (formulation 3) to make a 20 wt% solution (dry weight ratio of ASF to PEI was 6: 1). NaOH solution (1 N) was then added to the mixture in sufficient quantity to achieve a pH of 10.

The pH of each adhesive formulation was measured using a WTW 3310 pH meter (see Table 1).

2.2.2. Viscosity measurement

The viscosity of the adhesive formulations was measured using a Brookfield viscometer and determined by averaging data collected from 5 measurements in 2 min at ambient temperature (approximately 25 °C). Since the viscosity of the adhesives studied covered a wide range, different shear rates and spindles were used: For acetylated formulations shear rate was 10 rpm, and spindle cod was 02. For other formulations, shear rate was 1 rpm and spindle cod was 07.

2.2.3. Solid content measurement

Solid content of the adhesive formulations was measured according to the oven drying method. Five grams (α) of adhesive was placed into an oven at a temperature of 100 ± 2 °C until a constant weight (β) was obtained. The solid content was calculated using Eq. (1). An average of five replicates was used.

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

2.2.3.1. Assay of free amino group in acetylated formulations. The modified ninhydrine method was used according to a method as described by Xu et al. [25]. Two grams ninhydrine powder was dissolved in 100 ml of distilled water to prepare ninhydrine solution. One mililiter of ninhydrine solution was added to 1% (wt%) aqueous sample solution, and was then heated at 100 °C (in a boiling water bath) for 5 min and cooled to 25 °C. The absorbance of samples was determined at 580 nm against a water blank. The sample absorbance indicated the number of free amino groups available for reaction with the ninhydrine reagent, and the difference observed in absorbance of the unmodified and acetylated soy flours reflected the extent of acetylation.

2.2.4. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared spectroscopy (FTIR) studies were performed using a Thermo Nicolet 6700 Spectrometer (Thermo Scientific Co, US). in order to determine changes in functional groups which may have been caused by the treatments. Prior to the analysis, 100 mg of the freeze dried samples were mixed with KBr. The resultant powders were pressed into transparent pellets and analyzed in transmittance mode within the range of 4000–400 cm^{-1} with a 4 cm^{-1} resolution and 50 scans.

2.2.5. UV absorption spectra of adhesive formulations

To detect changes in protein structure, one method is the evaluation of changes in protein structure with the ultra violet spectra of protein. So, UV reflectance spectroscopy of native and modified solid samples was performed over the range from 200 to 500 nm.

2.2.6. Preparation of plywood composites

The adhesive was applied to both sides of a Beech (*Fagus orientalis*) veneer by a roller coater. The spread coverage of the