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Article

Improve Performance of Soy Flour Based-Adhesive with a Lignin Based Resin

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Abstract The aim of this study was to using a lignin based resin (LB) to improve the performance of the soy flour based adhesive. Soy flour (SF), polyamidoamine-epichlorohydrin (PAE), LB was used to develop a plywood adhesive. The solid content and viscosity of the adhesive, functional groups, thermo-stability, and crystallinity of the cured adhesive were characterized and the performance of the resultant adhesive was evaluated by fabricating three-ply plywood. Results showed using LB and PAE mixture to modify SF adhesive improves dry and wet bond strength by 66.3 and 184.2%. PAE contributed more for the wet bond strength improvement and the LB contributed more for the dry bond strength. The improvement was attributed to: 1) LB/PAE reacted with the functions of the soy protein and form a cross-linking network; 2) Polycondensation reaction between LB molecules further improved crosslinking density of the adhesive and formed a interpenetration structure with crosslinked protein; 3)The easy penetration of LB on wood surface and formed more interlock with wood. The denser structure created by LB and PAE mixture improved the thermal stability and decreased the crystallinity of cured adhesive. The usage of the LB and PAE mixture increased solid content by 35.5%, meanwhile, makes its viscosity acceptable for the industrial application.

Key words soy flour, lignin, adhesive, plywood, bond strength

Introduction

Formaldehyde-based resins, especially melamine-urea-formaldehyde resin, are widely used for fabricating plywood panels[1]. But they are non-biodegradable and petroleum-derived, leading to a environmental concern when they are prepared and used[2,3]. Therefore, there is an urgent need on developing adhesives based on ecological and renewable nature resources. Soy flour has been used as a wood adhesive for decades because it is a renewable, abundant, readily available and inexpensive raw material[4]. However, the poor water resistance of the soy flour-based adhesive limits their application. Many attempts have been used to improve the water resistance of soy flour-based adhesives, including protein denature agent modification and cross-linker modification. Denature agent, such as alkali[5], urea[6], and sodium dodecyl sulfate (SDS)[7], can unfold protein molecule and expose inside hydrophobicity groups to improve the water resistance of the adhesive. However, the water resistance of the resultant plywood cannot meet the interior use plywood requirement. Cross-linker modification, such as polyamidoamine-epichlorohydrin (PAE) resin[8], glycidyl methacrylate[8], and polyethylene glycol diacrylate [9], can cross-link protein molecule by react with the functions and form a net work to improve the water resistance of the adhesive. PAE were proved to be the most effective cross-linker to improve the water resistance of the adhesive. However, the soy flour-based adhesive with those crosslinkers have a low dry bonded strength, which limits its application, especially in the secondary operation process of its resultant plywood. This is because that the protein molecule is big and hard to penetrate into wood surface to form interlock. So that, it is important to improve the performance in dry and wet state for a soy flour-based adhesive.

In this study, a soy flour-based (SF) adhesive was synthesized by soy flour and PAE. A lignin based (LB) resin was synthesized in our lab with phenol and formaldehyde and acted as a modifier to improve the bond performance of the SF adhesive. Different addition of LB resin was used to develop

different adhesive samples. The performance of the resultant adhesive including the solid content and viscosity of the adhesive, and the functional groups, thermostability, and fracture surface of the cured adhesive was characterized. Three-ply plywood were fabricated with the resultant adhesives and their wet bond strength was tested.

Experimental Methods

Materials

Soy flour (200 mesh) was the meal after removing the oil from soybean and obtained from Fuda Protein Biotech Company in Zhejiang Province of China, and then milled to flour (SF). Components of the soy flour were: 52.2% soy protein, 38.2% saccharides, 7.5% moisture, 2.6% ash, and 0.5% fat. Phenol, formaldehyde solution (37-40 wt%) and sodium hydroxide were AR grade reagents were obtained from Zhejiang Chemical Reagent Co.. The lignin was produced from the Yongtai Paper co., LTD, which contained 82.5% acid-insoluble lignin, 4.7% acid-soluble lignin. PAE was obtained from Kaiyuan Chemical Ltd, solid content is 12.5%, and the viscosity ranges from 25 to 45 mPa·s. Eucalyptus veneer (60 × 60 × 1.7 cm, 5% of moisture content) was provided from Jiashan Province of China.

Lignin based resin (LB) Preparation

The LB resin was synthesized by batch copolymerization using the lignin, phenol, formaldehyde in weight ratio of 1:1:1 (100% solid content). In the first step, lignin (260g) and phenol (260g) with formaldehyde (400g, 37 wt%) and NaOH (100g, 50 wt%) were mixed and stirred in a flask. The mixture was heated to 80 °C and kept for 1 h. Then, the second portion of formaldehyde (300g, 37 wt%) and NaOH (80g, 50 wt%) was added into the flask and stirred for 1 h at 80 °C. Then the mixture was cooled down to 40 °C and through a vacuum distillation process removing the free formaldehyde to get the LB. The solid content of the resultant resin was 62.2% and the viscosity was 1080 mPa·s at 20 °C.

Adhesive preparation and measurement

For the different adhesive samples, soy flour was mix with water and stirred for 15 min at 30 °C. Then LB and PAE were added sequentially and further stirred for 15 min at 30 °C. The different adhesive formulations are shown in Table 1.

Table 1 Adhesive formulations.

Sample	Formulation
SF adhesive	Soy flour (30 g); Water (70 g)
SF/PAE adhesive	Soy flour (30 g); Water (40 g); PAE (30 g)
SF/LB adhesive	Soy flour (30 g); Water (70 g); LB (10 g)
SF/PAE/LB adhesive	Soy flour (30 g); Water (40 g); PAE (30 g); LB (10 g)

Solid content measurement. The adhesive solid content was measured using an weight method. About 3 g (α) of the adhesive was placed into an oven and dried at 102°C for 2 hours to get a weight (β). The value of the solid content was calculated using the following equation. The average value of the solid content was calculated from six parallel samples.

$$\text{Solid Content}\ (\%) = \frac{\beta\ (\text{g})}{\alpha\ (\text{g})} \times 100\% \qquad \text{Eq. (1)}$$

Dynamic viscoelastic measurement. The apparent viscosity of different adhesives was determined using a Brookfield viscometer with a spinning rate of 1 rpm and determined by averaging the date collected- 10 measurements in 3 minutes at 30℃.

Fourier Transform Infrared (FTIR) spectroscopy. The adhesive was cured in an oven at 130℃ for 1 hour and then ground into a 150 mesh powder. FTIR spectra of the cured adhesive was tested using a Nicolet 7600 spectrometer (Nicolet Instrument Corporation, Madison, WI) from 500 to 4000 cm^{-1} with a 4 cm^{-1} resolution using 16 scans.

Thermogravimetric (TG) measurement. The adhesive was cured in an oven at 130°C for 1 hour and then ground into a 150 mesh powder. The thermal stability of the cured adhesive samples was tested using a TGA instrument (TA Q50, WATERS Company, USA). About 3 mg powdered samples were weighed in a platinum cup and scanned from the 30 to 600 °C at a heating rate of 10 °C /min in a nitrogen environment while recording the weight change.

X-ray Diffraction (XRD) measurement. 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 a D8 advance diffractometer (Bruker, U.S.A) using a cobalt source and 0.02 theta scan ranging from 5°to 60°at 45 kV and 30 mA, the index of the sample determination was carried out by using a Jade 5.0 program

Plywood preparation and testing

Three-ply plywood were fabricated using the following conditions: 130 °C hot pressing temperature, 90 s/mm hot pressing time, 200 g/m^2 glue spreading, and 0.8 MPa hot pressing pressure.

Wet bond strength measurement. The wet bond strength test was in accordance with the description in China National Standards (GB/T 17657-2013). Twenty plywood specimens (2.5 cm × 10 cm) were cut from two parallel plywood panels and submerged into water at 63 ± 2°C for 3 h before a tension test. The wet bond strength was calculated by the following equation.

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

Results and Discussion

Solid content measurement

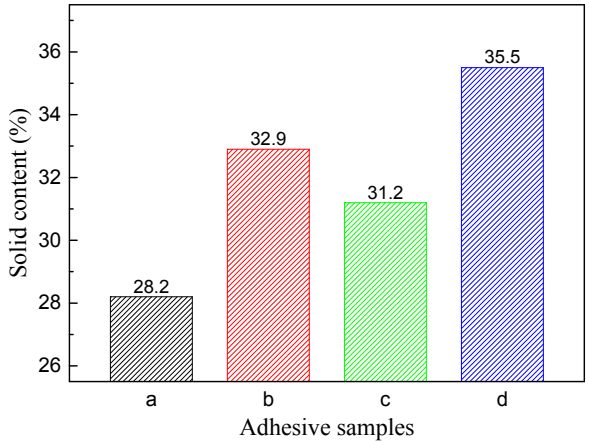

Fig. 1 The solid content of the different adhesives: a (SF adhesive), b (SF/LB adhesive), c (SF/PAE adhesive), and d (SF/LB/PAE adhesive)

The solid content of the adhesive is calculated from three parallel samples and shown in Fig. 1. For a water-based wood adhesive, the adhesive with a high solid content presents a better performance [10]. Soy protein based adhesive is water based adhesive, a low solid content means there are lots of water in the adhesive formulation, which leads to a low adhesive spreading. And the water should be remove during the hot pressing process, which costs energy and increase the interior force of the

resultant plywood. For the SF adhesive (adhesive a), the solid content was 28.2% and at that solid content, the adhesive have flow issue, indicating that further increase the solid content determined by the additives. When mixing with LB, the solid content of adhesive b reached at 32.9%, which increased by 16.7% when compare to adhesive a. After adding PAE, the solid content of the adhesive d increased to 35.5%, which was 25.9% higher than adhesive a. However, only mixing PAE and SF adhesive, the solid content of the adhesive c is 31.2%, which was 12.1% lower than that of adhesive d. According to the literature, the solid content of the soy protein-based adhesive was ranged from 32 to 36%. Therefore, the solid content of adhesive d meets the requirement of plywood adhesive application.

Dynamic viscoelastic measurement

Table 2 The viscosity of the adhesives: a (SF adhesive), b (SF/LB adhesive), c (SF/PAE adhesive), and d (SF/LB/PAE adhesive)

Adhesive sample	a	b	c	d
Initial viscosity (mPa·s)	28,510	687,500	19,840	541,200

The viscosity of the adhesives is shown in Table 2. The viscosity of the adhesive increased from 28,510 to 687,500 mPa·s after LB addition (adhesive b), which was attributed to that LB contained free sodium hydroxide (NaOH). NaOH is an effective protein denature agent, which can unfold the soy protein molecule and exposes the inside functions[11], which increases the friction between protein molecules and resulting in a huge increase on the adhesive viscosity. When PAE was added, the viscosity of the resultant adhesive decreased from 28,510 to 19,840 mPa·s, which may attributed to the low viscosity of PAE itself. In addition, the PAE has a smaller molecule compared with soy protein and it acts as a molecule lubricant to reduce friction between the molecules, resulting in the decreases of adhesive viscosity. The viscosity of adhesive d is 40% lower than that of adhesive b, which also proves the viscosity reduction effect of PAE.

Dry bond strength

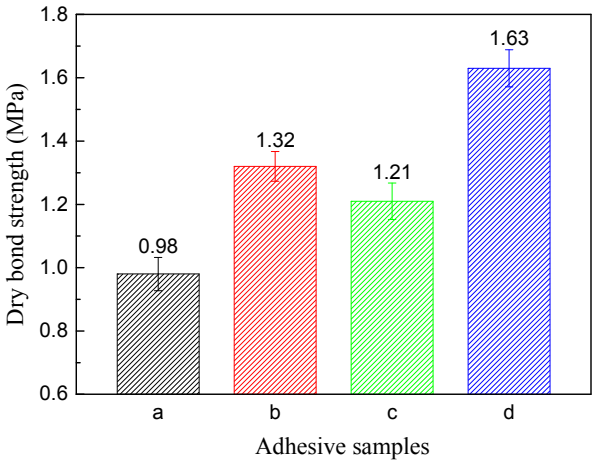

Fig. 2 The dry bond strength of the plywood with the different adhesives: a (SF adhesive), b (SF/LB adhesive), c (SF/PAE adhesive), and d (SF/LB/PAE adhesive)

The dry bond strength of plywood bonded the different adhesives is shown in Fig. 2. The dry bond strength of the plywood bonded with SF adhesive was 0.98 MPa. Protein molecule is big and hard to penetrate into wood surface to form a mechanically interlocked structure, resulting in a low dry bond

strength. Secondly, the interaction between soy protein molecule and wood was low, which further reduced the bond performance of the adhesive. After mixing with LB, the dry bond strength of the resultant plywood increased to 1.32MPa. When compared with protein molecule, the LB have smaller molecule and easy to form mechanically interlocking, thus improved the dry bond strength. In addition, the LB reacted with protein molecule and themselves to form a crosslinking structure, which increased the cohesive strength and improved the bond strength. This also happened in the adhesive c. When adding PAE in the adhesive formulation, the PAE crosslinked protein molecule and formed denser structure to improve the bond strength. But, PAE contributed less to form a mechanically interlocked structure, so that, the improvement of the plywood with adhesive c is lower than that of adhesive b. When mixing PAE and LB, the dry bond strength of plywood further increased to 1.63MPa, which was 66.3% higher than that of with adhesive a. This improvement was attributed to the following aspects: one is the small molecule subjects addition increased the interlock between wood and adhesive; secondly, the strength of the adhesive itself was enhanced; Chemical reaction took place between adhesive and wood by the phenolic hydroxyl methyl (adhesive) with hydroxyl (wood), which increased the interaction force between wood and adhesive.

Water shear strength

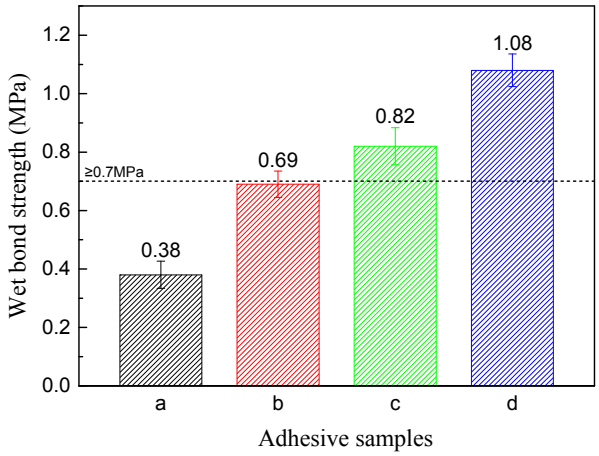

Fig. 3 The wet bond strength of the plywood with different adhesives: a (SF adhesive), b (SF/LB adhesive), c (SF/PAE adhesive), and d (SF/LB/PAE adhesive)

The wet bond strength of plywood bonded by the different adhesives is shown in Fig. 3. The wet bond strength of the plywood bonded with adhesive a was 0.38 MPa. The curing process of pure soy protein adhesive is the process of lost water and molecules twined with each other. During this curing process the main force for adhesive a is hydrogen bond, which is easy broken from moisture intrusion. When using LB, the wet bond strength of plywood with adhesive b reached at 0.69 MPa. This improvement is due to the following reasons: Firstly, the NaOH in LB is a effective denature agent, which unfolds the protein molecules and exposes the hydrophobicity groups, resulting in the improvement of the adhesive water resistance[12]. Secondly, the phenolic hydroxyl group on LB reacted with the functions of protein (such as, $-NH_2$, -COOH), forming a cross-linked network, thus further increasing the water resistance of the adhesive. Using PAE modified SF adhesive, the wet bond strength of plywood with adhesive c increased by 115.8% to 0.82 MPa. As a effective curing agent of soy protein, PAE effectively reacts with the functions of protein to form a denser structure to enhance the water resistance of the adhesive. After mixing PAE and LB, the wet bond strength of the plywood greatly increased to 1.08 MPa compared with the adhesive a, which increased by 184.2%. The NaOH in LB

unfolds the soy protein molecule and exposes active groups, which is promoted the reaction between protein molecule and PAE. In addition, the LB reacts with themselves by a polycondensation reaction to form a network, which penetrates with the PAE cross-linked soy protein network to form a interpenetrating network and improve the water resistance of the resultant plywood.

FTIR spectroscopic analysis

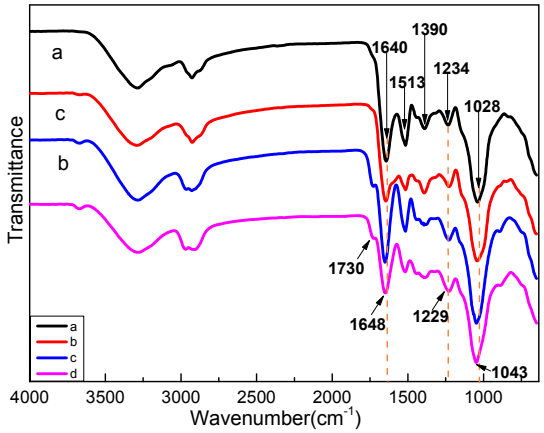

Fig. 4 FTIR spectra of the different adhesives: a (SF adhesive), b (SF/LB adhesive), c (SF/PAE adhesive), and d (SF/LB/PAE adhesive)

The FTIR spectra of the different adhesives are shown in Fig. 4. Peaks observing at 1640, 1513, and 1234 cm^{-1} was attributed to the characteristic peak of peptide, amide I (C=O stretching), amide II (N-H bending) and amide III (C-N and N-H stretching), respectively [13]. The peak at 1390, and 1028 cm^{-1} was attributed to COO– and C–O bending, respectively. After adding LB, the amide II (1513 cm^{-1}) of adhesive b decreased, indicating a reaction happened between LB and the –NH groups on soy protein. LB linked different protein molecules and formed a cross-linked network in the adhesive, which enhanced the water resistance of the adhesive. The absorption peak of C=O stretching (amide I) and C–O bending moved from 1640 to 1648 cm^{-1} and 1028 to 1043 cm^{-1}, respectively (blue shift), suggesting a denser structure was formed in the adhesive, which further improved the water resistance of adhesive. A same change was observed at the spectra of adhesive c, indicating PAE react with the –NH groups on soy protein molecule and form a denser crosslinking structure to resistant moisture intrusion. When using LB and PAE, the absorption peak of $–NH_2$ further decreased, suggesting a much denser structure formed in the adhesive, thus, further increased the water resistance of the adhesive.

TGA analysis

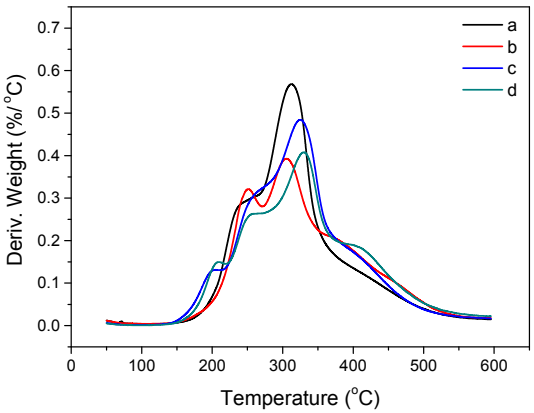

Fig. 5 The derivative thermogravimetric (DTG) curves of the different adhesives: a (SF adhesive), b (SF/LB adhesive), c (SF/PAE adhesive), and d (SF/LB/PAE adhesive)

The DTG curves of the different adhesives are shown in Fig. 5. After using LB to modified adhesive a, a obvious peaks observed at the DTG curve around 220 to 260 °C when compared that in the SF adhesive, indicating a different structure formed in the adhesive b. According to the FTIR analysis, the LB cross-linked protein molecule network played a major role in the adhesive system, which may have a lower thermal stability. A similar change observed at the curve of adhesive c proved that PAE also crosslinked with soy protein and formed a network. In the main structure degradation temperature ranged from 270-370 °C, the thermal degradation behavior of adhesive d was different from the other adhesives. The adhesive a had a highest degradation rate, which then decreased significantly with LB and PAE incorporation, suggesting a better thermal stability of the resultant adhesive. In addition, the peak of adhesive d in 220 to 260 °C temperature was increased and the peak in 270-370 °C moved to a low temperature, suggesting a interpenetration structure was formed besides the crosslinking structure.

Table 2 The crystallinity of different cured adhesives: a (SF adhesive), b (SF/LB adhesive), c (SF/PAE adhesive), and d (SF/LB/PAE adhesive)

Adhesive	a	b	c	d
The crystallinity (%)	15.5	14.6	13.1	11.6

The crystallinity of the different adhesive formulations is presented in Table 2. The crystallinity of the adhesive a was 15.5%. For a wood adhesive, a cross-linked structure formation in an adhesive reduces its crystallinity. After mixing with LB, the crystallinity decreased to 14.6%, probably due to the reaction between LB and soy protein, thus also increased the cross-linking density of the cured adhesive. The crystallinity decreased to 13.1% after using PAE, which was 10.3% lower than the adhesive b, indicating a more denser structure formed in the adhesive c and leading to a better water resistance. This was in accordance with the result of wet bond strength measurement. After mixing LB and PAE, the crystallinity further decreased to 11.6, indicating a more compact structure formation in the cured adhesive d. This attributed to the reaction between protein and LB/PAE, creating a cross-linking structure. In addition, the compact structure also came to the inter penetration network formation by the LB condensation, which further increased the density degree of the adhesive. The result of the adhesive crystallinity analysis was in accordance with the results in water resistance analysis and the result of FTIR analysis.

Conclusion

Using LB and PAE to modify SF adhesive improves dry and wet bond strength by 66.3 and 184.2%. PAE contributed more for the wet bond strength improvement and the LB contributed more for the dry bond strength. The improvement of the wet bond strength was attributed to: 1) Both of LB and PAE reacted with the functions of the soy protein and form a cross-linking network; 2) Polycondensation reaction between LB molecules further improved crosslinking density of the adhesive and formed a interpenetration structure with crosslinked protein. The dry bond strength improvement was attributed to the easy penetration of LB on wood surface and formed more interlock with wood. The crosslinked and interpenetration structure created by LB and PAE also improved the thermal stability and decreased the crystallinity of cured adhesive. The usage of the LB and PAE mixture increased solid content by 35.5%, meanwhile, makes its viscosity acceptable for the industrial application. It is an effective way to promote soy protein adhesive application.

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