



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



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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.

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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 bio-mimetic 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

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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 Shandong Province, China. Prior to use the soybean meal was milled into flour (≥ 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.

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

2.4. Preparation of plywood samples

Three-ply plywood samples were made under the following conditions: 180 g/m² 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

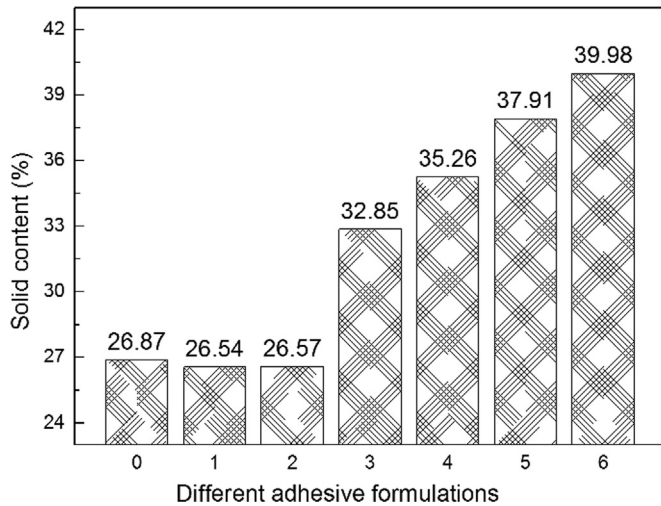


Fig. 1. Solid content of the different adhesive formulations: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/EP-5 g adhesive), 4 (SM/PAM/SDS/EP-10 g adhesive), 5 (SM/PAM/SDS/EP-15 g adhesive) and 6 (SM/PAM/SDS/EP-20 g adhesive).

index of the sample determination was carried out by using a Jade 5.0 program [18].

3. Results

3.1. Solids content

Solid content is important for a wood adhesive, since it determines adhesive behavior during the hot pressing process. In general, adhesive properties improve with increasing solid content. A lower solid content in the adhesive indicates that more volatiles need to be removed during the hot pressing process, which can damage the bond performance of the resulting plywood [19]. From the literature, the average solid content of soy protein-based adhesives is from 30 to 40% [20]. The solid content of different adhesives is shown in Fig. 1. For a soybean meal adhesive, a solids content of 30% will cause flow issues which can be of particular concern since additive incorporation could contribute to an increasing solids content. With the addition of both PAM and SDS, the solids content remains virtually unchanged due to the small amounts of both compounds added to the SM adhesive. As expected, the solids content of the adhesive increased with addition of M85 with solids content increasing from 32.85% to 39.98% with additions of 5 g and 20 g respectively i.e. significant enhancements in comparison to a solids content of 25.05% for the unmodified SM adhesive.

3.2. Water resistance

The wet shear strengths of the different adhesive formulations are shown in Fig. 2. The wet shear strength of plywood bonded by the SM adhesive was 0.31 MPa, which failed to meet the interior use panel requirement. After combination with PAM, the bonding strength increased by 19.4% to 0.37 MPa because of the lubrication effect of PAM [21]. After further mixing with SDS, the bonding strength was increased to 0.43 MPa an increase of 38.7% compared with the unmodified SM adhesive. SDS is an effective protein denature agent [11] and it releases soy protein molecules and exposes polar groups to enhance the water resistance of the adhesive. In general, when a higher proportion of cross-linking agent was incorporated, a lower apparent viscosity and an improved bonding strength was obtained [22]. The commercial

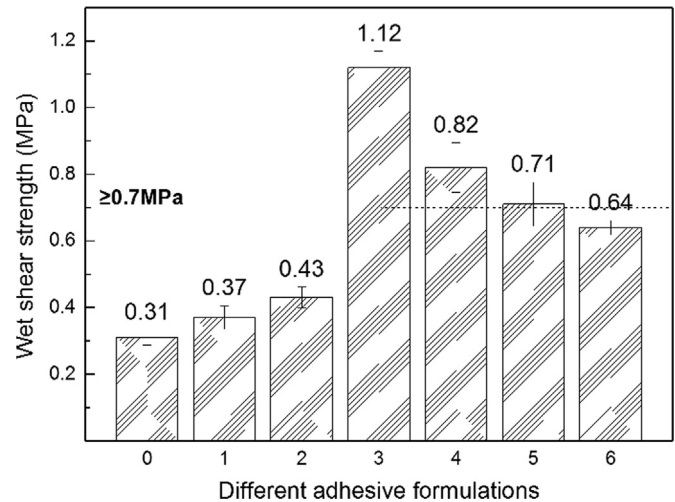


Fig. 2. Wet shear strength of the different adhesive formulations: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 [SM/PAM/SDS/EP-5 g adhesive], 4 [SM/PAM/SDS/EP-10 g adhesive], 5 [SM/PAM/SDS/EP-15 g adhesive] and 6 [SM/PAM/SDS/EP-20 g adhesive].

epoxy resin M85, when used as a cross-linker, can link soy protein molecules by reacting with the amino and hydroxyl groups to form a three dimensional cross-linked network structure which can in turn enhance water resistance. The wet shear strength increased significantly upon M85 addition, which was increased by 160.5% to 1.12 MPa compared with the SM/PAM/SDS adhesive. The average wet shear strength value of the plywood with addition of 5 g M85 was 1.12 MPa, which would meet the interior use panel requirement (≥ 0.7 MPa) according to the China National Standard (GB/T 9846.3-2004). Moreover, from the standard deviation for the SM/PAM/SDS/EP-10g adhesive formulation, the wet shear strength of the plywood specimens can be guaranteed over 0.70 MPa. Because SDS and PAM had opposite electrical charges, this could form an electrostatic attraction with amino acids with opposite charges, respectively. With the mesh structure becoming more dense, then more cross-linker could interact with the soy protein molecules, thereby enhancing the water resistance of the adhesive [21]. By increasing the M85 content to 10 g, the bonding strength decreased by 26.8% to 0.82 MPa, and was further decreased when M85 content was increased to 20 g. The reduction of the wet shear strength suggests that the epoxy resin is excessive in the adhesive formulation. The epoxy resin is oil soluble, so that, the residual epoxy resin in the adhesive reduces water resistance of the resulting adhesive. In addition, epoxy resin transfers to a rubbery state at 120 °C when hot pressing, and this will reverse when the resulting plywood is cooled down, which further decreases the water resistance of the resulting adhesive. Therefore, based on above discussing results and considering the production cost, the optimum M85 addition is 5 g.

3.3. Dynamic viscoelastic measurement

According to the solid content and water resistance analysis of the resulting adhesive, the optimum addition of M85 is 5 g. The SM/PAM/SDS/EP adhesive formulation was further characterized by a dynamic viscoelastic measurement, Fourier transform infrared (FTIR) spectroscopy and other relevant measurements together with the SM, SM/PAM, SM/PAM/SDS adhesives.

In the plywood fabrication industry, viscosity is a significant property, which largely governs the adhesive behavior during manufacture. The operating viscosity limits of the soy protein-based adhesive on plywood are very large ranging from 5000 to 25,000 mPa s depending on the application and the nature of the

materials [23]. The high viscosity of soy protein-based adhesives, especially after denaturing, not only causes difficulties in applying the adhesive on the veneer or particles, but also affects the adhesive distribution during hot press processing, which leads to a low bonding strength. The apparent viscosities of the different adhesives are shown in Table 1. The initial viscosity of the SM adhesive was 35,810 mPa s, which causes flow issues and will be hard to apply on the veneer surface uniformly. As PAM is a water-soluble polymer, it has a smaller molecule and can reduce frictional resistance among the soy protein molecules, hence, the viscosity of the SM/PAM adhesive decreased by 14.7% from 35,810 to 30,550 mPa s. As SDS was added, the viscosity of the SM/PAM/SDS adhesive increased by 32.7% from 30,550 to 40,550 mPa s. SDS acts as a denaturing agent for the soy protein. Thus, after using SDS, soy protein molecules unfold and the distance between protein molecules decreases, which increases the force acting between molecules, thus increasing the apparent viscosity of the soybean meal-based adhesive [24]. The incorporation of EP dramatically decreased the viscosity of the SM/PAM/SDS/EP adhesive by 49.7% from 40,550 to 20,415 mPa s, which was even lower than that of the SM adhesive by 43.0%. The probable reason is that EP could be used as a dispersant to decrease effective volume or hydrodynamic volume and thus to reduce the viscosity [25]. Therefore, EP acts as a cross-linker as well as viscosity reducer resulting in a low viscosity which allows easy handling and good flowability on the wood surface.

3.4. FTIR spectroscopic analysis

Water readily associates with hydrophilic groups (e.g., hydroxyl groups) via hydrogen bonds, resulting in poor water resistance of the adhesive. The FTIR spectra of the SM adhesive and its hybrids i.e. SM/PAM, SM/PAM/SDS, and SM/PAM/SDS/EP are presented in Fig. 3. The peak at 3327 cm^{-1} was assigned to the stretching vibration of N–H and O–H bonds in the primary amines and hydroxyl groups. The peaks at approximately 2930 cm^{-1} were attributed to the symmetric and asymmetric stretching vibrations of the $-\text{CH}_2$ group in the different adhesives. The main absorption bands of the peptide were related to the peaks at approximately 1660 , 1537 , and 1243 cm^{-1} , which were characteristic of amide I (C=O stretching), amide II (N–H bending) and amide III (C–N and N–H stretching), respectively [26]. The bands corresponding to COO⁻ and $-\text{C}-\text{NH}_2$ bending were located at 1397 and 1056 cm^{-1} , respectively. The peaks mentioned above were all observed in the four spectra with small variations on the exact position and relative intensity caused by the condensation and cross-linking reactions [27].

In the SM/PAM/SDS/EP adhesive, the absorption peaks for COO⁻ and $-\text{C}-\text{NH}_2$ (1397 cm^{-1} and 1056 cm^{-1}) decreased compared with the SM adhesive, which might be a result of a reaction between an epoxy group in the EP resin and N–H and COO⁻ groups in the soy protein molecule, implying that the amount of hydrophilic groups in the adhesive decreased upon EP addition [28]. A new peak appeared at 1738 cm^{-1} , which can be attributed to the stretching vibration of the ester carbonyl bond. This band indicated the formation of an ester linkage between the epoxy group and the hydroxyl group in soy protein [29]. The absorption peak at 910 cm^{-1} was assigned to the epoxy skeleton vibration [30]. After incorporation of EP, there would be a strong absorption peak at

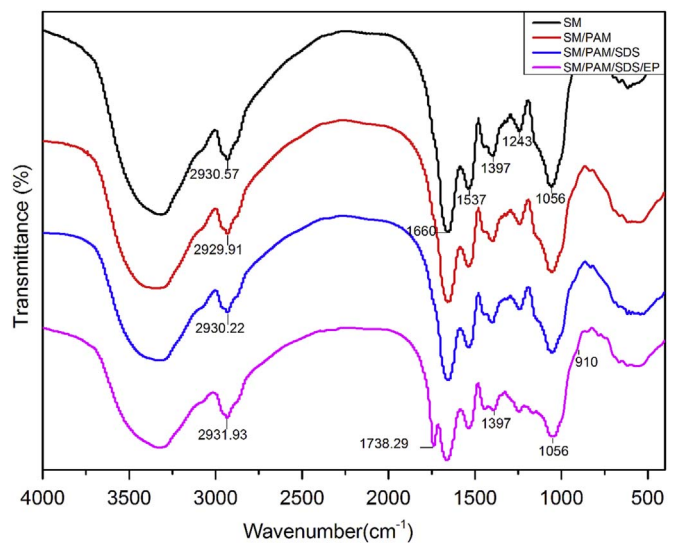


Fig. 3. FTIR spectra of the SM adhesive and its hybrid adhesive: the SM/PAM, SM/PAM/SDS, and SM/PAM/SDS/EP adhesive, respectively.

910 cm^{-1} . But in Fig. 3, it exhibited a minor peak (910 cm^{-1}) and even became negligible in the spectrum of the SM/PAM/SDS/EP adhesive formulation, indicating that the epoxy groups could react with the active hydrogen on $-\text{OH}$ and $-\text{NH}-$ groups in the protein molecules during the curing process by a ring-opening reaction [31]. In addition, the peak at 910 cm^{-1} also showed good dispersibility of the hydrophobic epoxy resin in the water soluble soy protein adhesive. This can be attributed to two reasons: first of all, the high viscosity of the soybean meal-based adhesive helps the hydrophobic epoxy resin to attach to the protein molecule and thus aid distribution. Secondly, the SDS in the formulation acts as an emulsifier, further enhancing epoxy resin distribution. The above-mentioned absorption peak changes coincided with the adhesive water resistance significantly. On the one hand, incorporation of SDS, PAM and EP tended to enhance the hydrophobic nature of the system whilst on the other EP addition increased the cross-linking density by chemical reaction. The likely reaction mechanism is shown in Fig. 4.

3.5. X-ray diffraction analysis

The x-ray diffraction pattern of the SM adhesive and its hybrid adhesives are shown in Fig. 5, and the crystallinity of the different adhesive formulations are presented in Table 2. On the (110) crystal face, the SM adhesive exhibited one strong characteristic peak at 2θ values near 8.8 . However, the crystallization peak disappeared in the X-ray diffraction pattern after the incorporation of EP, which indicated that a chemical reaction occurred between the EP and the soy protein. This confirmed the discussion above (FTIR analysis). As shown in Table 2, crystallinity increased from 14.5 to 16.5% following the incorporation of SDS, this likely being due to swelling and unfolding of the protein molecules and increasing the order region of the adhesive after curing. In general, increasing the cross-linking degree of the adhesive will lead to a crystallinity reduction. Using EP in the adhesive formulation decreased the crystallinity of the resulting adhesive from 16.7% to 11.1%, which was probably due to a ring-opening reaction between the EP and soy protein increasing the cross-linking density of the cured adhesive, thus decreasing the crystallinity. Comparing Figs. 2 and 5, there was a positive correlation between the adhesive cross-linking network formation and wet shear strength of the resulting plywood, which indicated that the elevated cross-linking network formed by reactions between EP and soy protein could minimize

Table 1

The initial viscosity of the SM adhesive and its hybrid adhesive: the SM/PAM, SM/PAM/SDS, and SM/PAM/SDS/EP adhesive, respectively.

Adhesive formulation	SM	SM/PAM	SM/PAM/SDS	SM/PAM/SDS/EP
Initial viscosity (mPa s)	35,810	30,550	40,550	20,415

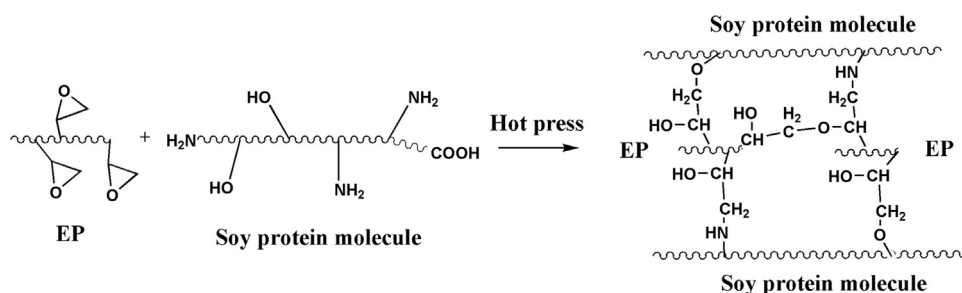


Fig. 4. The reaction process between the soy protein and epoxy resin.

Table 2

Crystallinity of the SM adhesive and its hybrid adhesive: the SM/PAM, SM/PAM/SDS, and SM/PAM/SDS/EP adhesive, respectively.

Adhesive formulation	SM	SM/PAM	SM/PAM/SDS	SM/PAM/SDS/EP
The crystallinity (%)	14.2	14.5	16.7	11.1

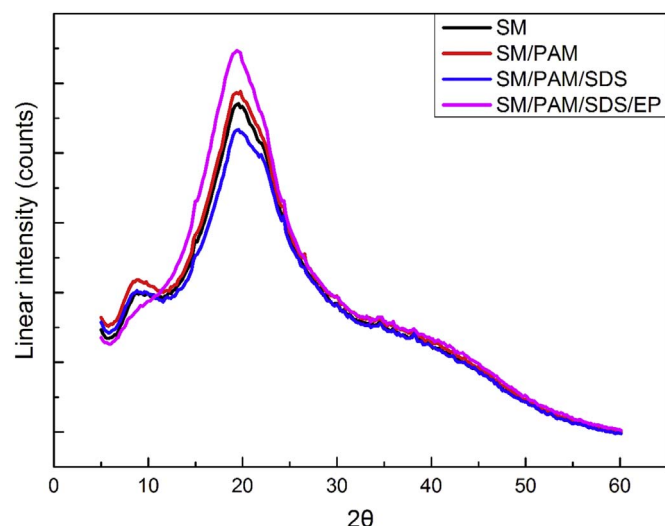


Fig. 5. X-ray diffraction pattern of the SM adhesive and its hybrid adhesive: the SM/PAM, SM/PAM/SDS and SM/PAM/SDS/EP adhesive, respectively.

moisture intrusion thus leading to an enhancement in the mechanical properties of the plywood.

4. Conclusions

Using PAM and SDS as retention and denature agents respectively, improves the water resistance of the resulting adhesive by 38.7%. Using 5 wt% of a commercial epoxy resin effectively improves the wet shear strength of the resulting adhesive by 261.3% to 1.12 MPa, while, the solid content of the resulting adhesive increased by 25.05% to 32.85 wt% and the viscosity decreased by 43% to 20415 mPa s. All properties of the resulting adhesives met the requirements for a plywood adhesive for industrial use. It is an effective solution for enhancing the properties of soybean meal-based adhesives for a range of applications.

Based on the FTIR and XRD analysis, chemical reactions clearly occurred between epoxy groups and the active groups on the soy protein molecule during the curing process, forming a solid crosslinked network to minimise moisture intrusion, thereby enhancing the water resistance of the resulting adhesives.

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