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A new soybean meal-based bio-adhesive enhanced with 5, 5 dimethyl hydantoin polyepoxide for the improved water resistance of plywood

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The primary goal of this study was to improve the water resistance of the soybean meal-based bio-adhesive and its resultant plywood with a water-soluble 5, 5 dimethyl hydantoin polyepoxide (DMHP). DMHP well distributed in the adhesive system and the water resistance of the adhesive/resultant plywood increased with the DMHP addition from 5 to 13 wt%. This improvement attributed to the following reason: 1) DMHP reacted with active groups on protein molecules to form a dense cross-linking network, improving the cross-linking degree of the cured adhesive; 2) adding DMHP decreased the adhesive viscosity, which benefited for the adhesive penetrating into wood surface and forming interlock; 3) the wettability of the adhesive increased after incorporating DMHP; 4) the adhesive with DMHP created a smooth surface with fewer holes and cracks to prevent moisture intrusion. Incorporating 13 wt% DMHP effectively improved the moisture resistance of the resultant adhesive by 38.7% and wet shear strength of the resultant plywood by 182.9%, upto 1.16 MPa, well within interior use plywood requirements. Adding DMHP also increased the adhesive solid content by 26.6% and decreased adhesive viscosity to 13,610 mPa·s, which would prove beneficial for industrial use plywood adhesive. Further increasing the DMHP addition to 17 wt%, the wet shear strength of the plywood with the resultant adhesive decreased by 40.5%, however, attributing to the significant penetration of the adhesive into wood surface caused by the low viscosity.

Introduction

Under increasing concern worldwide regarding environmental safety and sustainability, the development of biodegradable and renewable biomass for the production of wood adhesives is not only inevitable, but also a responsible response to environmental threat posed by formaldehyde-based adhesives.[1] Protein-based materials provide a favorable alternative, not only for wood adhesives but for use in medical applications, as label glues, paper adhesives and for underwater applications.[2] Soy protein has been utilized to produce wood adhesive ever since the 1920s/1930s when it was favored for its low cost and environmental friendliness.[3,4] Soy protein-based bio-adhesives show notable disadvantages, however, including low bond strength and poor water resistance.[5] After 1960, the low cost, high water resistant, and high curing condition adaptability of formaldehyde-based adhesives (petrochemical-based synthetic adhesive) caused them to take over the market.[6] More recently, issues regarding formaldehyde emissions and over-dependence on petrochemicals of the formaldehyde-based adhesive have created an urgent need for environmentally friendly adhesives from renewable resources; To this effect, many researchers and developers have begun to re-investigate soy protein-based adhesives, as they are abundant, potentially very effective, and low in cost.

Previous researchers have made many attempts to improve the water resistance of soy protein-based bio-adhesives. [7] Said attempts can be grouped into three main categories.

1) First is soy protein denaturing agent modification – most of the soy protein molecules are complex polypeptide agglomerates with a quaternary structure and breaking these agglomerates apart/retaining protein secondary structures improves the performance of the adhesive. Researchers have used alkali, [8] urea, [9] and sodium dodecyl sulfate (SDS)[10,11] to denature proteins and improve the water resistance of soy protein-based bio-adhesives. Improvement under this approach is limited, however, because soy protein also possesses many polar groups such as $-NH_2$, -COOH and -OH. Plywood treated in this manner does not meet interior use

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requirements. 2) Soy protein molecular modification, such as graft, acetylated, protein enzyme, and biomimetic modification[12] — this approach focuses primarily on grafting high-activity groups onto soy protein molecules. The activity groups react with polar groups in soy protein molecules and form a cross-linked network in the adhesive after curing. This process improves the water resistance of the adhesive, but is complex and quite costly, which makes it overall impractical for plywood fabrication.

3) Enhancing soy protein-based bio-adhesives using cross-linkers — researchers have used, maleic anhydride,[13] glycidyl methacrylate,[14] and polyethylene glycol diacrylate[15] as cross-linkers to improve the water resistance of soy protein-based bio-adhesives. These cross-linkers react with the -NH_2, -COOH and other exposed groups to increase the cross-linking density of the adhesive during a hot press process. The wet shear strength of plywood bonded with adhesives modified in such a manner does not usually meet requirements for interior use, however. Other researchers have mixed soy protein-based products (e. g. soybean meal and soy protein isolate flour) in combination with synthetic resins, such as phenol-formaldehyde (PF) resin,[16] melamine-urea-formaldehyde (MUF) resin,[9] and polyamidoamine-epichlorohydrin (PAE) resin[17] in effort to improve water resistance of the soy protein-based bio-adhesives. All of above have been proven useful curing agents for soy protein-based bio-adhesives; the resin molecules are small and react successfully with soy protein molecules to form a solid, interpenetrating network which prevents moisture intrusion.[18] This improves the water resistance of an adhesive to the point where the resultant plywood meets requirements for interior use. Soy-based bio-adhesives enhanced by the MUF and PF resin also create formaldehyde emissions, however, adhesives with PAE resin present low solid content, which increases transfer cost and thus limits the method's applicability.

5, 5 dimethyl hydantoin polyepoxide (DMHP) can be successfully used in advanced composites due to its many useful properties, such as water solubility, outstanding mechanical performance, high chemical resistance, and superior dimensional stability.[19,20] DMHP possesses epoxy groups that react with the active groups (–NH_2, -OH, -COOH) on proteins, and additionally is water soluble with high solid content. DMHP addition is thus a practical method of enhancing soy protein-based adhesive, though it has been only relatively recently studied in depth.

In this study, soybean meal flour (SM), polyacrylamide (PAM), sodium dodecyl sulfate (SDS), and DMHP were combined in different samples to develop soybean meal-based bio-adhesive samples. Differing structures and properties of the resultant adhesives were characterized by torque rheometer, contact angle, fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscopy (AFM) analyses. Three-ply plywood specimens were fabricated with the adhesive samples and the wet shear strength of each was tested according to Chinese National Standards (GB/T 17657-1999).

2. Experimental

2.1 Materials

Soybean meal was obtained from Xiangchi Grain and Oil Company in Shandong Province of China, and then milled to 250 mesh flour (SM). Components of the soybean meal flour were tested as follows: 46.8% soy protein, 5.86% moisture, 6.46% ash, and 0.56% fat. Polyacrylamide (PAM), sodium dodecyl sulfate (SDS), epichlorohydrin (ECH), sodium hydroxide (NaOH) were obtained from Tianjin Chemical Reagent Co.. The 5, 5 dimethyl hydantoin (DMH) was obtained from Tianjin institute of synthetic materials industry. Poplar veneer (40 × 40 × 1.5 cm, 8% of moisture content) was provided from Hebei Province of China.

2.2 Preparation of the DMHP

The DMHP was prepared according to the following procedure: the ECH was firstly heated to 80 °C, then the DMH and NaOH mixture was dropwise added into ECH in 2 h and then kept at 80 °C for 1 h to obtain the DMHP. The molar ratio of the DMH/ECH/NaOH was 1:8:1 and the concentration of the NaOH solution was 50 wt%. The reaction equation was presented in Fig. 1 and the resin properties was characterized and summarized in Table 1.

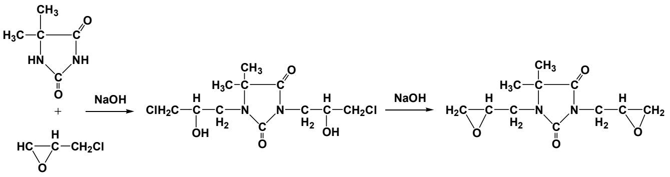


Fig. 1 The reaction equation of the DMHP.

Table 1 Properties of the DMHP.

Name	Weight per epoxide	Epoxy value	Active group number	Viscosity/ mPa·s
DMHP	0.69-0.75	0.62	2	2300-3500

2.3 Preparation of the different adhesives

For the different adhesive samples, soybean meal flour was added into deionized water/polyacrylamide solution and stirred for 10 min at 20 °C. Then sodium dodecyl sulfate and DMHP were added sequentially and further stirred for 10 min at 20 °C. The adhesive formulations are shown in Table 2.

2.4 Solid content measurement

The solid content of adhesive was determined using an oven-drying method according to the description in China National Standards (GB/T 17657-1999). Approximately 3 g (weight α) of the adhesive was placed into an oven and dried at 105°C for hours until a constant weight (weight β) was obtained. The value of the solid content was calculated using the following equation. The average value of the solid content was calculated from three parallel samples.

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

2.5 Preparation of the plywood sample

Three-ply plywood samples were prepared under the following conditions: 180 g/m^2 glue spreading for a single surface, 70 s/mm hot press time, 120 °C hot press temperature, and 1.0 MPa hot press pressure.[21] After hot press, the plywood samples were stored under ambient conditions for at least 12 h before testing.

Table 2 Different adhesive formulations.

Sample	Adhesive formulation
0 (SM adhesive)	Soybean meal flour (28 g); Deionized water (72 g)
1 (SM/PAM adhesive)	Soybean meal flour (28 g); Polyacrylamide solution (72 g, 0.01%)
2 (SM/PAM/SDS adhesive)	Soybean meal flour (28 g); Polyacrylamide solution (72 g, 0.01%); Sodium dodecyl Sulfate (1 g)
3 (SM/PAM/SDS/DMHP-5 wt% adhesive)	Soybean meal flour (28 g); Polyacrylamide solution (72 g, 0.01%); Sodium dodecyl Sulfate (1 g); 5 g DMHP
4 (SM/PAM/SDS/DMHP-9 wt% adhesive)	Soybean meal flour (28 g); Polyacrylamide solution (72 g, 0.01%); Sodium dodecyl Sulfate (1 g); 10 g DMHP
5 (SM/PAM/SDS/DMHP-13 wt% adhesive)	Soybean meal flour (28 g); Polyacrylamide solution (72 g, 0.01%); Sodium dodecyl Sulfate (1 g); 15 g DMHP
6 (SM/PAM/SDS/DMHP-17 wt% adhesive)	Soybean meal flour (28 g); Polyacrylamide solution (72 g, 0.01%); Sodium dodecyl Sulfate (1 g); 20 g DMHP

2.6 Wet shear strength measurement

The requirement of the interior use plywood (Type Ⅱ plywood) was determined using a wet shear strength test in accordance with the description in China National Standards (GB/T 17657-1999). Twelve plywood specimens (2.5 cm × 10 cm) were cut from two plywood panels and submerged into water at 63 ± 2°C for 3 h, and then dried at room temperature for 10 min before a tension test. The wet shear strength was calculated by the following equation.

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

2.7 Dry shear strength measurement

Twelve plywood specimens (2.5 cm × 10 cm) were cut from two plywood panels and then processing a tension test. The dry shear strength was calculated by the equation (2).

2.8 Moisture uptake measurement

The moisture uptake measurement of the cured adhesive was determined by gravimetric analysis. Twelve pieces of cured adhesive was placed into an constant temperature humidity chamber with 80% humidity and 50 ^{o}C temperature. The weight of the adhesive chunks was measured every two hours until a constant value obtained. The moisture uptake value was calculated by the following equation. (α:the adhesive before treatment; β: the adhesive after treatment)

$$\text{Moisture uptake value (\%)} = \frac{\text{Weight}(\beta) - \text{Weight}(\alpha)}{\text{Weight}(\alpha)} \qquad \text{Eq.(3)}$$

2.9 Contact angle measurement

Contact angle measurements on surfaces of samples parallel to the grain were performed with an optical contact angles apparatus (OCA 20 Data Physics Instruments GmbH, Filderstadt, Germany) equipped with a video measuring system with a high-resolution CCD camera and a high-performance digitizing adapter that enables instantaneous and frequency registration. SCA 20 software (Data Physics Instruments GmbH, Filderstadt, Germany) was used for data acquisition. The surfaces of veneers were sanded with 100 grit sandpaper after the oven-drying process. Sessile Droplets (5 µL, measured with a micro syringe) of adhesives were placed on the wood surface, right and left angles of drops on the surface were collected at intervals of 0.1 s for a total duration of 80 s. Contact angle measurements were made 5 s after adhesive drops were deposited. Three drops per sample were captured for all four adhesives, four samples were used per adhesive, and twelve measurements of contact angle were obtained. For increasing the adhesive flowability, each adhesive sample (10g) was added into 5g water.

2.10 Dynamic viscoelastic measurement

The apparent viscosity of adhesive was determined using a rheometer with a parallel plate fixture (20 mm diameter). The distance was set to 1 mm for all measurements. Experiments were conducted under a steady shear flow at 25°C. Shear rates ranged from 0.1 to 300 s^{-1} in 10 s^{-1} increments. All of measurements were conducted in triplicate, and the average value was reported.

2.11 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 the 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.

2.12 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 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 [18].

2.13 Atomic Force Microscopy (AFM)

The adhesives were cured in an oven at 120 ± 2°C until a constant weight was obtained and ground into a powder. The AFM sample prepared by pressed powder pellets using a compressing machine (Tianjin Tuopu instrument co., LTD). AFM measurements were performed with Shimadzu SPM-9600 equipment for evaluating the surface roughness of adhesive. AFM images were obtained at room temperature in the tapping mode with a scan rate of 1 Hz and using Si tips with a curvature radius of less than 10 nm and a spring constant of 42 $N\cdot m^{-1}$. Surface roughness of the samples were determined using the VectorScan software (software for Shimadzu's SPM-9600).

2.14 Scanning Electron Microscopy (SEM)

Adhesive sample was poured into a piece of aluminum foil and dried in an oven at 120 ± 2°C until a constant weight was achieved. A Hitachi S-3400N (Hitachi Science System, Ibaraki, Japan) scanning electron microscope was used to observe the fractured surface of adhesive. The surface was sputter coated with gold prior to examining it under the microscope.

3. Results and discussion

3.1 Solid content measurement

Solid content is a basic physical parameter for a wood adhesive which influences the performance of the adhesive during the hot press process. In general, adhesive properties are improved as solid content increases. Low solid content in an adhesive indicates that larger water content must be removed from the adhesive during the hot press process, which damages the bond of the resultant plywood.[23] The solid content of different adhesives tested in this study is shown in Fig. 2. The 30% solid content of the SM adhesive suggests a flow issue, and a further increase in the solid content which is determined by the additive in the SM adhesive system. After the addition of small amounts of PAM and SDS, solid content remained at basically the same level. As expected, the solid content of the SM/PAM/SDS/DMHP adhesive increased because increasing DMHP content is equivalent to increasing the mass of the adhesive. The solid content of the DMHP sample enhanced the adhesive's solid content gradually from 30.27 to 40.02% as DMHP addition was increased from 5 to 17 wt%. According to previous research, the solid content of soy protein-based adhesives should be over 35% to obtain favorable adhesive performance and prevent the plywood from breaking due to the water evaporation during the hot press process.[24] As DMHP addition rose to 13 wt%, the solid content of the adhesive reached 37.21% — a significant increase (38.5%) over the SM adhesive.

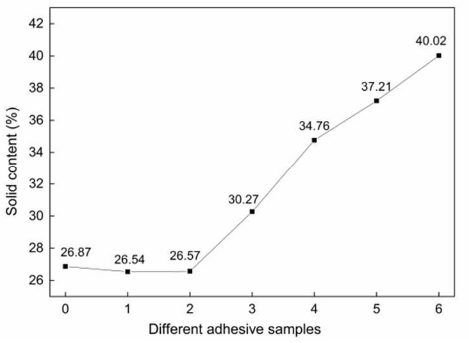


Fig. 2 The solid content of different adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive).

3.2 Water resistance measurement

The wet/dry shear strength of the plywood bonded by different adhesive samples is shown in Fig. 3. The wet shear strength of the plywood bonded by SM adhesive was 0.30 MPa, which failed to meet the interior use plywood requirement (≥0.7MPa). The wet shear strength of the plywood increased by 26.7%, to 0.38 MPa after PAM addition. Using PAM reduce the friction among protein molecules and increase the flowability during the hot press process, which benefits the adhesive distribution and penetration to form interlocking with wood. Thus the wet shear strength of the plywood bonded by the adhesive with PAM was increased. After the addition of SDS, wet shear strength increased to 0.41 MPa, up 36.7% compared to the SM adhesive sample. Denaturation of proteins is brought about with ionic surfactants, in general, both cationic and anionic. Denaturation is effectuated by perturbation of the electrostatic and nonpolar interactions which maintain the rigid tertiary structure of the protein. SDS is one of the most popular denaturants. Using SDS unfolds soy protein molecule and exposes non-polar groups, enhancing the water resistance of the adhesive.[25] The dry shear strength of the plywood showed a same tendency with wet shear strength. Comparing the wet and dry shear strength, the water resistance of the adhesive treated with PAM and SDS was improved. From another perspective of view, SDS and PAM possess electrical charges that formed a mesh structure by electrostatic attraction with charged amino acids. The cross-linker molecules easily cling into this mesh structure and create more chance to react with the soy protein molecules.[26] DMHP, which acts as a cross-linker, linked soy protein molecules by reacting with amino and hydroxyl groups to form three dimensional cross-linked networks among the macromolecules, improving water resistance. Comparing the wet and dry shear strength in Fig. 3, the water resistance of the adhesive was further improved by adding DMHP from 5 to 13 wt%. As a result, the Wet shear strength increased significantly upon 5 wt% DMHP addition – by 56.1%, to 0.64 MPa, compared to the SM/PAM/SDS adhesive. The wet shear strength of the plywood with addition of 9 wt% DMHP reached 0.76MPa, meeting the interior use plywood requirement. However, from the standard deviation at sample 4, the wet shear strength of the plywood specimens cannot be guaranteed over 0.70 MPa. As shown in Fig. 3, the wet shear strength of the plywood bonded by the adhesive with 13 wt% DMHP additions increased by 52.6%, reaching a maximum value of 1.16 MPa. By increasing the DMHP content to 17 wt%, the wet shear strength decreased to 0.69 MPa where it failed to meet the interior use plywood requirement (0.7 MPa), likely, due to low physical viscosity which caused the adhesive to significantly penetrate the veneer.

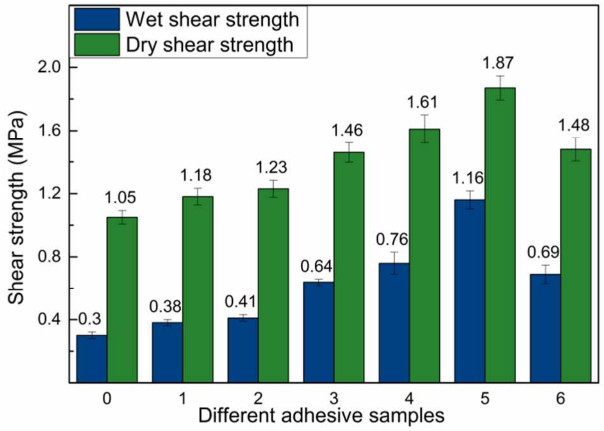
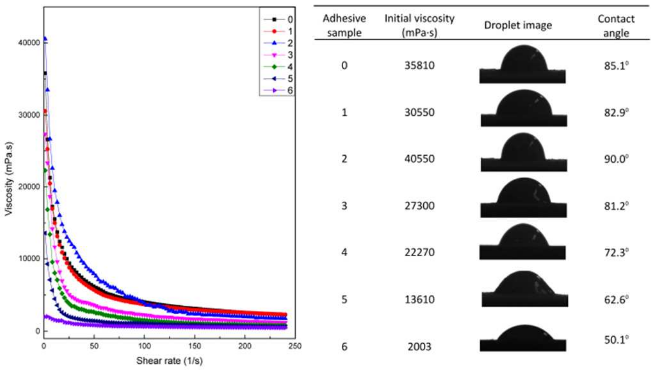


Fig. 3 The wet/dry shear strength of the plywood bonded by different adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive).

3.3 Wood wettability of the different adhesive samples

Contact angle is an indicator of an adhesive's affinity for an adherent,[27] where smaller contact angle indicates better wettability and adhesion.[28] Fig. 4 shows images and contact angles of droplets of different adhesives on the wood substrate. The SM adhesive droplets showed a hemisphere shape within 5 s and the contact angle of the SM adhesive was 85.1°. After addition of PAM and SDS, the contact angle of the adhesive was first reduced to 82.9° and then increased to 90.0°. The contact angle of the SM/PAM/SDS adhesive sample was even larger than that of the SM adhesive.

After adding DMHP (from 5 to 17%), the contact angle of the adhesive was significantly reduced from 81.2° to 50.1°, respectively.



Adhesive sample	Initial viscosity (mPa·s)	Droplet image	Contact angle
0	35810		85.1°
1	30550		82.9°
2	40550		90.0°
3	27300		81.2°
4	22270		72.3°
5	13610		62.6°
6	2003		50.1°

Fig. 4 The droplet picture on the wood substrate in 5 s after the deposition and apparent viscosity of different adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive).

The SM adhesive is a typical non-Newtonian fluid, like blood and starch solution, where shows a shear thinning behavior. As shown in Fig. 4, the apparent viscosity of the SM adhesive and hybrid adhesives decreased as the shear rate increased from 0.1 to 240 s^{-1}. The initial apparent viscosity was recorded and shown in Fig. 4, following a similar trend with the contact angles variation. Because PAM is a water-soluble polymer and can reduce frictional resistance within a liquid, thus the apparent viscosity of SM/PAM adhesive decreased by 14.7% and the contact angle decreased to 82.9°. A reduced contact angle means a good wettability for a wood adhesive, which improve the bond between wood and adhesive. After adding SDS, the soy protein molecules unfolded and the distance between them decreased, increasing the force between molecules[25] and thus increasing the apparent viscosity of the resultant adhesive by 32.7% (to 40,550 mPa·s). From the droplet image, the contact angle increased from 82.9° to 90.0° with the SDS addition, which caused by the increase of viscosity and exposed hydrophobicity groups after protein denaturing. In general, the operating viscosity limits of soybean meal-based bio-adhesive ranges from 5000 to 25,000 mPa·s – if an adhesive is overly viscous, adhesive flow and distribution problems result. Therefore, the viscosity of the SM/PAM/SDS adhesive is not acceptable for the industrial application.

After incorporating DMHP, the SM/PAM/SDS/DMHP-5 wt% adhesive showed much lower apparent viscosity, 27,300 mPa·s. The viscosity of the adhesive further decreased to 2,003 mPa·s with the DMHP addition reaching at 17%. Therefore, the contact angle of the adhesive decreased from 81.2° to 50.1° with the DMHP addition increase from 5 to 17 wt% in the adhesive sample. DMHP has a small molecular weight and can be used as a disperser to decrease the effective or hydrodynamic volume, reducing overall viscosity.[29] To this effect, DMHP acted as a cross-linker as well as viscosity reducer, allowing adhesive easy wetting and having high flowability on the wood surface, and ultimately benefiting the wet shear strength improvement of the plywood sample.

3.4 FTIR spectroscopic analysis

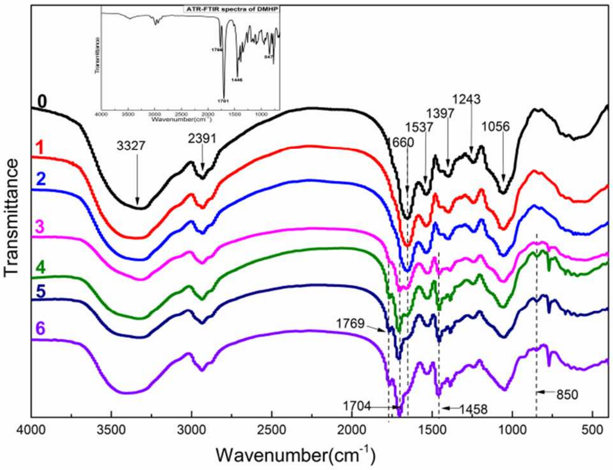


Fig. 5 FTIR spectra of of different adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive). And the curing process of the SM/PAM/SDS/DMHP adhesive.

Water readily associates with hydrophilic groups (e.g., hydroxyl groups) via hydrogen bonds, resulting in a poor water resistance of the adhesives. FTIR spectra of DMHP and its hybrid adhesives are presented in Fig. 5. A peak was observed at approximately 3327 cm^{-1}, related to free and bound O-H and N-H bending vibrations that formed hydrogen bonds with the carbonyl groups caused by peptide linkage in the protein. The peak observed at approximately 2930 cm^{-1} was attributed to symmetric and asymmetric stretching vibrations of the $–CH_2$ groups in the different adhesives. The main absorption bands of the peptide were related to peaks at approximately 1660, 1537, and 1396 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.[30] In the spectra of DMHP, a peak observed at approximately 1701 and 1766 cm^{-1}, related to characteristic of carbanyl group stretching vibration, and the peak at approximately 1447 cm^{-1} were attributed to characteristic of C-N stretching vibration. The absorption peak at 846 cm^{-1} was assigned to free epoxy group skeleton vibration.[31]

Amide I shifted from 1657-1659 to 1661-1668 cm^{-1} (blue shift) in the spectrum of the adhesive with DMHP, indicating that the soy protein molecule had more dense structure than in the SM adhesive. This dense structure caused by the chemical reaction between DMHP and soy protein molecule, which increased the adhesive's cross-linking density. The characteristic peaks of hydantoin ring, including 1701, 1766, and 1447 cm^{-1} were observed in the spectrum of the adhesive with DMHP and the signal intensity of these peaks increased with the DMHP addition increasing, which demonstrated the favorable dispersibility of the DMHP in the adhesive system. After incorporating DMHP, a strong absorption peak should have appeared at 846 cm^{-1}; but, as shown in Fig. 5, only a minor one (846 cm^{-1}) was present, which became even negligible in the spectrum of the adhesive with DMHP. This phenomenon suggests that epoxy group of the resin reacted with active hydrogen on –OH and $–NH_2$ groups in the protein molecules during the curing process in a ring-opening reaction. (most likely the specific reaction discussed in Fig. 6.)

From the above analysis, the water resistance of the adhesive should increase with the DMHP addition from 5 to 17 wt%. However, according to Fig. 3, the wet shear strength of the resultant plywood sample decreased when using the adhesive with 17 wt% DMHP addition, attributing to the very low viscosity of the adhesive caused by the DMHP (Fig. 4). A wood adhesive with low viscosity (≤3000 mPa·s) was easy to infiltrate the pores of wood, which reduced the bond and water resistance.

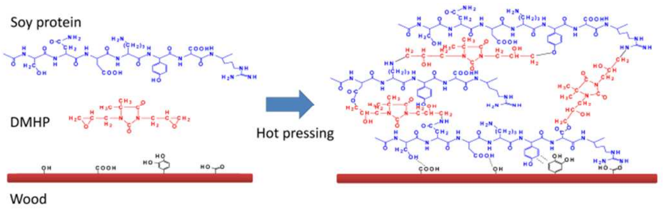


Fig. 6 The curing process of the SM/PAM/SDS/DMHP adhesive.

3.5 X-ray diffraction analysis

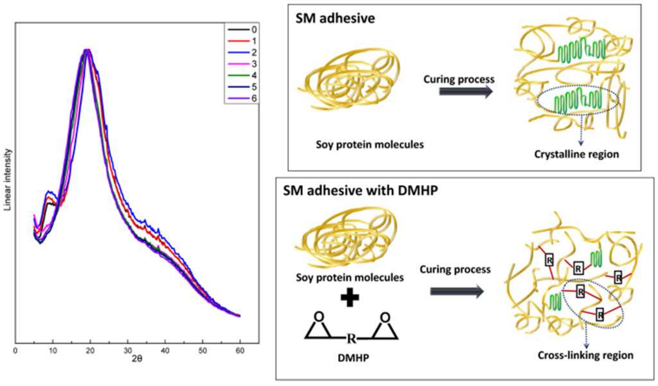


Fig. 7 The X-ray diffraction patterns of different adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive). And the effect of DMHP on adhesive crystallinity reduction.

Table 3 The crystallinity of different cured adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive).

Adhesive sample	0	1	2	3	4	5	6
The crystallinity (%)	14.3	14.5	16.5	13.9	11.3	10.1	7.2

X-ray diffraction patterns of the SM adhesive and its hybrid adhesives are shown in Fig. 7, and the crystallinity of the different adhesive samples is presented in Table 3. On the (110) crystal face, the SM adhesive exhibited one strong characteristic peak at 2θ values near 8.8. The crystallization peak was disappeared in the X-ray diffraction patterns after adding DMHP, however, suggesting that a chemical reaction had occurred between the DMHP and soy protein. This confirms the results discussed above (FTIR analysis).

As shown in Table 3, crystallinity increased from 14.5 to 16.5% after addition of SDS, which may attributed to the unfolded protein molecules after denaturing rearranging and forming more crystalline domain during hot press process. In general, increasing cross-linking in an adhesive reduces its crystallinity.[33] After adding DMHP to the adhesive sample, crystallinity decreased from 16.5 to 10.1%, probably due to the ring-opening reaction between DMHP and soy protein that had increased the cross-linking density of the cured adhesive, thus decreasing crystallinity (as shown in Fig. 7). Comparing Fig. 3 and 7 shows a negative correlation between adhesive crystallinity and wet shear strength, which validates the above analysis. The elevated cross-linking density of the cured adhesive, caused by the reaction between the DMHP and soy protein, prevented water intrusion and enhanced the mechanical properties of the plywood, which was in accordance with the result in Fig. 3 analysis.

3.6 AFM analysis

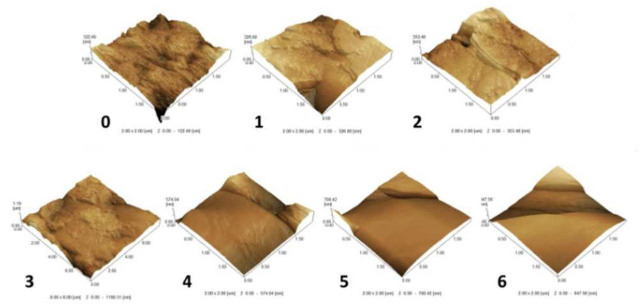


Fig. 8 AFM 3-dimensional image of different cured adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive).

When assessing adhesion quality, surface character must be taken into account because it determines the water resistance of the adhesive under a broad range of conditions. AFM analysis was conducted for this purpose, as it is a sensitive and reliable technique that offers a suitable means for acquiring qualitative and quantitative data concerning surface topography.[34,35] The typical surface topography of the cured SM adhesive and its hybrid adhesives are shown in Fig. 8. Careful evaluation of the images shows where DMHP addition generally facilitated a uniform surface morphology. Differences in surface morphologies of the SM adhesive and hybrid adhesives, which were measured and expressed in terms of surface roughness, are shown in Table 4. Surface roughness values fell into the following order: SM/PAM/SDS > SM > SM/PAM > SM/PAM/SDS/DMHP-5 wt% > SM/PAM/SDS/DMHP-9 wt% > SM/PAM/SDS/DMHP-13 wt% > SM/PAM/SDS/DMHP-17 wt% adhesive, in accordance with the viscosity and contact angle variations. PAM acted as an emulsifier, distributing the soybean meal flour uniformly to where the surface roughness (R_a) of the cured adhesive was reduced from 40.1 to 37.6. After adding SDS, the protein molecules were unfolded and inter-forces among soy protein molecules increased dramatically, which reduced the emulsification effects of PAM. At the same time, the unfolded soy protein molecules grew disordered during the curing process. The surface roughness of the cured SM/PAM/SDS adhesive thus increased from 37.6 to 69.1 compared to the SM/PAM adhesive. DMHP then reduced the surface roughness of the cured adhesive from 69.1 to 36.5 at the addition of 5%, and further reduced to 8.9 at the addition of 17 wt%, compared to the SM/PAM/SDS adhesive.

Table 4 The surface roughness of different cured adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive).

Adhesive sample	0	1	2	3	4	5	6
R_a (nm)	13.864	11.211	25.180	10.989	9.073	8.686	6.013

Table 5 Moisture uptake of different cured adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive).

Adhesive sample	0	1	2	3	4	5	6
Equilibrium moisture uptake (%)	15.5±0.2	14.1±0.3	14.6±0.3	10.2±0.1	9.6±0.1	9.5±0.2	9.3±0.2

Images of the SM, SM/PAM, and SM/PAM/SDS adhesives show more folds than the cured adhesive with DMHP, which has a much smoother surface. Table 5 showed the moisture uptake of different cured adhesive samples. Adding DMHP in the adhesive sample, the moisture uptake of the cured adhesive decreased, which meant the adhesive with DMHP efficiently prevented moisture intrusion and improved moisture resistance compared to adhesives lacking DMHP. This was in accordance with the result in Flauzino's research[36]. When incorporating 13 wt% of DMHP, the moisture uptake decreased from 15.5% to 9.5%. Compared Table 4 and 5, creating a reduced surface roughness benefited for the moisture resistance of the cured adhesive. The smooth surface of adhesive with DMHP can be attributed to adhesive flowability increasing after DMHP incorporating and the fact that DMHP cross-linked with soy protein molecules to form a solid, net-like system.

3.7 SEM analysis

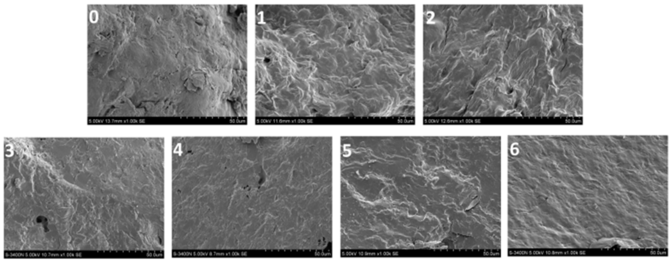


Fig. 9 The fracture surface micrograph of different cured adhesive samples: 0 (SM adhesive), 1 (SM/PAM adhesive), 2 (SM/PAM/SDS adhesive), 3 (SM/PAM/SDS/DMHP-5 wt% adhesive), 4 (SM/PAM/SDS/DMHP-9 wt% adhesive), 5 (SM/PAM/SDS/DMHP-13 wt% adhesive), 6 (SM/PAM/SDS/DMHP-17 wt% adhesive).

A fracture surface micrograph of the cured SM adhesive and its hybrid adhesives is shown in Fig. 9. A large number of holes and cracks were observed on the fracture surface of the SM adhesive, the entire fracture surface of which appeared very loose and disordered. Said holes and cracks were formed by water evaporation in the adhesive during the hot press process, which was easily intruded by moisture and caused the low water resistance of the SM adhesive (Fig. 3 and Table 5). This was in accordance with result in Zhang's research.[37] After DMHP was introduced, fewer holes and cracks were observed, and the fracture surface of the cured adhesive became smoother and more compact. This was caused by the reaction between the DMHP and soy protein molecules forming a cross-linking network, and improving the moisture resistance of the adhesive (Table 5). In theory, the adhesive with 17 wt% DMHP adhesive presented the best water resistance. But, according to Fig. 3, the wet shear strength of the plywood bonded by the adhesive with 17 wt% DMHP is lower than that with 13 wt% DMHP, even lower than that with 9 wt% DMHP, which was due to the very low viscosity of the adhesive caused by the DMHP addition further increase (Fig. 4).

Conclusions

Using DMHP effectively improved the water resistance of the soybean meal-based adhesive and its resultant plywood investigated in this study. This phenomenon was attributed to three reasons: the first one was the formation of a solid cross-linking network, caused by the reaction between the epoxy groups and active groups of soy protein molecule; the second one was the formation of smoother fracture surface which prevented moisture intrusion; the last one was the resultant appropriate viscosity and elevated wettability of the adhesive, which benefited adhesive distribution during the hot press process and formed more interlock with wood surface, thus created a better water resistance. Further increase the DMHP addition decrease the water resistance of the adhesive because the resultant the very low viscosity by adding DMHP over penetrated into wood surface and hard to form effective bond.

The wet shear strength of the plywood bonded by the adhesive with 13 wt% of DMHP increase by 182.9%, to 1.16 MPa, which met interior use plywood requirements. The solid content and viscosity was 37.21 wt% and 13,610 mPa·s, which met the requirement of plywood adhesive for industrial application. Overall, this study confirms that DMHP addition is an effective method of enhancing soybean meal-based bio-adhesive.

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