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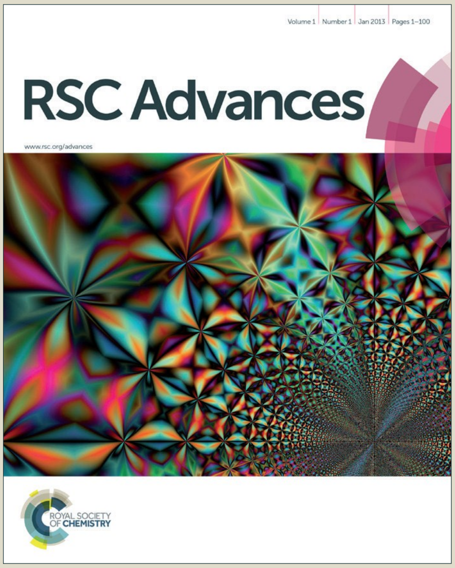

ROYAL SOCIETY OF CHEMISTRY

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Journal Name

ARTICLE

A sepiolite-based united cross-linked network in a soybean meal-based wood adhesive and its performance

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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In this study, soybean meal and triglycidylamine (TGA) was used to develop a soybean meal-based adhesive (as SM adhesive and TSM adhesive). The sepiolite (SEP) was initially treated with a KH-560 and then introduced into the soybean meal-based adhesive system to form a united cross-linked network (UCN) to compliment the water resistance of the resultant adhesive. Three-ply plywood was fabricated to measure the wet shear strength of the adhesive. The functional groups, cross section, crystallization property and degree of crosslinking of the resultant adhesives were characterized in detail. The experimental results showed that modified SEP (MSEP) could well distribute in the TSM adhesive system and improved the water resistance of the adhesive by 45.7%. The epoxy groups on the MSEP combined the cross linked protein network with the SEP system forming a UCN that increased the degree of crosslinking in the adhesive, which greatly improved the adhesive's water resistance. This UCN also produced a synergistic toughening effect and created a compact fracture to prevent moisture intrusion, which aided water resistance. The wet shear strength of the resultant plywood bonded by the TSM/MSEP adhesive with the UCN was improved by 228% (1.18 MPa) over that of the native SM adhesive, which met the interior use plywood requirement.

1. Introduction

Adhesives based on formaldehyde resins have dominated wood panel manufacturing field for many decades.[1] Resins such as urea-formaldehyde (UF), phenol-formaldehyde (PF), melamine-formaldehyde (MF) and melamine-urea-formaldehyde (MUF) play an important role in the wood composite industry due to their high adhesive strength and excellent water resistance. But these formaldehyde-based resins cause environmental pollution and are considered to be carcinogenic to humans.[2] In addition, most of the formaldehyde-based adhesives are derived from non-renewable petrochemicals and natural gas. With the increasing price and decreasing reserves of non-renewable fossil fuels, finding renewable and environmentally-friendly substitutions for petrochemicals is an urgent and serious problem.[3]

As a major agricultural crop, soybean has advantages, such as easy farming, year production, high productivity, so that, the soybean was cultivated worldwide, especially in the USA, Brazil, Argentina and China.[4] Therefore, biodegradable, abundant, non-toxic, renewable, commercially-available soy protein-based adhesives are consider to be one of the most promising alternatives to petroleum-based adhesives.[5] However, the low water resistance and the low bond strength of soy protein adhesives limit their application.[6] Many efforts have been made to improve the adhesive properties of soy protein adhesives including grafting of groups, using denaturing agents, cross linkers, and protein enzymes.[7-10] Of these approaches, it has been found that use of active synthesis resins and cross linkers were the most effective ways of improving the water resistance of soy protein based adhesives. This includes the phenol-formaldehyde resin,[11] melamine-urea-formaldehyde resin,[2] anethylene glycol diglycidyl ether,[12] 5,5-dimethyl hydantoin polyepoxide ,[13] and maleic anhydride.[14] These additives react with the functional groups in the protein molecules to form a dense network,[15] which resists water intrusion and improved the water resistance of the resultant adhesive.[16] Our previous research centered on the physical modification of a fibrous-shaped material such as attapulgite or cellulose nano-whiskers was used to modify the soy protein adhesive.[17,18] Experimental results showed that the fibrous shaped material dispersed well in the adhesive system and formed an interpenetration network with soy protein molecules. But there were no chemical reactions between the fibrous shaped material and the protein molecules. Thus the reinforcing effect for improving the water resistance of the adhesive was not significant. Therefore, if fibrous shaped material can be connected the soy protein molecules with chemical bonds to form a united crosslinked network, this may well improve the qualities of the adhesive.

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Sepiolite clay (SEP), a hydrated magnesium silicate with a microfibrous morphology (needle-like shape), has the theoretical unit-cell formula $Si_{12}O_{30}Mg_8(OH)_4\bullet(H_2O)_4\bullet 8H_2O$.[19,20] Alternating longitudinal blocks and channels (tunnels) are found in the SEP structure, which produce long needles with a high surface area (approximately 374 m^2/g).[21] Because of the small unit size, high surface area and good dispersion performance, SEP is able to uniformly disperse in a resin matrix producing a synergistic toughening effect.[22] Therefore, SEP has been used as a filler in natural rubber, plastics and formaldehyde-based resins. [23,24] Also, the numerous silanol groups on the surface of the sepiolite particles provide sites for hydrogen bonding and van der Waals interactions in composites, contributing to the reinforcing effect of SEP.[25] In particular, the silanol groups can graft to other active groups, such as the functional groups in the protein molecules which would form a cross linked interpenetrating network with the adhesive. Therefore, SEP may be useful as a reinforcing material for soy protein adhesives.

In this reported research, soybean meal and triglycidylamine (TGA) were used to develop a soybean meal-based adhesive. SEP was initially treated with KH-560 and then used to modify the soybean meal-based adhesive. Three-ply plywood specimens were fabricated using the modified adhesive to determine the water resistance of the adhesive. The functional groups, cross section, crystallization property and degree of crosslinking of the cured adhesives were determined to establish the relative performance of the adhesive.

2. Experimental

2.1. Materials

Soybean meal flour (SM) (46% soy protein, 5.86% moisture, 6.46% ash, 0.56% fat, and 38.12% carbohydrate milled to 200 mesh flour using a laboratory grinder) was obtained from Xiangchi Grain and Oil Company in Shandong Province of China. γ-(2,3-epoxypropoxy)propytrimethoxysilane (KH-560) and other chemical reagents used in this work were analytical grade and obtained from Beijing Chemical Reagents Co. Ltd. (Beijing, China). Poplar (*Populus tomentosa* Carr.) veneers (40 cm × 40 cm × 1.5 cm, 8% of moisture content) were purchased from Hebei province, China. SEP (moisture content ≤ 2%, 1 g/cm^3, 300-400 mesh) was purchased from the QiLiPing sepiolite factory, China.

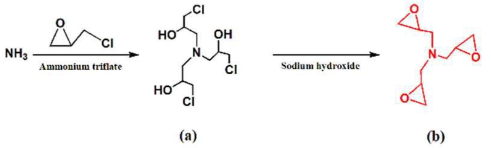
Pre-treatment of SEP clay. The SEP clay was treated with hydrochloric acid. Typically, 100 g of the SEP clay was dispersed in 1 M hydrochloric acid solution at the solid-liquid ratio of 1:10. The resultant suspension was mechanically stirred at 500 rpm for 4 hours at 70 °C and then left standing for 24 h. The resultant suspension was filtered, washed to neutrality with deionized water and dried at 80 °C to a constant weight. Finally, the dry product was ground and passed through a 300 mesh sieve.

2.2. Modification of sepiolite

Modification of the pre-treated SEP. Approximately 10 g of a silane coupling agent (KH-560) was dissolved in 4 g deionized water and 36 g (95%) of an aqueous ethyl alcohol solution. Dilute acetic acid solution （40%） was used to adjust the pH of the mixture to 4.5-5.5. Sepiolite was added to a flask containing 100 g of ethyl alcohol. The suspension was stirred vigorously to disperse the clay. Next a select amount of silane coupling agent (KH-560) solution (20%) was added to the suspension. The mixture was stirred for 1h at 70 °C, then filtered and washed several times with deionized water. The resulting filter cake was then air dried at 80 °C in an oven to a constant weight. Finally, the dry product was ground and passed through a 300 mesh sieve.

2.3. Preparation of the triglycidylamine

Triglycidylamine was synthesized according to a previous report[26] and the reaction pathway is illustrated in Scheme 1. Epichlorohydrin and aqueous ammonia with a mole ratio 5:1 were placed in a three-necked flask equipped with a condenser and stirrer. The mixture was stirred continuously with a rate of 800 rpm. Ammonium triflate was used to catalyze the reaction at 23 °C for 48 hours, then at 35 °C for 3 hours. The residual epichlorohydrin and ammonium hydroxide were removed by a vacuum distillation and the resulting colorless syrup consisted of tris-(3-chloro-2-hydroxypropyl) amine (Scheme 1(a)). An excess of sodium hydroxide solution (50%) was added to initiate the epoxy-ring closure reaction at 20 °C for 2 hours. Because the reaction was highly exo-thermic, an external ice-water cooling circulator was required to maintain the temperature. The precipitate of NaCl was filtered and the residue was vacuum-distilled to obtain pure viscous TGA (Scheme 1(b)).



Scheme 1 The synthesis procedure for triglycidylamine and its chemical structure.

2.4. Preparation of soybean meal-based adhesives

The SM adhesive. SM (30 g) was added to tap water (70 g) and stirred for 30 min at 20 °C.

The TSM adhesive. The SM adhesive (100 g) and TGA (8 g) were mixed and stirred for 30 min at 20 °C.

The TSM/SEP adhesive. SEP (2 g) was added into TSM (100 g) adhesive, stirred for 30 min at 20 °C, and ultrasonically dispersed for 3 min by VCX 800 of SONICS.

The TSM/MSEP adhesive. MSEP (2 g) was added to the TSM (100 g) adhesive, stirred for 30 min at 20 °C, and ultrasonically dispersed for 3 min by VCX 800 of SONICS.

The TSM/SEP/KH-560 adhesive. KH-560 (1 g) was added to the TSM/MSEP adhesive and stirred for 30 min at 20 °C.

2.5. Viscosity of the soybean meal-based adhesives

The apparent viscosity of the soybean meal-based adhesives was measured using a Brookfield DV-II viscometer employing the 64# rotor with a spinning rate of 100 rpm. An average of three replicate measurements was reported as the viscosity of each sample.

2.6. Preparation of three-ply plywood samples

Three-ply plywood samples were prepared using the following conditions. The select adhesive was applied with a loading of 180 g/m^2, which was evenly spread on a single plywood surface, 120 °C hot press temperature, 70 s/mm hot press time, and 1.0 MPa hot press pressure. After the hot press, the plywood samples were stored at ambient conditions for at least 12 h before testing.

2.7. Wet shear strength measurement

The properties of the bonded interior-use plywood (Type II plywood) were determined using a wet shear strength test in accordance with the requirements of the China National Standards (GB/T 17657-2013). Eight plywood specimens (2.5 cm×10 cm) were cut from two plywood panels and submerged in water at 63 ± 2 °C for 3 h and then dried at room temperature for 10 min before being subjected to tension test using a common tensile machine operating at a speed of 10.0 mm/min.

2.8. Residual rate test

The adhesive samples were placed in aluminum cups, which were then placed in an oven at 120 ± 2 °C until a constant weight (M) was obtained. The cured adhesives were soaked in tap water for 24 h at ambient temperature, then oven-dried at 105 ± 2 °C, until a constant weight was obtained (m). The residual rate is defined as m divided by M, as in eqn. (1). The average value of the residual rate was calculated from six parallel samples.

$$\text{Residual rate (\%)} = \frac{\text{m (g)}}{\text{M (g)}} \times 100 \qquad (1)$$

2.9. Fourier transform infrared (FTIR) spectroscopy

The adhesives were cured in an oven at 120 ± 2 °C until a constant weight was obtained. Then each was individually ground with a motor and pestle into a powder. Each powder was mixed with KBr and pressed into a pellet for analysis. FTIR spectra of the various cured adhesives were recorded using a Nicolet 6700 spectrometer (Nicolet Instrument Corporation, Madison, WI) from 500 to 4000 cm^{-1} with 4 cm^{-1} resolution using 32 scans.

2.10. X-ray diffraction (XRD)

The adhesives were cured in an oven at 120 ± 2 °C until a constant weight was obtained and then each was ground into a powder. X-ray diffraction (XRD) patterns of these powders were recorded on a D8 advance diffractometer (Bruker, U.S.A) using a cobalt source and 0.02 theta scan ranging from 5^o to 60^o at 45 kV and 30 mA.

2.11. Scanning electron microscopy (SEM)

Adhesive samples were placed on a piece of aluminum foil and dried in an oven at 120 ± 2 °C until reaching a constant weight, then sputter-coated with gold using an E-1010 Hitachi Ion Sputter (Japan). A Hitachi (Hitachi Science System, Ibaraki, Japan) scanning electron microscope was then used to observe the fractured surface of the adhesive.

3. Results and Discussion

3.1. Sepiolite modification

Organic modification of sepiolite can reduce the surface energy of the silicate layers and enhance the miscibility of the silicate in the polymer matrix. [27] There are many silanol groups on the surface of SEP, which can graft to silane coupling agents (KH-560) to promote the introduction of epoxy groups on the clay surface. The modified SEP can then react with the $-NH_2$, -COOH or other exposed groups on the protein molecules to increase the crosslink density of the resultant soy protein adhesive during the hot press process furthering enhancing the performance of the adhesive.

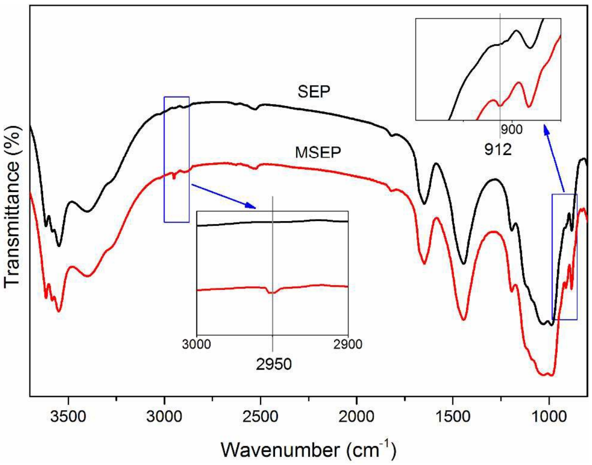


Fig. 1. FTIR spectra of SEP and MSEP.

Figure 1 depicts the FTIR spectra of sepiolite (SEP) and modified sepiolite (MSEP). Peaks in the 3401–3615 cm^{-1} region can be attributed to OH stretching vibrations of the zeolitic and Mg-coordinated water molecules inside the clay tunnels and bound to the magnesium ions in the mineral structure. Bending vibrations of the zeolitic or channel water molecules contributed to a signal at 1648 cm^{-1}. Peaks associated with Si-O bonds in the tetrahedral sheets were seen between 1300 and 800 cm^{-1}. Si-O-Si bonds produced absorption bands at 1029 and 987 cm^{-1}.[27] For the modified sepiolite, a new peak at 2950 cm^{-1} can be identified as the C-H stretching vibration belonging to the C-H stretching vibration mode of KH-560[28] and the new peak at 912 cm^{-1} is a characteristic peak for epoxy group.[29] These results are indicative of the successful grafting of KH-560 to the surface of SEP.[28]

The XRD curves of the sepiolite and the modified sepiolite are presented in Fig.2. Both samples generally exhibit a crystalline nature. The strong diffraction peak observed at 2θ = 8.4° for sepiolite is related to the primary diffraction of the (100) crystalline plane.[30,31] Since sepiolite is a non-swelling clay, organic modification occurs mainly through surface modification, so that it maintains its crystalline structure.[32] However, the organic modification can decrease the aggregation of fibers and result in a weak diffraction peak.[27] It can be clearly seen that crystallinity of the modified sample decreased in comparison to the natural SEP, indicating that important reactions had occurred at the sepiolite surface in the modified material.

The above analysis indicated clearly that chemical reaction occurred during the modification as shown in Scheme 2.

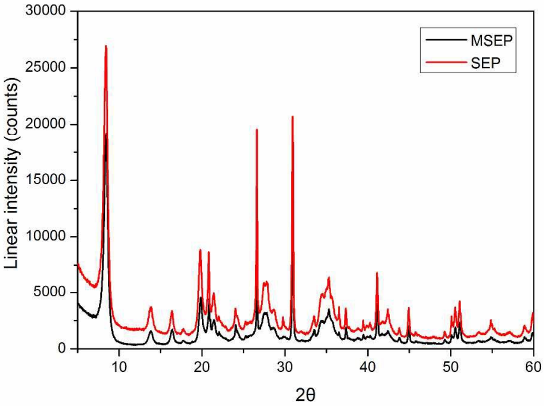
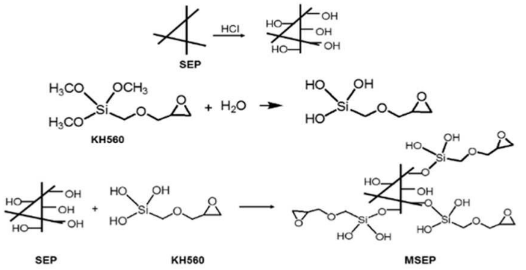


Fig. 2. XRD patterns of SEP and MSEP.



Scheme 2 Schematic illustration of the surface modification of sepiolite (SEP) by silane coupling agent KH-560.

3.2. Soybean meal-based adhesives

3.2.1. Viscosity

Viscosity largely governs the penetration and wetting of soy protein on the wood surface and into the wood interior, which can directly affect adhesion.[33] The operating viscosity limits of soybean glues are very large, ranging from 500 to 75,000 cP depending upon the application and the nature of the materials to be glued. A viscosity that is too high or too low is unfavorable for bonding. A soybean meal-based adhesives exhibiting a viscosity that is too high will cause adhesive flow and distribution issues and a viscosity that is too low will lead to over-penetration of the adhesive into wood surface during the hot press process.[34] The viscosity of the soybean meal-based adhesives is shown in Table 1. Considering the SM adhesive, incorporation of TGA decreased the viscosity of the SM adhesive by 58% from 36,980 to 15,520 mPa s. This result agreed with the research reported by Li et al.[12] and Wu et al.[35], who reported that a small molecular substance could distribute in SM as a molecular lubricant that would decrease the viscosity of the adhesive. After introducing SEP, the viscosity of the TSM/SEP adhesive increased to 68,520 mPa s, because of dispersion of the SEP fiber in the adhesive as reported by Moya et al.[36]. The small size of the SEP allowed it to be inserted into the protein molecular chains. Furthermore, the Si–OH groups on the surface of SEP formed hydrogen bonds with the –OH or –NH2 of the protein molecules, which increased intermolecular interactions and improved the viscosity of the soybean meal-based adhesive. This increased viscosity implied that the SEP dispersed well in the TSM adhesive system. When the SEP surface was functionalized, this induced changes in the type and strength of interactions between the particles and the monomers, which may have favored the breaking up of the SEP aggregates and the dispersion of SEP needles.[37] So, compared with the TSM/SEP adhesive, adding MSEP further increased the viscosity of the resultant TSM/MSEP adhesive to 73,040 mPa s.

Table 1 Viscosity of the soybean meal-based adhesives, (a) SM adhesive, (b) TSM adhesive, (c) TSM/SEP adhesive, (d) TSM/MSEP adhesive.

Adhesives	a	b	c	d
Viscosity (mPa s)	36,980	15,520	68,520	73,040

Table 2 The residual rate of the different soybean meal-based adhesives: (a) SM adhesive, (b) TSM adhesive, (c) TSM/SEP adhesive, (d) TSM/MSEP adhesive.

Samples	a	b	c	d
Residual rate (%)	72.2	75.1	76.8	78.9

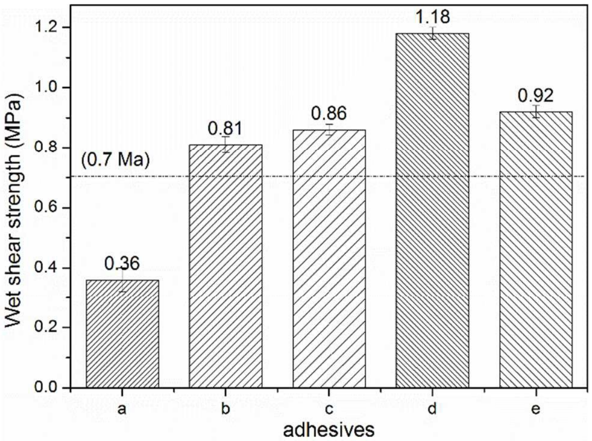


Fig.3. Wet shear strength of plywood bonded by the soybean meal-based adhesives: (a) SM adhesive, (b) TSM adhesive, (c) TSM/SEP adhesive, (d) TSM/MSEP, (e) TSM/SEP/KH-560.

3.2.2. Wet shear strength measurements

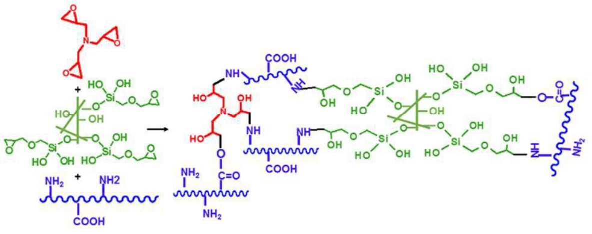
The wet shear strength of the soybean meal-based adhesive is shown in Fig.3. The wet shear strength of the plywood bonded by the SM adhesive was 0.36 MPa, which was far from compliance with the type Ⅱ requirement (⩾ 0.7 MPa) of the China National Standard (GB/T 17657-2013). In general, there was a positive correlation between the residual rate of the adhesive and the cross-linking degree.[38] The residual rate of shear strength of the different soybean meal-based adhesives is shown in Table 2. As can be seen in Table 2, the residual rate of the SM adhesive was the lowest, 72.2%, indicating that the SM adhesive had the lowest degree of cross-linking among all the soybean meal-based adhesives. Addition of TGA to the mixture caused the wet shear strength to increase by 125% to 0.81 MPa. This result was in agreement with other studies based on the effects of use of an epoxy cross-linking agent on the SM adhesive.[12] The epoxy groups in the cross linker reacted with active groups in the soy protein molecules (such as $-NH_2$,-COOH) to form a cross-linked structure, which resulted in increased water resistance in the adhesive (Scheme 3).

Compared with the SM adhesive, the increased residual rate (from 72.2% to 75.1%) of the TSM adhesive also implied that cross-linking formed between TGA and the SM adhesive. When SEP and MSEP were added to the TSM adhesive, the wet shear strength increased by 139% to 0.86 MPa and 228% to 1.18 MPa, by contrast with the SM adhesive, respectively. Meanwhile, when SEP and MSEP were added to the TSM adhesive, the residual rate increased to 76.8% and 78.9%, respectively. During the curing process of the adhesive, the fibre shape SEP well dispersed in the soybean meal-based adhesive and presented a physical filling effect. This filling effect improved the water resistance of the resultant adhesive. In the case of the TSM adhesive, adding SEP, caused the wet shear strength increased from 0.81 to 0.86 MPa, which implied that the SEP was uniformly and individual dispersed in the resin matrix resulting in a synergistic toughening effect. This caused the wet shear strength of the TSM/SEP adhesive to increase. Adding MSPE to the TSM adhesive further increased the wet shear strength to 1.18 MPa, which was 45.7% higher than that of adhesive b (TSM adhesive) and 37.2% higher than that of adhesive c (TSM/SEP adhesive). The epoxy groups of MSEP appeared to react with function groups in the protein molecules, which chemically connected the cross linked protein net system and the SEP. This connection combined two different systems and produced synergistic effect, which significantly improved the water resistance of the adhesive. After grafting KH560, the residual rate of the adhesive d was increased from 76.8 to 78.9%, which also validated that a united cross-linked network (UCN) had formed. And, this UCN greatly improved the water resistance of the soybean meal based adhesive. Compared adhesive e with adhesive d, the wet shear strength of the plywood bonded by adhesive e was 0.92 MPa, which is lower than adhesive d (1.18 MPa), implying the adhesion improvement of adhesive d was caused by the UCN structure formation, rather than simply elevating the number of epoxide groups after adding MSEP. The illustration of the UCN formation is shown in as Scheme 3.

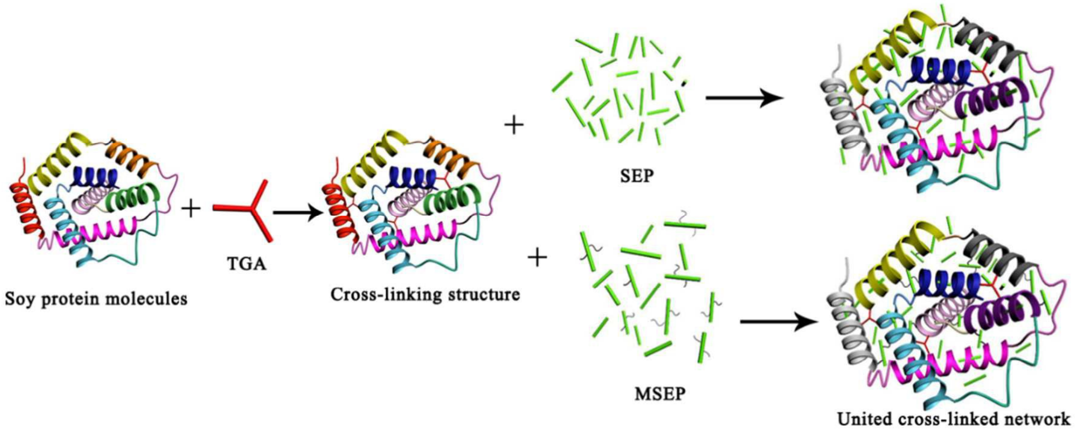
3.2.3. FTIR spectroscopic analysis

FTIR studies were conducted on the adhesives to reveal the possible chemical and physical interactions of the modified SM adhesives. Figure 4 shows FTIR spectra of soybean meal-based adhesives. All the samples' the spectra exhibited the relevant peaks at 1654, 1523 and 1232 cm^{-1} (Fig. 4), which are characteristic of amide I (C=O stretching), amide II (N–H bending), and amide III (C–N and N–H stretching), respectively.[39] The peak observed at approximately 2933 cm^{-1} was attributed to symmetric and asymmetric stretching vibrations of the $-CH_2$ groups in the different adhesives. The absorption peak near 3328 cm^{-1} corresponded to the N–H and O–H groups stretching vibrations of hydroxyl and amide groups. After introducing TGA, SEP, MSEP, this peak shifted from 3328 to 3350 cm^{-1} (blue shift), indicating that the resultant adhesive formed a more dense structure than that in the SM adhesive. This dense structure resulted from the chemical reaction between TGA/MSEP and soy protein molecules, which increased the adhesive's cross-link density.[13] The FTIR spectra also showed that the absorption peak of the epoxy group at 912 cm^{-1} disappeared for the adhesives containing TGA or MSEP, which indicated that all epoxy groups has participated in the curing reaction.[29] By comparison, a new peak appeared near about 1739 cm^{-1} with the addition of TGA and MSEP to the SM adhesive, which was related to the carbonyl group of the ester bond and originated from the esterification reaction between epoxy groups and carbonyl groups of the soy protein.[40] With the introduction of the TGA and MSEP, the absorption band at 1392 cm^{-1} in the spectrum of the resultant adhesive was significantly weakened. This suggested that the amino group was transformed by the reaction with epoxy group. Theoretically, if the –OH groups of sugar reacted with epoxide groups, it should form an ether bond and its absorption peak is observed around 1160 cm^{-1} in the FTIR spectrum. From the FTIR spectra of adhesive b, c, d (Figure 4), the intensity of ether bond absorption peak was not obvious increased, which couldn't prove the chemical reaction between sugar and epoxide group.

The above analysis indicated that the TGA, MSEP and SM were not simply blended into the adhesive, but that complex interactions existed between the two. The cross-linking reaction of the soy protein and TGA/MSEP generated a more stable chemical bond, which enhanced the performance of the soybean meal-based adhesive. The reaction mechanism of TGA, SEP, MSEP and soy protein molecule is showed in Scheme 4.



Scheme 4 Schematic illustration of the action mechanism of TGA, SEP, MSEP and soy protein molecule



Scheme 3. Schematic illustration of the UCN formation.

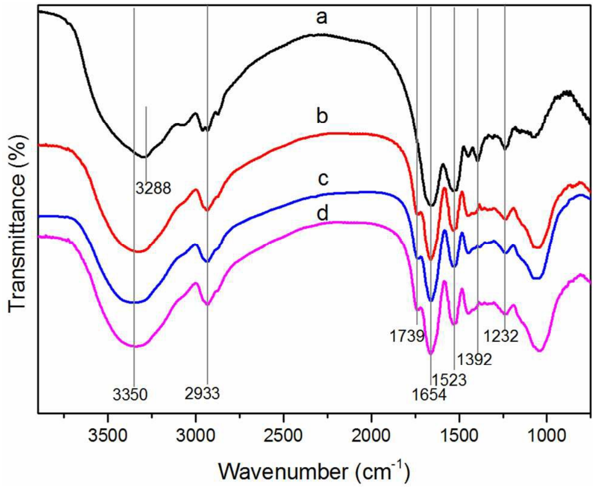


Fig.4. FTIR spectra of MSEP and soybean meal-based adhesives: (a) SM adhesive, (b) TSM adhesive, (c) TSM/SEP adhesive, (d) TSM/MSEP adhesive.

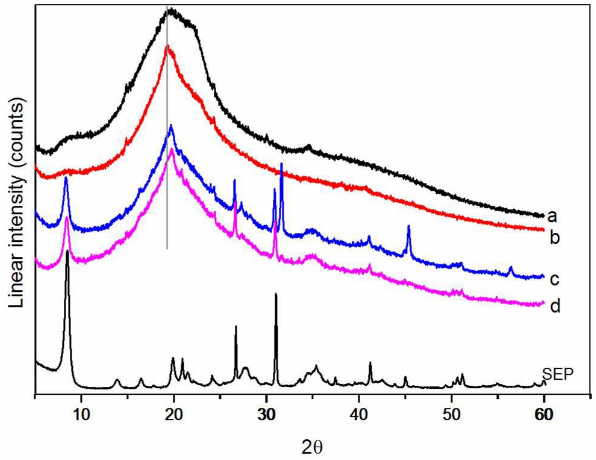


Fig.5. XRD patterns of MSEP and soybean meal-based adhesives: (a) SM adhesive, (b) TSM adhesive, (c) TSM/SEP adhesive, (d) TSM/MSEP adhesive.

3.2.4. X-ray diffraction analysis

The X-ray diffraction patterns of the various different adhesives is shown in Fig. 5. For the SM adhesive (a), the intensity of the peak (2θ = 9° and 19°) is due to the α-helix and β-sheet structure of protein molecules.[41] The crystallization peak at 2θ = 9° nearly disappeared in the X-ray diffraction patterns after addition of TGA, which suggests that a chemical reaction occurred between the TGA and soy protein. This confirmed the FTIR results previously detailed and is in accordance with Luo's research.[13] The crystallinity of the various adhesives was calculated and is presented in Table 3. The crystallinity of the SM adhesive was 36.9%. After addition of TGA, the crystallinity of the TSM adhesive decreased to 24.7%, which was due to the ring-opening reaction between TGA and soy protein molecule. This result also agrees with the report of Lou et al.[13], who detailed that the increased cross-linking density of the cured adhesive decreases the crystallinity of resultant adhesive. When SEP was added, the X-ray pattern exhibited the characteristic peaks of the SEP, indicating that the SEP was well dispersed in the adhesive system. And the broad peak at 2θ =19° shifted slightly towards a higher angle after addition of SEP indicating that the physical filling effect of SEP may have affected the crystalline orientation or constriction of the cured TSM/SEP adhesive. In the case of the TSM adhesive, addition of SEP, caused crystallinity of the TSM/SEP adhesive to increase from 24.7% to 32.5%. One reason for this may have been that the well dispersed SEP prevented the TGA from interacting with the protein molecules, which decreased the crosslink density of the resultant adhesive. Also, the high crystallinity of SEP contributed to the higher crystallinity of the resultant adhesive. After the SEP was modified with KH-560, the crystallinity of the TSM/MSEP adhesive containing MSEP declined from 32.5% to 23.7% compared with the TSM/SEP adhesive and was 4% lower than the crystallinity of the TSM adhesive, indicating formation of a high cross linked UCN. This UCN resisted water intrusion and improved the water resistance of the resultant adhesive, which was in accordance with the results of the wet shear.

Table 3 The crystallinity of different soybean meal-based adhesives: (a) SM adhesive, (b) TSM adhesive, (c) TSM/SEP adhesive, (d) TSM/MSEP adhesive.

Samples	a	b	c	d
Crystallinity (%)	36.9	24.7	32.5	23.7

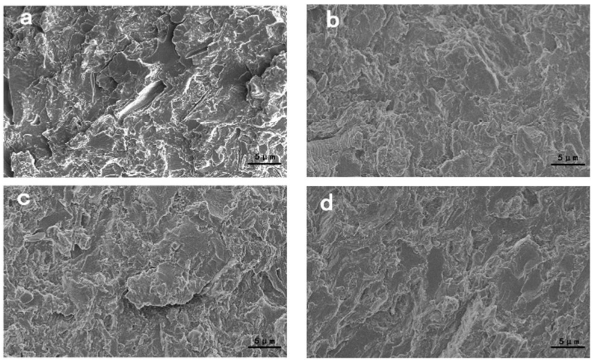


Fig.6. SEM micrograph of soybean meal-based adhesives: (a) SM adhesive, (b) TSM adhesive, (c) TSM/SEP adhesive, (d) TSM/MSEP adhesive.

3.2.5. SEM analysis

The morphology of the fracture surface of the cured adhesives was observed using SEM (Fig. 6). For the SM adhesive (a), a loose fracture with many cracks was found. Since soy protein-based adhesive is a water-based adhesive, water will be introduced into the plywood. Generally, the cohesion of the native SM adhesive is very low, during the hot pressing, the water ejected out and resulted cracks and holes. Hence, after curing, moisture easily intruded into these imperfections in the cured adhesive layer which caused adhesive failure, so that, the wet shear strength was relatively low.[39] After TGA was introduced, few cracks occurred in the TSM adhesive, which was a direct result of the cross-linking reaction that occurred between the TGA and the protein molecules in the SM adhesive. The cross-linked structure increased the cohesion of the adhesive, which can resist the damage caused by the water ejection during the curing process, so that, the holes and cracks decreased. By contrast, introduction of the SEP into the TSM adhesive resulted in a tough fracture without cracks. Introduction of MSEP caused the resultant TSM/MSEP adhesive (d) to exhibit a compact and tough fracture, resulting from the chemical cross-linking reaction and the physical filling effect formed by the MSEP and SM adhesive. During the curing process of the adhesive, the fibre shaped SEP filling in the molecular chains of soybean based adhesive produced a toughness fracture. The buffer action of the toughness structure for the water ejection certainly decreased the formation of cracks and holes during the hot press process, which further improved the water resistant of the resultant adhesive. After cuing, the smooth and compact fracture implied that the MSEP and soy protein formed a uniform system leading to synergistic, toughening effects. In addition, this compact fracture effectively prevented moisture penetration, which improved the water resistance of the adhesive. This tough UCN balanced a high interior force of the plywood caused by an extreme condition (like a boiling process or an impact external force). Hence, the wet shear strength of the plywood was effectively improved by introducing the MSEP, which was in accordance with the results of wet shear strength and XRD analysis.

Conclusions

The following conclusions can be drawn from the results obtained in this current study:

1. Using KH560 successful introduced epoxy groups onto SEP.
2. The fiber shaped SEP was well dispersed in the TSM adhesive system and formed a physical filling effect creating a 76.8% residual rate, compact shear fracture and good water resistance. This produced a wet shear strength that increased from 0.81 to 0.86 MPa.
3. The epoxy groups of MSEP reacted with function groups in the protein molecules, which chemically connected the cross linked protein net system with SEP, formed a united cross-linked network (UCN) in the adhesive system and produced a synergistic effect, which greatly increased the crosslink density of the adhesive and generated a compact shear fracture that prevented moisture intrusion. Therefore, the wet shear strength of the resultant plywood was increased by 37.2% to 1.18 MPa compared to the adhesive with untreated SEP, which met the interior use plywood requirement.
4. The incorporation of modified low-cost SEP is a feasible way to enhance soybean meal-based bio-adhesives.

Acknowledgements

The authors are grateful for financial support from Beijing Natural Science Foundation (2151003) and the Special Fund for Forestry Research in the Public Interest (Project 201404501).

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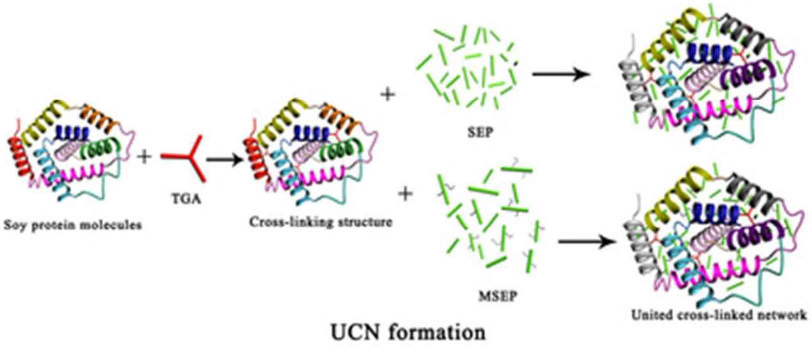

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