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ARTICLE

## An eco-friendly wood adhesive from soy protein and lignin: Performance properties

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The aim of this study was to improve the water resistance of the soybean meal-based adhesive with a low cost lignin-based (LR) resin. The LR could react with active groups on the protein molecule and itself to form a cross-linking and interpenetrating network, which improved the water resistance of the resultant adhesive. In addition, adding LR increased the thermal ability of the cured adhesive, forming a cross-linked protein molecule based structure, created a smooth surface with less holes and cracks to prevent moisture intrusion, which further improved the water resistance of the resultant adhesive. Using LR also resulted an appropriate viscosity which benefited adhesive distribution during the hot press process and formed more interlock with wood, thus created a good wet shear strength of the resultant plywood. Incorporating 10 wt% LR effectively improved the wet shear strength of the resultant plywood by 200% to 1.05 MPa, which met interior use plywood bond strength requirement. The resultant adhesive have the solid content of 32.65% and viscosity of 499,400 mPa·s, which was acceptable for the industrial application of plywood fabrication.

### Introduction

Formaldehyde-based resins, such as urea-, phenol-, and melamine-formaldehyde resin, are present common wood adhesives. They perform very well, but one of their major disadvantages, from the environmental point of view, is that they are derived from the non-renewable and limited fossil sources. Furthermore, urea- and melamine-formaldehyde resin also have formaldehyde emission issue, which are hazardous to human health.<sup>1</sup> Therefore, there is an urgent need on developing adhesives based on environmentally friendly and renewable resources.<sup>2</sup>

Soy protein-based adhesive is one of the researchers' focuses since soybean is abundant, inexpensive, and environmentally friendly.<sup>3</sup> However, the low bond strength and water resistance of the soy protein-based adhesives limit their application.<sup>4</sup> The efforts to improve adhesion properties of the soy protein-based adhesives include using denaturants and cross-linking agents.<sup>5</sup> Denaturants, such as urea, sodium dodecyl sulfate (SDS), alkali, can unfold the protein molecule and these molecules rearranged during the hot press process, which improves the water resistance of the adhesive.<sup>6</sup> But the resultant plywood bonded by the adhesive with the denaturants cannot meet the bond strength requirement of interior use. Using crosslinking agents, such as, glycidyl methacrylate, polyamidoamine-epichlorohydrin resin, polyethylene glycol diacrylate, latex-based adhesive could effectively improve the water resistance of the soy protein-based adhesive and the

resultant plywood meet the interior use bond strength requirement.<sup>7-10</sup> However, those additives are expensive and greatly increase the cost of the resultant adhesive, which limits the industrial application of soy protein-based adhesives.

As the third most abundant natural biological macro-molecule, lignin widely exists in the plant resource, such as wood, corncob, sorghum. It is a low value by-products of the paper-making industry and lignocellulosic ethanol industries. Lignin has an aromatic and cross-linked structure comprising of three main lignin building units, p-hydroxyphenyl, guaiacyl, and syringylunits, linked by carbon-carbon and ether bonds. As an aromatic compound available from renewable resources, the depolymerization of lignin was potentially used to produce bio-based polymers. Since some parts of lignin structure are similar to phenol, it is a potential substitution for phenol in phenol formaldehyde resin synthesis.<sup>11</sup> However, the fewer reactive sites and the stronger steric hindrance effect of lignin make its low reactivity and the resultant resin with high lignin content have a poor performance. Considering the possibility of the generating the coupling reactions of side chains and link-bonds of functional groups, a raw sorghum lignin was used to mix with defatted soy flour to improve the water resistance of the soy protein based adhesive.<sup>12, 13</sup> But the improvement was not significant and the resultant adhesive was hard to meet the bond strength requirement of industrial use.

In this study, corncob lignin was used to synthesis a lignin-based resin (LR). And then, the LR resin mixed with soybean meal-based adhesive to develop a plywood adhesive. The performance of the resultant adhesive including the viscosity of the adhesive, and the functional groups, thermostability, and fracture surface of the cured adhesive was characterized. Three-ply plywood specimens were fabricated with the resultant adhesives and their wet shear strength was tested.

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## Experimental

### 2.1 Materials

Soybean meal (SM) was obtained from Xiangchi Grain and Oil Company in Shandong Province of China, and then milled to 200 mesh flour. Components of the soybean meal flour were tested as follows: 46.88% soy protein, 40.24% saccharides, 5.86% moisture, 6.46% ash, and 0.56% fat. Phenol, formaldehyde solution (37–40 wt%) and sodium hydroxide were AR grade reagents and purchased from Tianjin Chemical Reagent Co.. Corncob lignin was purchased from Shandong Long Li Biological Technology Co., LTD, China. The lignin was produced from the corncob residue after hydrolysis of hemicelluloses, which contained 88.5% acid-insoluble lignin, 4.7% acid-soluble lignin, 0.10% arabinose, 0.12% glucose, and 0.08% xylose. The ash and moisture contents of the lignin were 1.3% and 5.2%, respectively. Poplar veneer (40 × 40 × 1.5 cm, 8% of moisture content) was provided from Hebei Province of China.

### 2.2 Preparation of the lignin-based resin (LR)

The lignin-based resin (LR) was synthesized by batch copolymerization according to the lignin, phenol, formaldehyde in weight ratio of 150:140:132 (100% solid content). In the first step, lignin (150g) and phenol (140g) with formaldehyde (146g, 37 wt%) and NaOH (45g, 50 wt%) were mixed and stirred in a flask. The mixture was heated to 80 °C and kept for 1 h. In the second step, the second portion of formaldehyde (97g, 37 wt%) and NaOH (20g, 50 wt%) was added into the flask and stirred for 1 h at 80 °C. In the last step, the rest formaldehyde(113g, 37 wt%) and NaOH(20g, 50 wt%) were added in the flask and further stirred for 1 h at 80 °C. Then the mixture was cooled down to 40 °C and through a vacuum distillation process removing the free formaldehyde to get the LR. The solid content of the resultant resin was 60% and the viscosity was 380 mPa·s at 20 °C. The reaction equation is presented in Fig. 1.

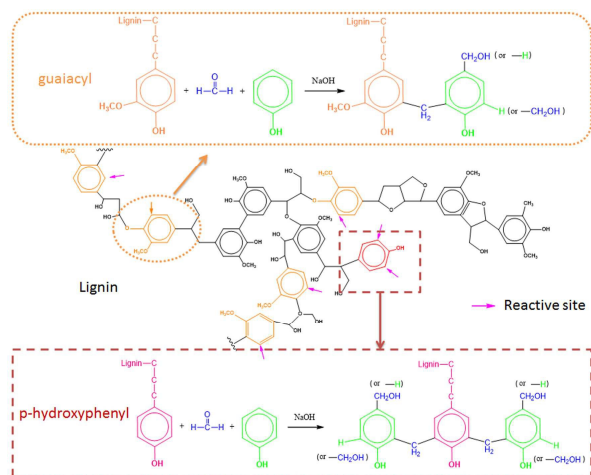


Fig. 1 The reaction equation for the formation of LR.

### 2.3 Preparation of soybean meal-based adhesives

For the soybean meal (SM) adhesive: soybean meal flour (28 g) was added into deionized water (72 g) and stirred for 10 min at 20 °C. 5, 10, 15, 20 wt% of LR were mixed with the SM adhesive, and further stirred for 10 min at 20 °C to develop the SM/LR5% adhesive, the

SM/LR10% adhesive, the SM/LR15% adhesive, the SM/LR20% adhesive, the SM/LR25% adhesive, respectively.

### 2.4 Preparation of the plywood sample

Three-ply plywood samples were prepared under the following conditions: 180 g/m<sup>2</sup> glue spreading for a single surface, 70 s/mm hot press time, 135 °C hot press temperature, and 1.2 MPa hot press pressure.<sup>14</sup> After hot pressing, the plywood samples were stored under ambient conditions for at least 12 h before testing.

### 2.5 Solid content measurement

The adhesive solid content was determined using an oven-drying method. Approximately 3 g (weight  $\alpha$ ) of the adhesive was placed into an oven and dried at 105 °C for several hours until a constant weight (weight  $\beta$ ) 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.

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

### 2.6 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 measurements. Experiments were conducted under a steady shear flow at 25 °C. Shear rates ranged from 0.1 to 240 s<sup>-1</sup> in 10 s<sup>-1</sup> increments. All of the measurements were conducted in triplicate, and the average value was reported.

### 2.7 Wet shear strength measurement

The wet shear strength of the interior use plywood (Type II plywood) was determined using a 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 a room temperature for 10 min before a tension testing. The wet shear strength was calculated by the following equation.

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

### 2.8 Residual Rate Test

The adhesive samples were 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 for 5 h in an oven, until a constant weight was obtained (m). The residual rate is defined as m divided by M, as shown in Eq. (3). The average value of the residual rate was calculated from six parallel samples.

$$\text{Residual Rate (\%)} = \frac{m \text{ (g)}}{M \text{ (g)}} \times 100\% \quad \text{Eq. (3)}$$

### 2.9 Fourier Transform Infrared (FTIR) Spectroscopy

The different adhesive samples prepared in 2.4 were cured in an oven at 120 ± 2 °C until a constant weight was obtained and then 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  $\text{cm}^{-1}$  with a 4  $\text{cm}^{-1}$  resolution using 32 scans.

### 2.10 Thermogravimetric (TG) measurement

The different adhesives were cured in an oven at  $120 \pm 2^\circ\text{C}$  until a constant weight was obtained and ground into a powder. The thermal stability of the cured adhesive samples were tested using a TGA instrument (TA Q50, WATERS Company, USA). About 5 mg powdered samples were weighed in a platinum cup and scanned from the 30 to 600  $^\circ\text{C}$  at a heating rate of 10  $^\circ\text{C}/\text{min}$  in a nitrogen environment while recording the weight change.

### 2.11 Scanning Electron Microscopy (SEM)

The different samples were poured into a piece of aluminum foil and dried in an oven at  $120 \pm 2^\circ\text{C}$  until a constant weight was achieved. A Hitachi S-3400N (Hitachi Science System, Ibaraki, Japan) scanning electron microscope was used to observe fractured surfaces of the different adhesive samples. The surface was sputter coated with gold prior to examining it under the microscope.

## Results and Discussion

### 3.1 Solid content measurement

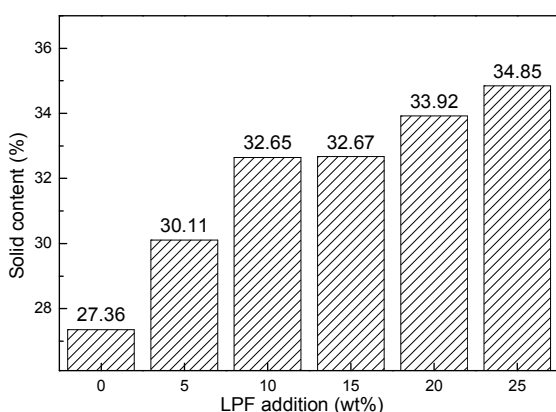


Fig. 2 The solid content of the different adhesive samples.

Solid content is a basic physical parameter for a wood adhesive that influences the performance of the adhesive during the hot press process. In general, the adhesive properties are improved with the solid content. A low solid content of the adhesive indicates that a larger water content leads to an excessive diffusion into the veneer resulting in poor bond at the interface due to insufficient adhesive.<sup>15, 16</sup> The average value of solid content of the different SM/LR adhesive formulations was calculated from three parallel samples and shown in Fig. 2. Soy protein has a big molecule with a complex structure and easy to swell in the water, which presents a high viscosity. As expected, for the SM adhesive, the 27.36% solid content caused a significant viscosity and a further increase in the solid content will be determined by the additive in the SM adhesive system. The low solid content of SM adhesive also lead to the lack of adhesive in plywood and a long hot press time, which is not appreciated in plywood fabrication industry.<sup>17</sup> Because of LR's high solid content, the solid content of the SM/LR adhesive increased from 30.11 to 34.85% with the LR addition from 5 to 25 wt%.

Moreover, with the LR addition up to 10 wt%, the solid content of the adhesive was 32.65%, which was increased by 19.3% compared to the SM adhesive. According to the literature review, the solid content of the soy protein-based adhesive was ranged from 32 to 36%.<sup>15</sup> Therefore, the adhesive with more than 10 wt% LR addition meets the requirement of plywood adhesive application.

### 3.2 Dynamic viscoelastic measurement

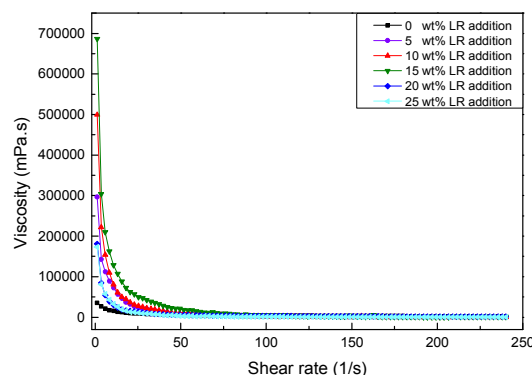


Fig. 3 The apparent viscosity of the different adhesive samples.

Table 1 The initial viscosity of the different adhesive samples.

LR addition (%)	0	5	10	15	20	25
Initial viscosity (mPa.s)	35,810	296,700	499,400	686,600	181,200	73,300
	0	00	00	00	00	0

The apparent viscosity of the SM/LR adhesives is shown in Fig. 3 and the initial viscosity of the different adhesive was summarized and presented in table 1. As the LR addition was from 5 to 15 wt%, the initial viscosity of the resultant adhesive increased from 35,810 to 686,600  $\text{mPa}\cdot\text{s}$  (Table 1). This is because that the LR contains free sodium hydroxide which is an effective protein denature agent. With the increase of the LR addition, more protein molecules unfold and increase the friction among these molecules, which greatly increases the adhesive viscosity. In addition, this denature process also exposes lots of interior function groups to form large number of the intermolecular forces (hydrogen bonds, hydrophobic interactions) between protein molecules, which further increases the viscosity of the adhesives. The viscosity of the adhesive decreased from 686,600 to 173,300  $\text{mPa}\cdot\text{s}$  when the addition of LR increase from 15 to 25 wt%. This attributed to two reasons: the first one is the low viscosity of the LR itself. The other one is that the protein molecule begins to degradation as the sodium hydroxide addition increase, which further decreases the viscosity of the resultant adhesive.

### 3.3 Wet shear strength measurement

Soy protein can be used as an adhesive because the protein molecules are able to disperse and unfold in solution. The unfolded molecules increase the contact area and adhesion to other surfaces. In addition, these molecules entangle with each other during the curing process to produce bond strength<sup>18</sup>. However, this kind of bond was easy to be broken by moisture, which was the main disadvantage of the adhesive. The wet shear strength of the

plywood bonded by the different adhesive and the residual rate of the different adhesive are shown in Fig. 4 and 5, respectively. The wet shear strength of the plywood bonded by the SM adhesive was 0.35 MPa, which failed to meet the interior use bond strength requirement ( $\geq 0.7$  MPa). From Fig. 5 the residual rate of the SM adhesive presented the lowest one, 76.6%, indicating that SM adhesive had the lowest cross-linking structure among all the adhesive formulation. The wet shear strength of the plywood with addition of 5 wt% LR was 0.78 MPa, which met the interior use panel bond strength requirement. However, from the standard deviation at 5 wt% addition, the wet shear strength of the plywood specimens cannot be guaranteed over 0.70 MPa. After further increasing the LR addition to 10 wt%, the wet shear strength increased by 200.0% compared with the SM adhesive and reached a maximum value of 1.05 MPa which met the interior use plywood bond strength requirement. Also, the residual rate of the adhesive was improved by 3.8% with the LR addition from 5 to 10%. This was due to three reasons: First of all, the denature process caused by the NaOH in the LR. Native soy proteins have a highly ordered global structure with hydrophilic groups exposed outside and hydrophobic groups buried inside. NaOH, as a effective protein denature agent, unfold the soy protein molecule and expose the inside hydrophobic groups, which could prevent moisture intrusion to improve the water resistance of the adhesive<sup>19</sup>. In addition, according to our previous research on X-ray diffraction patterns of the soy protein adhesive and its denatured adhesive,<sup>20</sup> after using denature agent, the unfolded molecule of the protein rearranged during the curing process and formed more crystalline structure which improved the water resistance of the adhesive. The second one was the cross-linking effect of LR. The amino acids could dominate soy protein properties because many side chains connect to these molecules and interact with various inorganic, organic materials and cellulosic fibers. In this adhesive formulation, the functional groups in lignin, such as phenolic, alcoholic hydroxyl group, active hydrogen of benzene ring, are transferred to phenolic hydroxyl methyl groups (Fig. 1) which could react with the amino and hydroxyl groups on the soy protein molecule and form a cross-linking network between LR and soy protein molecule, which brought a solid structure to improve the water resistance. The last was the LR molecules also could react with themselves to form a interpenetration structure with soy protein molecules, which further increased the water resistance of the adhesive (Fig. 7). The cross-linked structure caused by LR/protein and LR itself also increased the residual rate of the adhesive.

By increasing the LR content to 15 wt%, the residual rate of the adhesive further increased by 2.9% when compared with the adhesive with 10% LR, indicating more cross-linked structure in the adhesive. In general, the water resistance of the adhesive increased with the cross-linking structure in the adhesive. However, from Fig. 4, the wet shear strength of the plywood bonded by the adhesive with 15% LR addition decreased to 0.91 MPa and the viscosity of the adhesive increased by 37.5% compare with the adhesive upon 10 wt% LR (Table 1). This was because a very high viscosity was detrimental to the flowability of the adhesive and caused an adhesive distribution issue which reduced the wet shear strength of the plywood. Also, the adhesive with a very high viscosity was hard to penetrate into wood gaps and form

interlock with wood, which further reduced the wet shear strength of the resultant plywood. By further increasing the LR content to 25 wt%, the wet shear strength continued decreasing and then levelled off (0.65 MPa). This was attributed to three reasons. One was that the excess NaOH along with LR addition decomposed the soy protein molecule into small pieces and reduced the bond property of the adhesive. The second was because using the LR only as a wood adhesive, had a low water resistance. The last one was the very low viscosity of the adhesive, which caused an over penetration into wood and low bond strength.

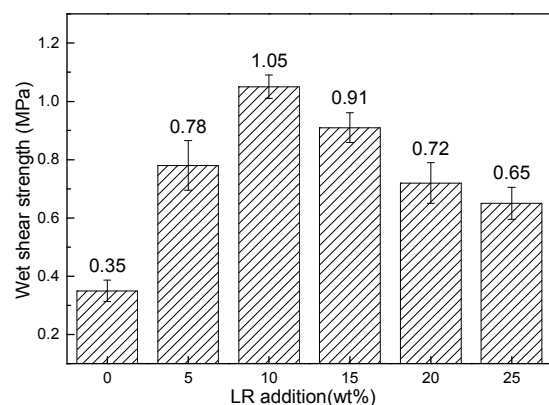


Fig. 4 The wet shear strength of the different adhesive samples (error bars represent standard deviations from twelve replicates).

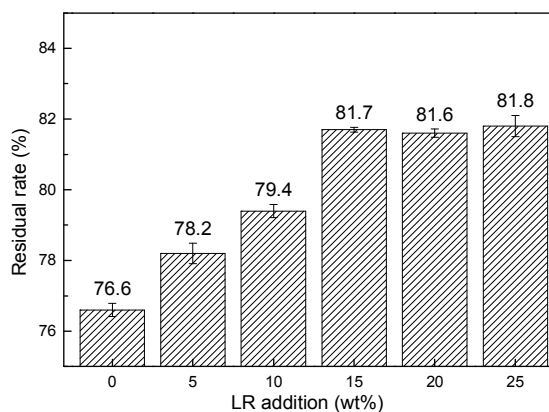


Fig. 5 The residual rate of the different adhesive samples (error bars represent standard deviations from six replicates).

### 3.4 FTIR spectroscopic analysis

The FTIR spectra of the SM adhesive and its hybrid adhesives are presented in Fig. 6. A peak was observed at approximately  $3319\text{ cm}^{-1}$  was related to the free and bound O-H and N-H bending vibrations, which could form hydrogen bonds with the carbonyl group of the peptide linkage in the protein. The peak observed at approximately  $2930\text{ cm}^{-1}$  was 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 peaks approximately at  $1656$ ,  $1536$ , and  $1241\text{ cm}^{-1}$ , which were characteristic of amide I (C=O stretching), amide II (N-H bending)



and amide III (C-N and N-H stretching), respectively<sup>21</sup>. The bands corresponding to C-O bending were located at 1052 cm<sup>-1</sup>.

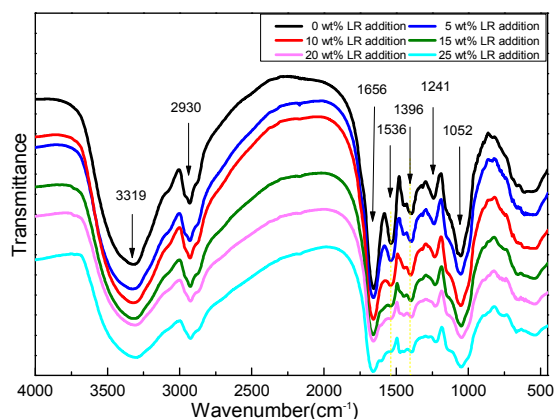


Fig. 6 FTIR spectra of the different adhesive samples.

With LR addition increasing from 0 to 10 wt% in the adhesive, the absorption peak of amide II and amide III (1536 and 1396 cm<sup>-1</sup>) gradually decreased, which was attributed to the reaction between functions of the LR and the -NH groups on soy protein molecule. This reaction decreased the amount of hydrophilic groups in the adhesive, which increased the water resistance of the adhesive. In addition, LR cross-linked the soy protein molecule to form a solid network, which increased the crosslinking degree of the adhesive and the water resistance of the adhesive was further improved<sup>22</sup>. (Most likely the specific reaction discussed in Fig. 7.) Furthermore, as the LR increasing, the LR could react with themselves to form a LR-network and penetrate with soy protein-network to form a interpenetrating network, which also improved the water

resistance of the adhesive. After further increasing the LR addition to 25 wt%, the absorption peak of amide II became neglectable and eventually disappeared in the spectrum of the SM/LR adhesive with 25 wt% LR addition, indicating that the addition of LR was excessive. Those excessive LR formed a key structure with low water resistance, so that, the water resistance of the adhesive system was reduced. The absorption peak of amide I had a minor decrease with the increasing of LR content, which was attributed to the protein content in the adhesive formulation decreased with the LR content increase.

### 3.5 TGA analysis

Compared Fig. 8 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the SM/LR adhesives. The thermal degradation process of the adhesives could be divided into three stages. The first stage (I) was attributable to the evaporation of residual moisture at a temperature region of 50-220 °C. No degradation of soy protein was found and the weight loss ratio was very small. The second stage (II) was initial degradation stage from 210 °C to 280 °C, which resulted from the weight loss of the small molecule subject degradation and the break of some unstable chemical bonds. The third stage (III) was the skeleton structure degradation stage, at a temperature region of 280-360 °C, which attributed to the cross-linking network structure degradation. Before the first degradation stage, the small weight loss was attributable to the evaporation of residual moisture.<sup>23</sup> After the third degradation stage, a further heating caused breakages of C-C, C-N, and C-O linkages, and soy protein backbone peptide bonds were decomposed, the gases such as CO, CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>S were produced.<sup>24</sup> The decomposition of residual modifier should be taken into consideration and belonged to this degradation stage.

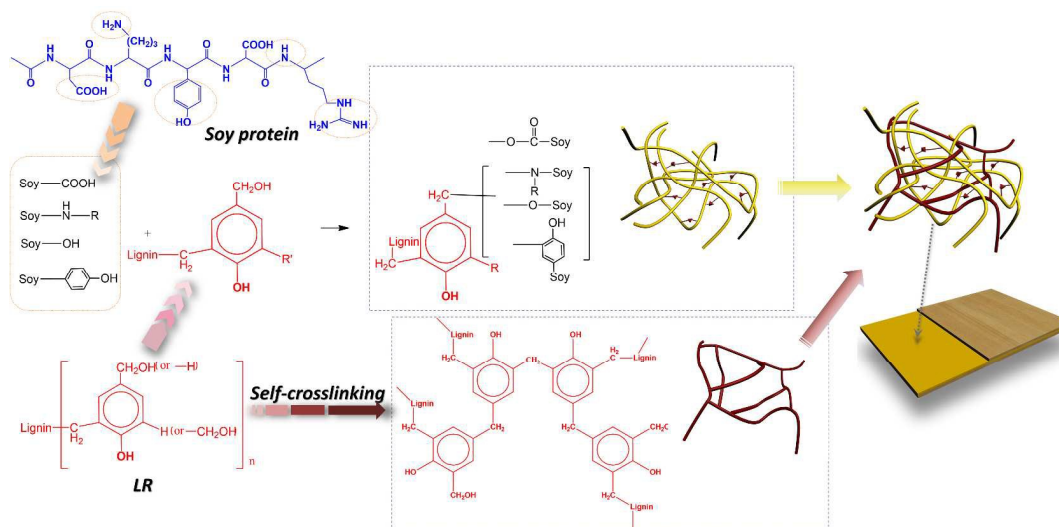


Fig. 7 The curing process of the adhesive enhanced with LR.

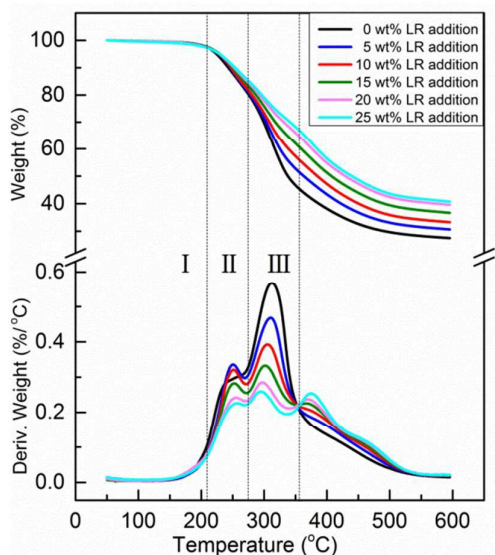


Fig. 8 The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the different adhesive samples.

Compared with SM adhesive, the adhesive with 5 and 10 wt% LR additions showed a strong peak (Deriv. weight) in stage (II), which was attributed to the unstable bond formed by LR and protein molecule during the curing process of the resultant adhesive. Further increasing the LR addition decreased that peak, which meant the main structure of cured structure changed as the LR addition increasing. For the adhesive with 5 and 10 wt% LR addition, LR reacted with protein molecule and formed a cross-linked protein molecule network presenting a major structure in the adhesive system, which improved the water resistance of the resultant adhesive. As the LR addition further increasing, the reactive groups on the protein decreased (FTIR analysis) and the protein decomposed (viscosity analysis), so that, the LR self-cross-linked and formed a network which played a major structure in the adhesive system. This LR network was easily broken by moisture, which presented a low water resistance. In addition, the protein was more likely acting as filler in the adhesive system in the adhesive with 25% LR addition, which further decreased the water resistance of the adhesive.

In the third stage, the thermal degradation behavior showed evident distinction with and without LR. The SM adhesive had the highest degradation rate and then it was decreased significantly with LR addition gradually increasing in the adhesive formulations. The relative weight loss in the third stage of the adhesive with LR addition from 0 to 25 wt% were 37.6, 32.0, 25.6, 22.8, 17.2 and 15.5%, respectively, which suggested a better thermal stability of the SM/LR adhesive.

### 3.6 SEM analysis

The fracture surface micrograph of the cured SM/LR adhesives is shown in Fig. 9. A large number of holes and cracks were observed on the fracture surface of the SM adhesive. In addition, the whole fracture surface appeared very loose and disordered. These holes and cracks were formed by water evaporation in the adhesive during the hot press process. Moisture could intrude into those

cracks and swell to break the bond, which reduced the water resistance of the SM adhesive.<sup>25</sup> After the 10 wt% LR was introduced, no 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 LR and soy protein to form a cross-linked network, which could effectively prevent moisture intrusion to improve the water resistance of the adhesive. Further increase the LR addition to 25%, holes, cracks, and disorder surface were observed again on the fracture surface. This is because that the soy protein molecule decomposed with the LR addition increased. These decomposed protein molecules with lot of hydrophilic groups, acting as filler, filled in the LR and reduced the water resistance of the composite adhesive. Also, the holes and cracks helped moisture attaching and swelling, which further decrease the water resistance of the adhesive.

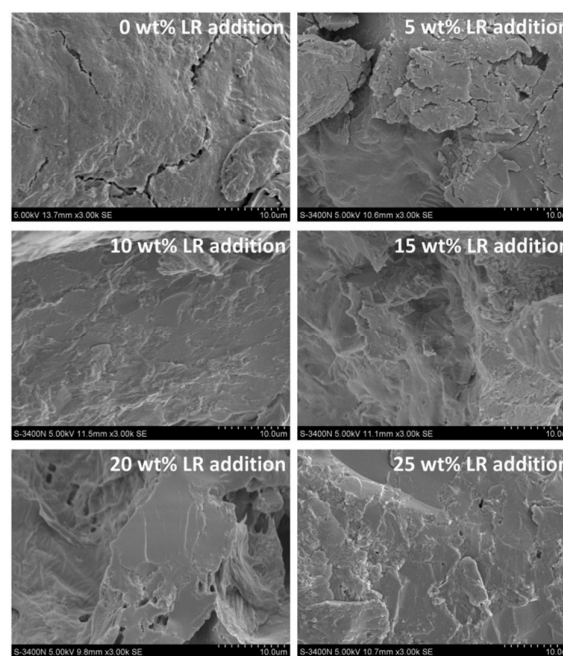


Fig. 9 The fracture surface micrograph of the different cured adhesive samples.

### Conclusions

Using LR at an appropriate level effectively increased the water resistance of the soybean meal-based adhesive and the wet shear strength of the resultant plywood. This is attributed to the following reasons: 1) a cross-linking network formed by the reaction between the LR and the active groups on soy protein molecule; 2) a smoother fracture surface formed to prevent moisture intruding; 3) a interpenetrated network formation by cross-linked protein molecules and self-crosslinking LR molecules; 4) the improved thermal stability of the adhesive; 5) the resultant appropriate viscosity 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 LR addition decrease the water resistance of the adhesive because the resultant very low viscosity by adding LR and protein decomposition over penetrated into wood surface and hard to form effective bond.

Using 10 wt % the LR effectively improved the water resistance of the adhesive by 3.7 % and the wet shear strength of the plywood bonded by the resultant adhesive by 200 % to 1.05 MPa, which met interior use plywood bond strength requirements. The solid content and viscosity of the resultant adhesive was 32.65 wt% and 499,400 mPa·s, respectively, which was acceptable for the industrial use of plywood adhesive. It is an effective solution for promoting soybean meal-based adhesive application.

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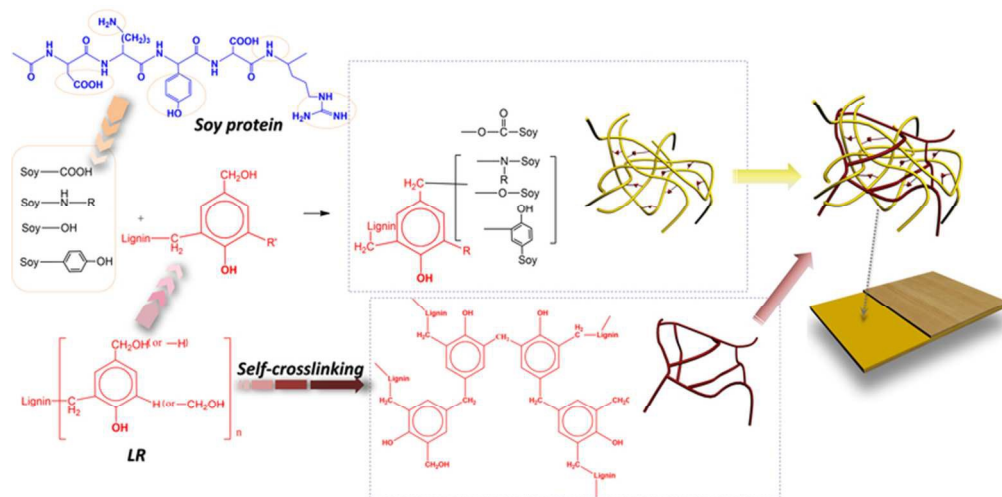
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