Improve performance of soy protein adhesives with a low molar ratio melamine-urea-formaldehyde resin

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Abstract. In this study, the low molar ratio melamine-urea-formaldehyde (MUF) resin and sodium hydroxide were used to modify soy protein adhesives, and the addition of MUF was studied as the influencing factor, the properties of soy protein adhesives, formaldehyde emission and bonding strength were studied. The results showed that the solid content and viscosity of the adhesives were suitable for the application of wood adhesives, the formaldehyde emission and wet shear strength of plywood prepared by soybean protein adhesive modified by MUF with 30% addition were 0.38mg/L and 1.25 MPa. Moreover, based on the analysis of the free formaldehyde content of the adhesive and the formaldehyde emission of plywood, it can be inferred that most of the free formaldehyde in the plywood was derived from the unreacted methyl group during the hot pressing process.

1. Introduction
The formaldehyde-based adhesives such as phenolic resins, urea-formaldehyde resins, and melamine-formaldehyde resins had played an important role in wood industry. However, the free formaldehyde released from the formaldehyde-based adhesives is harmful to people's health \cite{1, 2}. Moreover, most of the raw materials for formaldehyde-based adhesives came from non-renewable fossil resources \cite{3}. With the strengthening of public environmental awareness and the improvement of environmental protection grade requirements for man-made panels, environmentally-friendly bio-based adhesives, such as lignin adhesives, tannin adhesives, protein adhesives and starch adhesives, had been increasingly concerned. The main ingredients of bio-based adhesives were usually natural polymers, and soy protein adhesive has received the most attention in the wood-based panel industry in recent years.

In natural state, the structure of soy protein is dense globular formed by a polypeptide chain of 18 kinds of amino acids through the action of secondary bonds such as disulfide bonds, hydrogen bonds, hydrophobic interactions, ionic bonds, and van der waals forces. Moreover, soy protein is renewable, multifunctional, process able and environmentally compatible \cite{4-7}. However, compared with formaldehyde-based adhesives, soy-based adhesives have poorer properties, especially the water resistance and the bonding strength \cite{8}. The main reason for the poor water resistance and low...
bonding strength of soy protein adhesives is as follows: The curing mechanism of soy protein adhesive is the intertwining of soy protein molecules and the evaporation of water, but the functional groups on the soy protein molecular chain hardly chemically react with each other. The adhesive force mainly comes from the hydrogen bonds generated between these functional groups, and these hydrogen bonds are easily broken in a humid environment.

In order to improve the water resistance and the bonding strength of soy protein adhesives, low molar ratio melamine-urea-formaldehyde (MUF) resin was used to modify the soy protein adhesive in this study. The effect of the MUF additive amount on the properties of the soy protein adhesives and plywood prepared by it were studied.

2. Materials and Methods

2.1. Materials
Soy protein isolate (SPI) (≥90% protein content) was obtained from Shansong Biological Co., Ltd (Shandong, China). Sodium hydroxide, melamine, urea and formaldehyde aqueous solution (37 wt%) were purchased from Chronchem Co., Ltd (Sichuan, China), they are all analytically pure.

2.2. Preparation of MUF resin
The MUF resin made by laboratory. The molar ratio of (melamine urea): formaldehyde of MUF resin is 1: 1.1. The prepared MUF resin was named Adhesive G.

2.3. Preparation of Soy Protein Adhesives
The formulas of the adhesives were showed in Table 1. 10g soy protein isolate (SPI) was added to a beaker containing 90g of distilled water, the solution was stirred evenly at room temperature. The prepared adhesive was named Adhesive A. Based on the same materials and methods as Adhesive A, the solution pH was adjusted to 9.0-10.0 by sodium hydroxide (NaOH), and the solution was stirred evenly at room temperature, the prepared adhesive was named Adhesive B. Based on the same materials and methods as Adhesive B, MUF resin with addition of 10, 20, 30, 40% (of the final adhesives mass) were added to Adhesive B, the adhesive was stirred at room temperature for 30 min, and the obtained adhesives were named Adhesive C, Adhesive D, Adhesive E, and Adhesive F, respectively.

| Table 1. Formulations used for adhesive fabrication. |
|-----------------------------------------------|
| Adhesive sample | Adhesive formulation |
| A         | SPI (10g); Distilled water (90g) |
| B         | SPI (10g); Distilled water (90g); NaOH |
| C         | SPI (9g); Distilled water (81g); MUF (10g); NaOH |
| D         | SPI (8g); Distilled water (72g); MUF (20g); NaOH |
| E         | SPI (7g); Distilled water (63g); MUF (30g); NaOH |
| F         | SPI (6g); Distilled water (54g); MUF (40g); NaOH |
| G         | MUF |

2.4. Adhesives performance measurement
The solid content, viscosity and free formaldehyde content of the adhesives were carried out according to the method in GB/T 14074-2017 "Testing methods for wood adhesives and their resins".

2.5. Preparation of plywood
Eucalyptus veneer with dimension of 300mm (length)* 300mm (width) were used to produce three-layer plywood. Adhesive G was used mixed with 30% (of the final adhesives mass) flour. Other adhesives are used directly. The adhesives were evenly painted on the eucalyptus veneer according to
the sizing amount of 330g / m². Hot pressing temperature, pressure and time were 130℃, 1.2 MPa and 6min respectively.

2.6. Plywood performance measurement
The wet shear strength and formaldehyde emission of plywood were carried out according to the provisions of level II plywood in GB/T17657-2013 "Test methods for physical and chemical properties of artificial panels and finished panels".

3. Results and discussion

3.1. Solid content measurement
The effect of solid content of adhesive on the properties of sheet metal is significant. The lower the solid content of the adhesive, the more moisture it contains, high moisture content of adhesive is not conducive to its curing, and increases the internal stress of plywood at the same time. The solid content of the adhesives were shown in Figure 1, the solids content of each adhesive was calculated from three parallel samples. The solid content of Adhesive A and B were 9.9% and 10.2%, respectively. The results showed that the effect alkali modification on the solid content of the soy protein adhesives was non-significant. The solid content of Adhesive C, D, E, and F were 16.8%, 19.4%, 21.1%, and 22.9%, respectively. The solid content of Adhesive E and F were suitable for the producing of plywood.

![Figure 1. The solid content of adhesives.](image1)

![Figure 2. The viscosity measurement of adhesives.](image2)

3.2. Viscosity measurement
The effect of viscosity measurement of adhesive on the properties of bonding strength was significant. The fluidity of adhesives with high viscosity was poor and cannot be evenly coated on plywood. And the adhesive with low viscosity will penetrate into the wood excessively, leading to lack of glue of the plywood. The viscosity of different adhesives were shown in Figure 2. The viscosity of the adhesive was improved significantly by alkali modification treatment, the viscosity of Adhesive B was 11300 mPa·s which was 1.97 times compared with that of the Adhesive A. The fluidity of Adhesive B was extremely poor, because the internal hydrogen bonds of soy protein was destroyed by NaOH, and most of the chemical groups were exposed, resulting in excessive viscosity. The viscosity of the adhesives was reduced with the addition of the small molecular weight MUF resin. Viscosity decreased with the increase of MUF resin addition, the lowest value was 5233mPa·s. Adhesives A, D, E, F were suitable for the applications of plywood adhesive.
3.3. **Free formaldehyde measurement**

Free formaldehyde in adhesives was one of the main sources of formaldehyde emission from plywood. The free formaldehyde of different adhesive was shown in Figure 3. Free formaldehyde of Adhesives A and B were not tested in this study for formaldehyde was not used in the raw material of them. The free formaldehyde of Adhesive G was the highest. The free formaldehyde content of all MUF modified adhesive were less than 0.1%, and the value increased with the increase of the MUF resin additive amount.

![Figure 3.](image)

**Figure 3.** The free formaldehyde content of different adhesives.

3.4. **Wet shear strength measurement**

The wet shear strength was shown in Figure 4. The wet shear strength of plywood prepared by Adhesive A was 0.44 MPa, which was lower than the standard requirement for level II plywood (≥0.7 MPa). The wet shear strength of plywood prepared by Adhesive B was 0.67 MPa, which was 52% higher than that of plywood prepared by Adhesive A. This was because the secondary bonds in the soy protein molecule was broken by NaOH, releasing a lot of polar and non-polar groups, which improved the water resistance of the adhesive. However, the plywood was still lower than the standard requirement for level II plywood, indicating that the alkali modification effect was limited. The wet shear strength of all plywood prepared by the adhesive C, D, E, and F were higher than the standard requirement of Class II plywood. The results showed that the wet shear strength increased with the increase of the amount of MUF resin added, the highest value was 1.34 MPa, which due to the methyl group of MUF resin crosslinked with the amino and amide bonds of soy protein. Therefore, water molecules were prevented entering into adhesive by the cross-linking networks, and covalent bonds formed by the reaction provided higher bonding forces than hydrogen bonds.
3.5. Formaldehyde emission measurement

The formaldehyde emission of the plywood produced by different adhesives were shown in Figure 5. Formaldehyde emission from plywood produced by Adhesive A and B came from wood and air, which were less than 0.1mg/L. The formaldehyde emission of the plywood prepared by the adhesive C, D, E were less than the Chinese National Standard E0 level for formaldehyde emission (≤0.5mg/L). The results showed that the formaldehyde emission of the plywood prepared by the modified soy protein adhesive increased with the increase of addition amount the MUF resin, and the plywood prepared by the adhesive F was higher than 0.5 mg/L. Surprisingly, the formaldehyde emission of plywood prepared by the adhesive C, D, E, F were all higher than that of the plywood prepared by adhesive G. The reason was speculated as follows, the moisture of modified soy protein adhesive contained were higher than that of the MUF resin, which leading to insufficient curing reaction of adhesive. Therefore, most of the free formaldehyde in the plywood was derived from the unreacted methylol group during the hot pressing process.

4. Conclusion

The performance of soy protein adhesives was significantly improved by the addition of MUF resin. When the amount of MUF resin was 30% and 40%, the solid content and viscosity of the adhesives were suitable for the application of wood adhesives. When the addition amount of MUF resin was 40%, the wet shear strength of plywood prepared by modified soy protein adhesive was increased by 204% to 1.34 MPa compared to that of the plywood prepared by unmodified soy protein adhesive. However, the formaldehyde emission of the soy protein adhesive with 40% MUF was 0.53 mg/L, which was higher than the national standard E0 level. When the addition amount of MUF resin was 30%, the formaldehyde emission of the prepared plywood was less than the E0 level standard and the wet shear strength was 1.25 MPa. Therefore, 30% was the optimal amount of MUF resin.

Moreover, based on the analysis of the free formaldehyde content of the adhesive and the formaldehyde emission of plywood, it was inferred that most of the free formaldehyde in the plywood was derived from the unreacted methyl group during the hot pressing procedure.

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