Preparation and Properties of Five Biomass-based Melamine Modified Urea Formaldehyde Resins

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Abstract. In this paper, shell (PS), rice husk (RH), rapeseed stalk (RS), toonaciliata wood (TW) and Sinocalamus affinis (SA) were served as the modifier to modify the melamine modified urea-formaldehyde resin (MUF). The PS, RH, RS, TW, SA were ultra-fine crushed to be the powder with less than 48 um. The reactivity of PS, RH, RS, TW, SA and formaldehyde solution was measured, and PS, RH, RS, TW, SA were added in the third stage of synthesis process of the MUF resin. The basic properties of the resin and plywood were tested. The results showed that, with addition of the PS, RH, RS, TW, SA, the reactivity with formaldehyde solution became better, while the gel time became longer, the resin viscosity and the solid content increased, and the free formaldehyde content of the resin decreased. The formaldehyde emission of the plywood decreased by 60.53%, 48.25%, 41.23%, 44.74%, 56.14%, respectively, and the wet ply strength of the plywood increased by 40.00%, 56.19%, 16.19%, 24.76%, 54.29%, respectively. The use of the ultra-fined PS, RH, RS, TW, and SA showed good effects on the formaldehyde elimination of the MUF resin.

1. Introduction
Urea formaldehyde resin (UF) is widely used in the wood bonding industry because of high bonding strength, low cost and easy processing. The introduction of melamine (M) during UF synthesis is the main method to modify the UF resin [2, 3]. Melamine-modified urea-formaldehyde (MUF) resin has better bonding properties, but the MUF resin is more expensive than UF resin, so the production and modification for the polymers have gradually turned to bio-based materials [4].

Peanut shells (PS), rice husk (RH), rapeseed stalk (RS), toonaciliata wood (TW), Sinocalamus affinis (SA) are common agricultural and forestry products, with huge annual output and low prices. Ultrafine pulverization is an efficient way to use PS, RH, RS, TW and SA. After being micro-pulverized, the particle size and the specific surface area of these powders were decreased and increased, respectively [5]. In this paper, PS, RH, RS, TW and SA were blended with formaldehyde solution, and the reaction capacity of PS, RH, RS, TW, SA and formaldehyde solution was measured. PS, RH, RS, TW, SA as additive of MUF resin, the preparation of peanut shells base melamine modified urea formaldehyde resin (PS+MUF), the RH+MUF resin, the RS+MUF, the TW+MUF resin and the SA+MUF resin were also prepared with the same method. The effects of the addition of PS, RH, RS, TW and SA on the properties of urea-formaldehyde resin and plywood were investigated.
2. Materials and methods

2.1. Experimental materials
Formaldehyde (37% aqueous solution), urea (>99%), melamine (>98.5%), sodium hydroxide (>96%), ammonium chloride (NH₄Cl) (98%), formic acid (>98%). All reagents are for analytical purity, provided by Chengdu Kelong Chemical Co., Ltd. PS were collected from Anju District, Suining City, Sichuan. RH were collected in Leshan, Sichuan. RS, TW and SA were collected in Yucheng District, Ya'an, Sichuan. All are crushed to more than 300 mesh, ready for use.

2.2. Study on the reaction capabilities of PS, RH, RS, TW, SA and formaldehyde

2.2.1. Calibration of formaldehyde solution. The formaldehyde content was determined according to the method for measuring the formaldehyde content in "GBT685-2013".

2.2.2. Response time. Add PS, RH, RS, TW, SA, and formaldehyde to the three-necked flask at a mass ratio of 22.5: 273, adjust the solution pH to 8.0 with NaOH (40% concentration), and keep the water bath temperature at 90 °C. Reaction 0.5h, 1h, 1.5h, 2h, 2.5h, 3h, 3.5h, 4h, 4.5h, 5h. The formaldehyde content of the solution was measured immediately after the reaction.

2.2.3. Reaction temperature. Add PS, RH, RS, TW, SA and formaldehyde to a three-necked flask at a mass ratio of 22.5: 273, and adjust the solution pH to 8.0 with NaOH (40% concentration) at 45 °C, 60 °C, The reaction was performed at 75 °C and 90 °C for 1h, and the formaldehyde content of the solution was measured immediately after the reaction.

2.3. Resin preparation
In total, 255 g of formaldehyde (37%), 88 g of urea and 3.95 g melamine of urea were placed in the reactor and then the reaction pH was adjusted to 7.8–8.0 with NaOH (40% aqueous solutions). The temperature was set to 90 oC in about 40 min and maintained for 30 min. Subsequently, the pH was adjusted to 4.0–4.5 until the turbidity point appeared, and then the pH was adjusted to 7.0–7.5, and the second urea and formaldehyde were placed in the reactor and maintained for another 30 min. Then set the pH value to 7.5-8.0, add 22.5 g of PS, RH, RS, TW and SA, and react for 30 min, then cool down the glue. The resin was named as PS+MUF, RH+MUF, RS+MUF, TW+MUF and SA+MUF, and the resin without PS, RH, RS, TW, and SA was named as MUF-a.

2.4. Type II plywood production
Eucalyptus twirl veneer (300 mm × 300 mm × 1.7 mm) with 8% moisture content was used to produce Type II plywood. The resin content in the plywood was controlled at 300 g/m². The plywood was compressed at 0.8 MPa for 60 min at room temperature, and then hot pressing (125 °C) was carried out at 1.2 MPa with a fixed loading speed (60 s/mm). Thereafter, the plywood samples were stored under ambient condition for further testing.

2.5. Performance measurement

2.5.1. Basic resin performance testing. WS+MUF, WD+MUF, PS+MUF, RH+MUF, RS+MUF, TW+MUF, SA+MUF resins mainly examine the resin properties such as gel time, pH, viscosity, solid content and free formaldehyde content, and the resin curing performance has curing time. Determined according to GB/T 14074-2006 "Test methods for wood adhesives and resins".

2.5.2. Performance testing of plywood. The pressed plywood is placed in the room for 1 to 2 days and then tested. The bonding strength is tested by universal material testing machine in accordance with GBT 17657-2013 "Test Methods for Physical and Chemical Properties of Wood-based Panels and Facing Wood-based Panels". The formaldehyde emission of the board is tested by the dryer method in
GB/T 17657-1999 "Test Methods for Physical and Chemical Properties of Wood-Based Panels and Facing Wood-Based Panels".

3. Results and discussion

3.1. Determination of PS, RH, RS, TW, SA and formaldehyde reaction capabilities

3.1.1. The effect of the reaction time on formaldehyde reaction capabilities.

The effect of reaction time on the reaction capabilities of PS, RH, RS, TW, SA and formaldehyde are shown in figure 1. Under alkaline conditions, PS, RH, RS, TW, SA and formaldehyde react well. It can be seen from figure 2 that the reaction mainly occurs in the early stage of the reaction and gradually weakens in the later stage. When the reaction time is 1 h, the amounts of formaldehyde consumed per 100 g of PS, RH, RS, TW, and SA are 0.72 mol, 0.60 mol, 0.59 mol, 0.48 mol, and 0.44 mol, respectively. When the reaction time is 5 h, the amount of formaldehyde consum ed per 100 g of PS, RH, RS, TW, and SA is 1.57 mol, 1.14 mol, 0.99 mol, 1.56 mol, and 1.01 mol, respectively. The peak time of PS, RH,
RS, TW, SA formaldehyde consumption appeared at 0.5h, 0.5h, 0.5h, 1.5h, 1h. With the extension of reaction time, the reaction ability of PS, RH, RS, TW, SA and formaldehyde showed a downward trend. When the reaction time is 5h, PS and TW consume more formaldehyde than RH, RS, SA.

PS, RH, RS, TW, and SA all belong to lignin-based biomass. Lignin contains more phenolic hydroxyl groups and alcoholic hydroxyl groups, and is a good raw material for synthetic wood adhesives [7]. Therefore, it is feasible to prepare MUF resin using RH, RS, SA, PS, TW as additives.

3.1.2. Effect of reaction temperature on the ability of PS, RH, RS, TW, SA to react with formaldehyde.

Figure 3 shows the effect of different reaction temperatures on the reaction capabilities of PS, RH, RS, TW, and SA. As the reaction temperature increasing, the amount of formaldehyde consumed by PS, RH, RS, TW, and SA were continued to increase. When the reaction temperature is 90 °C, 100 g of PS, RH, RS, TW, and SA can react with 0.72 mol, 0.60 mol, 0.59 mol, 0.72 mol, and 0.44 mol formaldehyde, respectively.

3.2. Effect of PS, RH, RS, TW, SA as additives on resin properties

The effects of PS, RH, RS, TW, SA as additives on resin properties are shown in Table 1.

| Resin category | pH     | Viscosity /mPa·s | Solid content /% | Gel time /s | Storage life /d | Free formaldehyde /% |
|---------------|--------|------------------|-----------------|------------|----------------|---------------------|
| MUF-a         | 8.19   | 35               | 51.73           | 112        | 29             | 0.28                |
| PS+MUF        | 7.95   | 185              | 52.36           | 156        | 12             | 0.23                |
| RH+MUF        | 8.27   | 139              | 53.28           | 166        | 41             | 0.23                |
| RS+MUF        | 7.45   | 187              | 52.61           | 144        | 35             | 0.22                |
| TW+MUF        | 8.01   | 279              | 64.94           | 134        | 23             | 0.25                |
| SA+MUF        | 8.41   | 238              | 61.51           | 178        | 39             | 0.25                |

The increase of resin viscosity will help to improve the pre-pressing performance of plywood, shorten the pre-pressing time, improve production efficiency and plywood quality. The gel time is extended, which indicates that the curing temperature of PS+MUF, RH+MUF, RS+MUF, TW+MUF, SA+MUF
resins increases, more energy is required for curing, and curing becomes more difficult. Compared with MUF-a resin, the free formaldehyde content of PS+MUF, RH+MUF, RS+MUF, TW+MUF, and SA+MUF resins is slightly reduced, which indicates that PS, RH, RS, TW, and SA have certain aldehyde elimination effect.

3.3. Effect of PS, RH, RS, TW, SA as additives on plywood performance

3.3.1. Effects of PS, RH, RS, TW, and SA on formaldehyde release from plywood. Weigh the same amount of PS+MUF, RH+MUF, RS+MUF, TW+MUF, SA+MUF resin, add 10% flour of resin mass, and add 2% NH4Cl as the curing agent. Stir evenly after mixing. The plywood was made according to the method of preparing plywood. After the plate was finished, the plate was left to stand for 7 days for constant weight treatment, and then the formaldehyde emission of the plywood was measured. The results are as follows:

![Figure 4. Effect of PS, RH, RS, TW, and SA on formaldehyde release from plywood](image)

From the test results of formaldehyde release from plywood, it can be seen that the formaldehyde release from plywood made of PS+MUF, RH+MUF, RS+MUF, TW+MUF, SA+MUF resins is significantly reduced. Compared with MUF-a resin, PS+MUF, RH+MUF, RS+MUF, TW+MUF, SA+MUF resins reduce formaldehyde emissions from plywood by 60.53%, 48.25%, 41.23%, 44.74%, 56.14%, respectively. PS+MUF, RH+MUF, RS+MUF, TW+MUF, SA+MUF resins reduce the formaldehyde emission of plywood for two reasons: First, active groups such as lignin in PS, RH, RS, TW, and SA Groups can react with free formaldehyde in urea-formaldehyde resin and free formaldehyde released when the resin cures [8, 9], thereby absorbing most of the free formaldehyde. Another reason is that after adding PS, RH, RS, TW, and SA, the resins of the same quality in PS+MUF, RH+MUF, RS+MUF, TW+MUF, and SA+MUF resins have a relatively low content of active ingredients, so Reduced formaldehyde emissions from plywood.

3.3.2. Effects of PS, RH, RS, TW, and SA on plywood bonding strength. The measurement result of the plywood wet bonding strength is shown in figure 5.
Effects of PS, RH, RS, TW, and SA on the wet bond strength of plywood

From the test results of plywood wet gluing strength, it can be known that different types of additives have different effects on plywood wet gluing strength. Compared with MUF-a resin, PS+MUF, RH+MUF, RS+MUF, TW+MUF, SA+MUF resins have improved the wet bonding strength of plywood by 40.00%, 56.19%, 16.19%, 24.76%, 54.29%, respectively.

PS, RH, RS, TW, SA are lignin-based additives. When PS, RH, RS, TW, and SA are used as additives, under a certain amount of addition, the wet bonding strength of plywood can be improved. The reason is that the lignin reactive groups in PS, RH, RS, TW, and SA can crosslink with free formaldehyde in urea-formaldehyde resin and free formaldehyde released when the resin is cured [8, 9], which improves the moisture of plywood. Adhesive strength. Another reason is that after adding PS, RH, RS, TW, SA, it prevents excessive penetration of the glue solution, fills tiny voids generated by shrinking and curing of the resin, and reduces curing stress.

4. Conclusion

The optimal conditions for the reaction efficiency of PS, RH, RS, TW, SA and formaldehyde are: the reaction temperature is 90 °C, and the reaction time is 0.5-1.5 h.

MUF resin prepared by adding PS, RH, RS, TW, and SA has longer gel time, increased resin viscosity and solid content, and reduced free formaldehyde content of resin. The formaldehyde emission of the prepared plywood decreased by 60.53%, 48.25%, 41.23%, 44.74%, and 56.14%, respectively, and the wet bonding strength of the plywood increased by 40.00%, 56.19%, 16.19%, 24.76%, and 54.29%, respectively.

PS, RH, RS, TW, and SA have good aldehyde elimination effects, and can be used in the preparation of MUF resin.

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