Effects of Three Biomass Fillers on the Properties of Melamine Modified Urea-Formaldehyde Resin

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Abstract. In this paper, the ultra-pulverized walnut shell (WS), walnut dregs (WD), and tea (T) were blended with formaldehyde solution. Based on the determination of the reactivity of WS, WD, T and formaldehyde solution, WS, WD, T was respectively blended with melamine modified urea-formaldehyde resin (MUF) as fillers, and the properties of the resin and plywood were analyzed. The results showed that under the conditions of blending, the pot life and gel time of MUF resin are prolonged, the viscosity is increased, while the pH value, the free formaldehyde content and the methylol content are decreased. The formaldehyde emission of the prepared plywood decreased with the amount of WS, WD, and T increased. When the added amounts of WS, WD, and T were 30%, 30%, and 10%, respectively, the wet bond strength of plywood increased by 120.00%, 47.27%, and 50.91%, respectively. The optimal amount of WS, WD, and T is 20%, 30%, and 10%.

Key words: melamine modified urea-formaldehyde resin, Biomass, filler.

1. Introduction

Urea-formaldehyde resin is a large amount of synthetic resin adhesive which is currently used in the wood industry. During the use of urea-formaldehyde resin, a certain amount of filler needs to be added to improve the process performance and the bonding strength, and ensure product quality [1, 2]. The foreign filler market has developed towards diversification, and a lot of work has been done on the research and development of fillers. At this stage, coconut shell powder, bark powder, mineral powder, and soybean powder are commonly used as fillers for urea-formaldehyde resins [3, 4]. In China, wheat flour (WF) is mainly used as the resin filler, and the variety is single, which is easily restricted by many factors such as nature and society. Of course, some research work has focused on the use of flour fillers as resin fillers in the production of plywood [6]. In recent years, there have been many studies on biomass fillers: agricultural and forestry wastes are used as woodworking adhesive fillers [5], wood flour is used as fillers for the production of plywood [7], and walnut shells are used as raw materials for phenolic resins. [3] Use fenugreek wet slag as a urea-formaldehyde resin extender [8], peanut shell whole powder as a phenolic resin enhancer, etc. [9].
Walnut shell (WS), walnut dregs (WD), and tea (T) are common forestry processing wastes with large annual outputs and low prices [10]. There has been increasing interest for greater economic utilization of WS, WD, and T. Ultrafine powder of WS, WD, and T enhance solubility, dispersibility, and chemical reactivity. After the ultrafine grinding treatment of WS, WD and T, the particle size is small, the specific surface area increased, the active group exposed on the surface increased, and the reaction was easier to react with other substances [11]. Therefore, in this paper, WS, WD and T were used as the filler of the melamine modified urea-formaldehyde resin (MUF) by blending the ultra-micro-pulverized WS, WD, and T with the formaldehyde solution. The effects of WS, WD and T on MUF resin properties and plywood properties were discussed.

2. Experimental

2.1. Materials
Formaldehyde (37% aqueous solution), urea (>99%), melamine (>98.5%), sodium hydroxide (>96%), ammonium chloride (NH4CL) (98%), and formic acid (>98%) were purchased from Chengdu Cologne Chemical Co., Ltd. without further purification. Walnut shells were collected in shanyang county, shanxi province and walnut dregs were purchased from xi’an broad well biological co., LTD. Tea was supplied by Shaanxi Xixiang Baiyan Tea Co., Ltd. All fillers were grounded to particle with size smaller than 48 μm.

2.2. 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 ℃ in about 40 min and maintained for 30 min. Subsequently, the pH was adjusted to 4.0–4.5 until the turbidity point appeared, then the pH was adjusted to 7.0–7.5, and the second urea (55 g) and formaldehyde (18 g) were placed in the reactor and maintained for another 30 min. After that, the third urea (45 g) was added and maintained for 30 min, and then the pH was adjusted to 8.0-8.5. The prepared resin was named MUF6.

2.3. Basic Performance Test of Resin
The basic properties of the resin include gel time, viscosity, solid content, free formaldehyde content, and hydroxymethyl content. According to "GBT14074-2006 Wood Adhesive and Resin Inspection Method" for relevant performance measurement.

2.4. Plywood Production
Eucalyptus twirl veneer (300 mm × 300 mm × 1.7 mm) with 8% moisture content was used to produce 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 (125oC) 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 testing of plywood
The formaldehyde emission test on plywood was conducted according to GB/T 17657-2013 "Test Methods for Physical and Chemical Properties of Wood-based Panels and Veneered Panels." The wet bonding strength of plywood was determined in accordance to a GB/T 17657-2013 "Test Methods for Physical and Chemical Properties of Wood-based Panels and Veneered Panels."
3. Results and Discussion

3.1. Determination of the Reactivity of WS, WD and T with Formaldehyde

3.1.1. Effect of Reaction Time on Reactivity of WS, WD and T with Formaldehyde.

![Fig. 1 Effect of different reaction time on the reactivity of WS, WD, T and formaldehyde](image1.png)

![Fig. 2 WS, WD, T formaldehyde consumption (time interval 0.5 h)](image2.png)

The effects of different reaction times on the reactivity of WS, WD, and T with formaldehyde are shown in Fig.1. Under alkaline conditions, WS, WD, and T had good reaction activity with formaldehyde, and the reaction mainly occurred in the early stage of the reaction, which gradually weakened in the later stage. When the reaction time was 1 h, the formaldehyde consumption per 100 g WS, WD, and T was 0.58 mol, 0.78 mol, and 0.78 mol, respectively. When the reaction time was 5 h, the formaldehyde consumption per 100 g WS, WD, and T was 1.17 mol, 1.48 mol, and 1.71 mol, respectively.

With the extension of the reaction time, the formaldehyde consumption of WS, WD, and T increased at first and then decreased (Fig.2). The peak time of formaldehyde consumption of WS, WD, and T appeared at 1h, 1h, and 0.5h, respectively. With the increase of reaction time, the reactivity of WS, WD and T with formaldehyde showed a downward trend.

WS lignin belongs to GS-type lignin and contains more G-type lignin. The GS position of G-type lignin is a vacancy that can be methylolated. In addition, WS lignin contains more phenolic hydroxyl groups and alcoholic hydroxyl groups, which is a good raw material for synthetic adhesives [12]. One of the main components of WD is protein. The amino groups on protein macromolecules can undergo nucleophilic addition reaction with formaldehyde [13], and can consume some formaldehyde. The main
components of WD dietary fiber are lignin, cellulose and hemicellulose. Lignin can also consume a part of formaldehyde. T contains 20% to 35% of tea polyphenols and other active substances [14]. As one of the main components of tea polyphenols, catechins can react with formaldehyde, and the reaction is mainly in the A ring containing resorcinol structure. The active site of the flavonoid unit forms a methylene bond between the active sites of the flavonoid unit to polymerize it [15]. The polyphenols contained in tea can react with formaldehyde to capture formaldehyde [16]. It is worth mentioning that when the reaction time was 0.5 h, compared with WS and T, WD had the best reactivity with formaldehyde. This might be related to the rate of extraction (leaching) of tea polyphenols, lignin and other substances.

3.1.2. Effect of Reaction Temperature on the Ability of WS, WD, T to React with Formaldehyde.

![Graph](image)

**Fig. 3** Effect of different reaction temperatures on the reactivity of WS, WD, T and formaldehyde

The effects of different reaction temperatures on the reactivity of WS, WD, and T with formaldehyde are shown in Figure 3. As the reaction temperature increased, the amount of formaldehyde consumed by WS, WD and T increased. When the reaction temperature is 90 °C, 0.58 mol, 0.78 mol, and 0.78 mol of formaldehyde can be consumed per 100 g of WS, WD, and T, respectively. This is mainly due to the continuous increase in reaction temperature, which accelerates the rate of precipitation of active groups such as lignin and tea polyphenols, increases the number of effective collisions, and thus accelerates the rate of chemical reactions.

3.2. Effect of WS, WD, and T as Fillers on Resin Properties

The effects of WS, WD and T as fillers on the resin properties are shown in Tab.1.

| Resin | Filler Category | Add Amount (%) | pH  | Viscosity/ (mPa·s) | Gel Time /s | Free Formaldehyde /% | Hydroxymethyl Content /% |
|-------|-----------------|----------------|-----|--------------------|-------------|----------------------|--------------------------|
| MUF6  | 0               | 0              | 8.23| 26                 | 133         | 0.15                 | 9.65                     |
| WS    | 10              | 6.84           | 32  | 280                | 228         | 0.14                 | 8.76                     |
| WD    | 10              | 6.29           | 28  | 228                | 273         | 0.13                 | 7.96                     |
| T     | 10              | 6.73           | 39  | 273                | 273         | 0.13                 | 8.57                     |
| WF    | 10              | 7.19           | 65  | 104                | 104         | 0.14                 | 8.79                     |
The effects of WS, WD, and T on resin properties are shown in Table 2. Adding 10% WS, WD, T, and WF to MUF6 resin significantly reduced the pH of the resin and prolonged the gel time of the resin, but WF shortened the gel time of the resin. The cause of this phenomenon may be that WS, WD, T and WF have different biomass characteristics. The groups on the WF molecular chain (the active ingredient is starch) can react with the methylol and amino groups on the resin to form a network structure, which promotes the resin gel curing [17]. Adding WS, WD, T, and WF increased the viscosity of the resin and reduced the free formaldehyde and methylol content in the resin. Reducing the methylol content is beneficial to improve the water resistance of resins and plywood.

3.3. Effect of WS, WD, and T as Fillers on Plywood Properties

3.3.1. Effects of WS, WD, and T on Formaldehyde Release from Plywood. Weigh the same amount of resin, add 5%, 10%, 15%, 20%, 25%, 30% of WS, WD, T, and WF respectively, and add 2% NH₄Cl as the curing agent. The sizing amount is 300 g/m². The measurement results of the formaldehyde emission of the plywood are as follows.

![Fig. 4 Effects of Different Additions of WS, WD, and T on the Formaldehyde Release from Plywood](image)

As can be seen from the formaldehyde emission test results of plywood, the formaldehyde emission of plywood decreased with increasing of filler. When addition amount of the filler reached 10%, the formaldehyde release amount of the plywood was less than 0.5%, which met the requirement of E0 grade of the plywood formaldehyde release amount.

There are two reasons for the continuous decrease in formaldehyde emissions from plywood: First, reactive groups in WS, WD, T and WF can crosslink with formaldehyde [8, 12, 18], thereby reducing the formaldehyde emission of plywood. Another reason is that after adding WS, WD, T, and WF, the urea-formaldehyde resin content in the glue solution is reduced. When the glue consumption remains unchanged, the urea-formaldehyde resin amount is relatively reduced, so the formaldehyde release amount of plywood is reduced.
3.3.2. Effects of WS, WD, and T on Plywood Bonding Strength. The wet bonding strength of the plywood is shown in Fig. 5.

![Graph showing the effects of WS, WD, T, and WF on plywood bonding strength.](image)

**Fig. 5** Effects of Different Additions of WS, WD, and T on Wet Adhesive Strength of Plywood

It can be known from the test results of plywood wet bonding strength that different fillers have different effects on plywood wet bonding strength. When the added amounts of WS, WD, T, and WF were 20%, 30%, 10%, and 25%, respectively, the plywood wet bond strength reached the maximum and the formaldehyde release amount was minimized. At this time, the plywood wet gluing strength was increased by 103.8%, 47.27%, 50.91%, and 63.64%, respectively, and the formaldehyde emission of the plywood was less than 0.5mg/L. Therefore, the optimal amounts of WS, WD, T and WF are 20%, 30%, 10%, and 25%, respectively.

WS, WD, T, WF are used as fillers for MUF6 resin, which can improve the wet bonding strength of plywood. This may be the cross-linking reaction between the active groups in WS, WD, T, and WF with formaldehyde [8, 12, 18]. At the same time, after the introduction of WS, WD, T, and WF, excessive penetration of the glue is avoided, and tiny voids generated by the resin are filled, which reduces the curing stress. However, when the amount of T added exceeds 10%, the wet gluing strength of the plywood continues to decrease, which may be due to the increase of the amount of T added, resulting in incomplete curing of the resin [18]. When the amount of WF is more than 20%, the wet gluing strength of plywood continuously decreases. The main reason is that starch is the main ingredient in flour. The crosslinkability between starch and hydroxymethyl in urea resin is relatively weak. The effective ingredients are reduced, and the bonding strength is significantly reduced.

In conclusion, it can be seen that when WS, WD, and T are used as the filler of MUF6 resin, the formaldehyde release of plywood can be reduced to less than 0.5 mg/L, and the wet bonding strength of plywood is greater than 0.7 MPa. WS, WD, and T can be used as fillers for MUF resin instead of WF.

4. Conclusion

(1) The best conditions for the reaction of WS, WD and T with formaldehyde are: the reaction temperature is 90 °C, and the reaction time is 0.5-1.5 h.

(2) The optimal dosages of WS, WD, T, and WF as fillers are 20%, 30%, 10%, and 25%, respectively; the plywood wet gluing strength is greater than 0.7 MPa, and the formaldehyde release of plywood is less than 0.5%, in accordance E0 level plywood requirements for formaldehyde release.

(3) WS, WD, and T have good aldehyde elimination effect and ability to improve the wet bonding strength of plywood, and can be used as fillers of MUF resin to replace WF.
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