The effect of the amount and type of curing agent on the basic properties of UF resin

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Abstract. In this study, the effects of four single-component curing agents on the basic properties of UF resins were investigated. The basic properties include pH, gel time and valid period. The studies have shown that different curing agent types and additions have different effects on the basic properties of urea-formaldehyde resins. The degree of influence of different curing agents of the same addition amounts: APS>AC>AS>AP, the degree of influence of different addition amounts of the same curing agent: 5%>2%>1%. Comprehensive comparison of four single-component curing agents, the optimal curing agent is AC, the optimal addition amount is 2%. This study laid the foundation for the subsequent study of the effects of multi-component curing agents on the properties of resins.

1. Introduction

Urea-formaldehyde resin (UF for short) is a thermosetting synthetic resin, which is a polycondensate formed by the reaction of addition and polycondensation of urea and formaldehyde under the action of a series of catalysts. UF is rich in raw materials, low in price, good in adhesion to wood fiber, high in cohesive strength, widely used in wood processing industry, accounting for 65%~75% of total synthetic resin for wood-based panel industry [1].

Curing is the key to gluing. The curing of UF plays an important role in the quality of the gluing process and the comprehensive properties of the bonded products [2]. As shown in the reaction formula below, the initial resin of the synthesis is cross-linked and cured under the condition of acidic auxiliary or heating, and the resin molecular chain continues to undergo polycondensation reaction, that is, the molecular weight is rapidly increased while being crosslinked into insoluble and infusible polymer [3].

The pH of the finished resin is generally between 7.5 and 9.0. Under such conditions, the resin is difficult to completely cure only by the acidity of the wood itself, and the cured product has a low crosslink density and poor adhesion quality. Therefore, it is necessary to add a curing agent to rapidly cure the resin to ensure the quality of the bonding.
The core of the resin cure is the enhancement of the acidity of the glue. Therefore, according to this curing mechanism, the curing agent should be an acidic substance or a substance capable of releasing acid when mixed with a resin. If the curing agent itself is a strong acidic substance, the pH of the glue solution drops sharply after the addition, and the rate of decline is too fast, which easily causes the pre-cure phenomenon of the glue. Therefore, a strong acid ammonium salt is generally added, which can chemically react with formaldehyde to form an acidic substance to promote curing of the resin [4].

In this paper, four kinds of ammonium salts were selected as curing agents, and the added amount was 1%, 2%, and 5% of the mass of the resin. The effect of the amount and type of curing agent on the basic properties of urea-formaldehyde resin was studied. By analyzing and evaluating the pH, gel time and valid period of the corresponding UF resin, the optimal curing agent type and addition amount were selected for subsequent research.

2. Materials and methods

2.1. UF resin preparation
Adding the first batch of formaldehyde and urea to the reaction kettle, adjusting the pH to 7.5-8.0, heating to 90℃ for 40 minutes, adjusting the pH to 4.5-5.0, and adjusting the pH to 8.0-8.5 after reacting to the desired viscosity. Add the second batch of urea, adjust the pH value to 5.0-5.5 after 25 minutes of reaction, adjust the pH to 7.5-8.0 after the reaction to the desired viscosity, add the third batch of urea, react for 30 min, and cool and pour out. The initial pH of the resin is 9.0 and the solids content was 51.4%.

2.2. Curing agent preparation
Ammonium chloride (AC for short), Ammonium sulfate (AS for short), ammonium phosphate (AP for short), and ammonium persulfate (APS for short) are all formulated into a solution having a mass fraction of 25%.

2.3. Sample Preparation
Take the same amount of UF resin, add four curing agents and mix them evenly. The addition amount gradient is set to 1%, 2%, 5% of the resin quality.

2.4. Performance test
The basic properties of the resin are carried out in accordance with the national standard GB/T 14074-2006 "Test methods for wood adhesives and resins".
3. Results and discussion

3.1. The effect of different curing agents on the pH of UF resin

Table 1. Change in pH of four curing agents within 15 seconds

| Time(s) | AC 1% | AC 2% | AC 5% | AP 1% | AP 2% | AP 5% | AS 1% | AS 2% | AS 5% | APS 1% | APS 2% | APS 5% |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 5       | 8.42  | 8.21  | 7.84  | 8.68  | 8.45  | 8.06  | 8.49  | 8.31  | 7.90  | 8.24  | 8.09  | 7.43  |
| 10      | 7.24  | 7.06  | 6.28  | 7.68  | 7.42  | 7.08  | 7.36  | 7.12  | 6.41  | 7.17  | 6.92  | 6.12  |
| 15      | 6.85  | 6.63  | 5.98  | 7.18  | 6.97  | 6.53  | 6.90  | 6.69  | 6.01  | 6.65  | 6.37  | 5.64  |

Table 1 shows the change in pH of the resin of the four curing agents in an amount of 1%, 2%, and 5% in 15 seconds. As can be seen from Table 1, the pH of the resin decreases with time. Since the four ammonium salts can react with the free formaldehyde in the resin, the reaction formula is: \(4\text{NH}_4^+ + 6\text{CH}_2\text{O} \rightarrow (\text{CH}_2)_6\text{N}_4 + 4\text{H}^+ + 6\text{H}_2\text{O}\), which indirectly produces acidic substances. The more the curing agent is added, the stronger the acidity of the resin, the faster the pH value decreases, and the lower the final pH value.

The pH value of the system is one of the keys to the curing of urea-formaldehyde resin [5]. The rate of decrease in pH affects the curing reaction and affects the performance of the sheet after hot pressing. If the rate of change of PH value is too fast, the resin cures too quickly, and the degree of pre-cure is more serious. The plate after hot pressing will cause problems such as aging and brittleness. If it is too slow, the reaction rate is slower, and the slow curing speed will result in incomplete curing of the resin, which may result in the resin and the sheet not being completely bonded during the production process.

Fig. 1 shows the change in pH of the resin in which the amount of the curing agent added is 2%. The rate of pH drop of the resin with different curing agents is significantly different. Within 5s-10s, the pH decline is the fastest, because the curing agent in 0s-5s reacts with the free formaldehyde in the resin, the reaction takes time, and the free formaldehyde which can react with the curing agent in 0s-5s resin is the most. And the most acidic substances are formed. In general, the pH of UF+APS changes the fastest, and the UF+AP is the slowest. Because APS can decompose to produce \(\text{S}_2\text{O}_8^{2-}\), \(\text{S}_2\text{O}_8^{2-}\) has strong oxidation properties and can directly oxidize formaldehyde to formic acid [6]. The substances which generate acid when AC, AP and AS are used as a curing agent are HCl, H_3PO_4 and H_2SO_4, respectively. The acidity of H_3PO_4 is weaker than H_3PO_4 and H_2SO_4. In the case of the same mass fraction, the H^+ provided by HCl is 1.36 times that of H_2SO_4. The ability of four identical mass fraction curing agents to affect the rate of change of resin pH is APS>AC≈AS>AP.

![Figure 1](image_url)

**Figure 1.** Change in pH of the four resin with 2% curing agent

3.2. The effect of different curing agents on the gel time of UF resin

Table 2. Gel time of resin with four curing agents added.

| Add amount | AC | AP | AS | APS |
|------------|----|----|----|-----|
| 1%         | 214| 265| 208| 168 |
| 2%         | 150| 195| 146| 124 |
| 5%         | 124| 145| 118| 75  |
Table 2 shows the gel time of the resin of the four curing agents in an amount of 1%, 2%, and 5%. It can be seen from the table that the more the amount of the same curing agent, the shorter the gel time of the resin. The more the curing agent is added, the stronger the acidity of the resin, and the faster the molecular weight of the resin grows, so that the faster the crosslinking cure occurs, the shorter the gel time.

![Figure 2. Gel time of the four resin with 2% curing agent](image)

As shown in Figure 2, the gel time of the resin with the addition of 4 different curing agents of 2% was 150s, 195s, 146s and 124s, respectively. Among them, Gel time of UF+ APS is the shortest, and that of UF+AP is the longest, UF+AC and UF+AS are similar in time, which is consistent with the change of pH value. APS is more susceptible to hydrolysis under the measured boiling water conditions, which greatly reduces the gel time. The faster the pH drops, the faster the cross-linking reaction takes place.

### 3.3. The effect of different curing agents on the valid period of UF resin

| Add amount | AC | AP | AS | APS |
|------------|----|----|----|-----|
| 1%         | 12 | 14 | 11 | 11  |
| 2%         | 7  | 10 | 8  | 8   |
| 5%         | 4  | 7  | 4  | 5   |

Table 3 shows the valid period of the resin of the four curing agents in an amount of 1%, 2%, and 5%. It can be seen from Table 3 that the more the same kind of curing agent is added, the shorter the valid period of the resin. The valid period of the four resins with a curing agent addition of 1% is 12h, 14h, 11h, 11h, and of 2% is 7h, 10h, 8h, 8h, and of 5% is 4h, 7h, 4h, 6h. In summary, The ability of four identical mass fraction curing agents to affect the rate of change of resin gel time is AC > AS ≈ APS > AP.

Fig. 3 shows the valid period of the resin in which the amount of the curing agent added is 2%. The valid period of adding AS and APS is the same. It may be because the determination of the valid period is performed at room temperature after the resin is cooled. The decomposition rate of APS is slow at normal temperature, which causes the acidity of the two glues to be similar. In order to meet the production needs, the valid period of the resin is as short as possible while meeting 6 hours. Comprehensive comparison of four curing agents, the effect of adding AC is the best.
Figure 3. Valid period of the four resin with 2% curing agent

4. Conclusion
Different curing agents have different degrees of influence on the basic properties of urea-formaldehyde resins, and the same amount of curing agents have different degrees of influence: APS > AC > AS > AP. The effect of different additions of the same curing agent: 5% > 2% > 1%.

In comparison, among the four single-component curing agents, the optimum curing agent is ammonium chloride, and the optimum addition amount is 2%. However, there are shortcomings in the single-component curing agent, which lays a foundation for the subsequent study of the effect of the multi-component curing agent on the properties of the resin.

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