Curing Characteristics of Low Molar Ratio Urea-Formaldehyde Resins

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(Received November 2, 2006, Accepted November 21, 2006)

Abstract: Five low molar ratio urea-formaldehyde (LUF) resins were synthesized in this study. The effects of molar ratio, free formaldehyde content, and catalysts on the curing characteristics of LUF resins were studied by measuring its free formaldehyde content, pH value change after catalysts added, curing rate, and pot life, observing its cured appearance, and analyzing its thermal behavior. The results indicate that: 1) The LUF resin with lower molar ratio than 1.0 can still cure; 2) Free formaldehyde content is not the main factor in affecting curing rate of LUF resin; 3) Compared with ammonium chloride as a traditional catalyst, persulfate salts markedly accelerate the curing rate of LUF resin, and result in the different appearance; 4) the addition of sodium chloride to catalysts can accelerate the curing rate of LUF resin, but the effect is moderate.

Keywords: *low molar ratio, urea-formaldehyde, curing characteristics, thermal analysis*

1. Introduction

Urea-formaldehyde (UF) resins have been greatly used in the production of wood-based panels, which are also one of the main sources of formaldehyde pollution from new decorated house, seriously harming people's physical and mental health [1-3]. In general, most widely used approaches for reducing formaldehyde emission of UF resin bonded products are either lowering the formaldehyde to urea (F/U) molar ratio or modifying the synthesis process of UF resins [4,5]. However, the curing rate of UF resin with low free formaldehyde content is usually slower and the bond strength of the UF resin bonded products is also lower, which limits its use. In addition, the performance of UF resins cured with different catalysts shows great differences. Correlative researches have indicated that different types of catalysts directly influenced UF resin's curing, formaldehyde emission, and bonding strength of the bonded products [6-8]. Consequently, to study the curing characteristics of LUF resins with different catalysts, will be helpful to solve the problems of formaldehyde emission.

Five LUF resins were synthesized in this study. The effects of molar ratio, free formaldehyde content, and types of catalysts on the curing characteristics of LUF resins were studied by measuring its free formaldehyde content, pH value change after catalysts added, curing rate, and pot life, observing its cured appearance, and analyzing its thermal behavior.

2. Materials and Methods

2.1. Materials

Formaldehyde solution and urea were of industrial grade respectively from Xilong Chemical Industries and Zhong'an Chemical Industries, China. Formic acid (HCOOH) and all the other chemicals used were of AR grade from Beijing Chemical Industries, China.

2.2. Methods

2.2.1. Synthesis of LUF Resins

Five types of LUF resins with formaldehyde to urea (F/U) ratio (0.8～1.2) were synthesized using the same synthesis procedure. Synthesis procedure of five typical resins was shown as follows:

The calculated amount of formaldehyde aqueous solution (37%) was charged into a stirred reactor and the reaction system was adjusted to the target pH value with 30% NaOH solution when the temperature was heated to 30°C, and the first urea was charged in. Then the tem-

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Table 1. Characteristics of LUF resins

F/U molar ratio	Properties			
	Non-volatile solids content (%)	Viscosity (mPa.s)	pH	Free formaldehyde content (%)
0.8	60	190	7.8	0.04
0.9	58	193	7.8	0.05
1.0	57	189	7.8	0.09
1.1	56	195	7.8	0.15
1.2	55	185	7.8	0.22

perature was slowly raised to 90°C within about 30 min and maintained at 90°C for a period of time, and then the pH value was adjusted to a weak acid value with 20% formic acid solution and the reaction was kept for 45 min. The second urea was added into reactor followed after adjusting the pH to a weak alkaline value, and the reaction was continued for 30 min. Then adjusting the pH value to 7.5～8.0 and cooling the temperature to 70°C, the last urea was added. The temperature was then set back to 70°C and the reaction was continued at this constant temperature for 30 min. At last, the system was cooled to room temperature and the sample was taken after the pH value reached about 7.8.

2.2.2. Catalysts

20% solution of ammonium chloride, 20% solution of ammonium persulphate, and 10% solution of potassium persulphate were used as single component catalysts. The adding amount of the catalysts was 1 g in solid per 100 g liquid LUF resin.

In addition, three composite catalysts were prepared by adding sodium chloride to the single component catalysts. The adding amount of the composite catalysts was 1 g of ammonium chloride (ammonium persulphate or potassium persulphate) and 3 g of sodium chloride in solid per 100 g of liquid LUF resin.

2.2.3. Measurement of Curing Rate and Pot Life

The curing rate and pot life of LUF resins were measured according to GB/T 14074.7-93 and GB/T 14074. 8-93 [9].

2.2.4. pH Value Changes of LUF Resins

A LUF resin with a catalyst was poured into a beaker at 25 ± 0.5°C, and the pH value change of the LUF resin was recorded using a pH meter (PHS-3C).

2.2.5. Appearances of Cured LUF Resins

Five LUF resins with catalysts were placed at room temperature (about 25°C) for 15 days, and the appearances of cured LUF resins were observed.

2.2.6. Thermal Behaviors of LUF Resins

LUF resins and catalysts were completely mixed, and their thermal curing behaviors were measured using a DSC (DSC-60/60A, SHIMADZU, Japan).

DSC measurements were performed on 10 to 20 mg of sample contained in an aluminum pan, and at a heating rate of 10°C/min from 30 to 150°C.

3. Results and Discussion

3.1. Characteristics of LUF Resins

Table 1 showed the properties of five LUF resins. With increasing F/U molar ratio, free formaldehyde content of five LUF resins increased, whereas the solids content decreased.

3.2. Curing Characteristics of LUF Resins with Different Catalysts

Classical polymer chemistry theory believes that the curing process of UF resin is condensing liner structure of resin into a three-dimensionally crosslinked network, and is very important for bonding qualities during curing and overall properties of bonded products.

It is generally considered that the reaction of traditional catalyst (ammonium chloride) with free formaldehyde of UF resin yields acids during curing, which results in the acceleration of condensation reaction and makes the resin cured. The chemical reaction [10] is presented as follows:

$$4NH_4Cl + 6CH_2O = (CH_2)_6N_4 + 6H_2O + 4HCl \quad (1)$$

Table 2. Curing rate and pot life of LUF resins using single component catalysts

F/U ratio	Ammonium chloride		Ammonium persulphate		Potassium persulphate	
	Curing rate (s)	Pot life (h)	Curing rate (s)	Pot life (h)	Curing rate (s)	Pot life (h)
0.8	143	19	48	6	55	9
0.9	75	13	47	5.5	52	8.8
1.0	68	11	45	5.3	50	8.6
1.1	66	10.3	42	4.5	49	8.5
1.2	63	10	38	4.2	48	8.3

Consequently, free formaldehyde in UF resin can accelerate the resin curing reactions, but free formaldehyde in LUF resins is usually very low, which results in formaldehyde in reaction being insufficient and thus affecting the resin curing rate. Therefore, LUF resins using ammonium chloride as catalyst have disadvantages. Ammonium persulphate and potassium persulphate possess rather stronger oxidation ability, and their aqueous solution show lower pH value than those of ammonium chloride. So, they can be expected to accelerate LUF resins cure. Therefore, ammonium persulphate and potassium persulphate were employed as catalysts in this study.

According to classical polymer chemistry theory, the LUF resin's characteristics and many phenomenon of LUF resin during synthesizing and after cured were hardly explained [11]. Thus, Pratt suggested a new colloid theory for UF resins, and subsequently Dunker and John further advanced this theory [12,13].

In this study, sodium chloride was used as one component of composite catalysts to investigate the effects of electrolyte on the curing characteristics of LUF resins to study the real curing mechanism of LUF resins.

3.3. Single Component Catalysts

The gel time and pot life of five LUF resins with single component catalysts were showed in Table 2.

After measuring curing rate of five LUF resins with different types of catalysts, it was found that the cured LUF resins show a very different state. For example, when ammonium persulphate (or potassium persulphate) was as a catalyst, the cured UF resin was rigid; however, the UF resin cured with ammonium chloride catalyst was very soft. And the LUF resins catalyzed by ammonium persulphate (or potassium persulphate) with lower molar ratio than 1.0 can still cure to be a solid.

3.4. Curing Rate

The results (Table 2) indicated that both ammonium persulphate and potassium persulphate as catalysts were significantly more effective than ammonium chloride in accelerating LUF resin catalytic curing, and especially the curing time of LUF resins with a molar ratio of 0.8 was shortened about 65% (from 143s to 48s or 54s). This is because ammonium persulphate and potassium persulphate aqueous solutions show lower pH value than ammonium chloride, and they all have oxidation ability which can oxidize free formaldehyde in UF resin into formic acid; during curing, ammonium persulphate can be hydrolyzed to form ammonium sulfate and hydrogen peroxide, which can also react with free formaldehyde to yield acid [14,15].

All of ammonium chloride, ammonium persulphate, and potassium persulphate can react with free formaldehyde to yield acid and thereby make resins cured. In general, free formaldehyde content of resins is very important for the curing rate of UF resins. Comparing Table 1 with Table 2, it was found that both free formaldehyde content and curing rate of resins increased with increasing molar ratio of UF resin. But, the Table 2 also showed that the curing rate of resins catalyzed by ammonium persulphate (or potassium persulphate) was not remarkably influenced by free formaldehyde content.

In addition, we added formaldehyde to the UF resin with molar ratio 0.8 to increase its free formaldehyde content to be as same as that of the UF resin with molar ratio of 1.2, then the curing rates of them using different catalysts were measured, and the results were shown in Table 3. The results showed that although the curing rate of UF resin with molar ratio 0.8 was increased, it was still slower than that of UF resin with molar ratio of 1.2 remarkably. Therefore, it can be concluded that free formaldehyde content is not the main factor in affecting LUF resin curing rate, while molar

Table 3. Curing rates of UF resins of molar ratio 0.8 and 1.2 with same free formaldehyde content

F/U ratio	Ammonium chloride	Ammonium persulphate	Potassium persulphate
	Curing rate（s）	Curing rate（s）	Curing rate（s）
0.8 → 1.2	103	43	54
1.2	63	38	48

Table 4. Curing rate and pot life of five LUF resins using composite catalysts

F/U ratio	Ammonium chloride + sodium chloride		Ammonium persulphate + sodium chloride		Potassium persulphate + sodium chloride	
	Curing rate (s)	Pot life (h)	Curing rate (s)	Pot life (h)	Curing rate (s)	Pot life (h)
0.8	137	17.5	44	5.3	50	8.5
0.9	71	12	42	4.5	49	8.2
1.0	65	10	38	4.4	47	8
1.1	64	9.5	37	4.2	46	7.7
1.2	60	8	35	4	44	7.5

ratio and pH value of catalyst aqueous solution have more effective influence on the curing rate.

3.5. Pot Life

From the results in Table 1, it could be found that the pot life of LUF resin with ammonium chloride as catalyst was the longest among three single component catalysts. Under different molar ratios, the lower molar ratio was, the longer the pot life was. Table 1 also instructed that persulfate salts markedly accelerated LUF resin curing rate, while consequently shortened its pot life. However, the pot life of five LUF resins with potassium persulphate was more than 8 hours, which could satisfy the practical production requirements.

3.6. Composite Catalysts

Comparing Table 2 with Table 4, it could be concluded that the addition of sodium chloride to catalysts could accelerate curing rate and shorten pot life of five LUF resins, but with mild effect. In a word, sodium chloride can accelerate LUF resins curing rate, but the effect is moderate. The reasons for above-mentioned results are possibly that LUF resins indeed have a certain colloid component. Due to the fact that curing rate and pot life have few changes, even if colloid theory worked in the LUF resins, it was not totally decisive. Furthermore, sodium chloride added to UF resin during or after synthesis does not shorten the storage period of resin markedly.

3.7. pH Value Changes of LUF Resins with Single Component Catalysts

In this study, the LUF resins with molar ratio of 0.8, 1.0, and 1.2 were used, and their pH value changes after adding catalyst within 8 hours were measured.

From Figures 1～3, it was found that after adding single-component catalysts, the pH value of all three LUF resins decreased very sharply during the first 30 minutes. The pH value of the resin of molar ratio of 1.2 catalyzed by ammonium persulphate decreased fastest, from 7.80 to 5.53, but that of the resin of molar ratio of 0.8 with ammonium chloride catalyst changed most slowly, from 7.80 to 7.17. After 30 minutes later, the changes of pH values of the three resins decreased gently. The main possible reason is that three types of catalysts can react with the free formaldehyde of LUF resins to yield acids. In the initial stage of curing reaction, there is much free formaldehyde reacting with catalyst, thus yielding plenty of acids; with the free formaldehyde decreasing, the yielding rate of acid slows down, resulting in slower decreasing rate of pH value.

In addition, it was also found that the LUF resin using ammonium chloride or ammonium persulphate as a catalyst with higher molar ratio showed lower pH value at the same curing time. This was consistent with the changes of pot life and curing rate of UF resin using ammonium chloride or ammonium persulphate as a catalyst. But the LUF resins using potassium persulphate as a catalyst with higher molar ratio showed higher pH

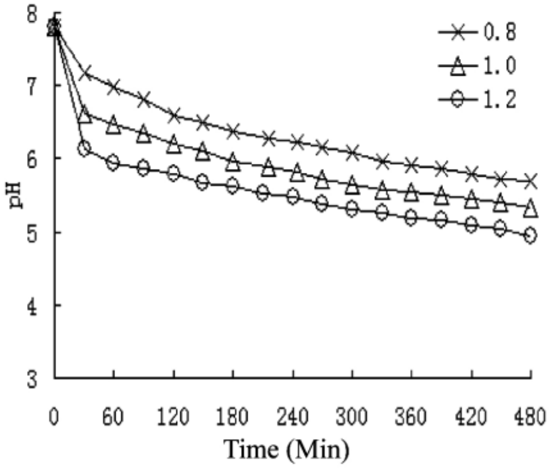

Figure 1. The pH changes of UF resins with ammonium chloride catalyst.

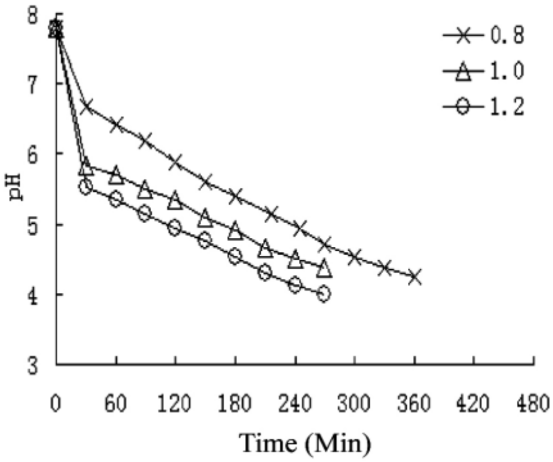

Figure 2. The pH changes of UF resins with ammonium persulphate catalyst.

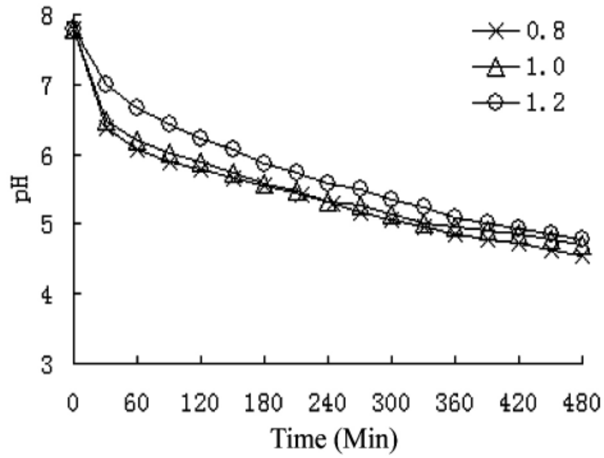

Figure 3. The pH changes of UF resins with potassium persulphate catalyst.

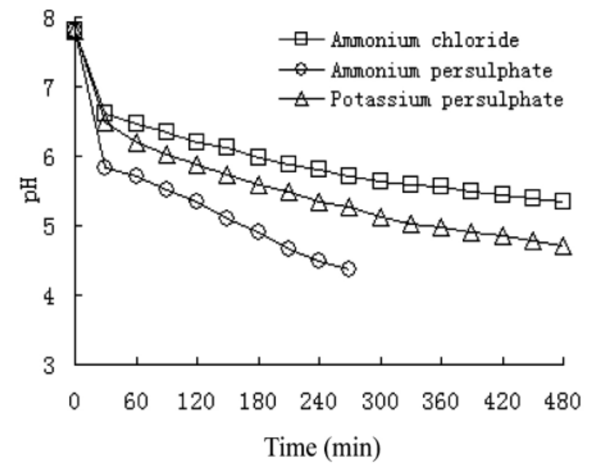

Figure 4. The pH changes of UF resin with single component catalysts.

value. The reason is yet unknown, and further research is needed.

In order to study the pH value changes of LUF resin during curing with different catalysts, we chose the LUF resin with molar ratio of 1.0 as the study object, and the experimental results were shown in Figure 4.

The pH value change of LUF resin using ammonium chloride as a catalyst were similar to that of potassium persulphate as a catalyst. However, the range of pH value change using ammonium persulphate as a catalyst was higher than that of the other two. This is why the resin using ammonium persulphate as a catalyst has the shortest pot life.

3.8. pH Value Changes of LUF Resin with Composite Components Catalysts

Comparing the effects of single component catalysts with composite component catalysts on pH value in Figure 5, we could conclude that sodium chloride had no significant influence on pH value change of LUF resin.

3.9. pH Value Changes of Single Component Catalyst Solution with or without Formaldehyde

In order to study the effects of formaldehyde content on pH value change, we added formaldehyde to 1% catalyst aqueous solution to make the free formaldehyde concentration to be 0.2%, and the pH value changes of the solution in 480 minutes at room temperature were

Table 5. Appearances of five LUF resins using different catalysts after cured for 15 days

F/U ratio	Appearances		
	Ammonium chloride	Ammonium persulphate	Potassium persulphate
0.8	Appearance: non-white Section: rough	Appearance: transparent Section: series, smoothness	Appearance: off-white with little transparence Section: series, flatness
0.9	Appearance: non-white Section: rough	Appearance: transparent Section: series, smoothness	Appearance: off-white with little transparence Section: series, flatness
1.0	Appearance: white Section: series, flatness	Appearance: transparent Section: series, smoothness	Appearance: white Section: series, flatness
1.1	Appearance: white Section: series, flatness	Appearance: white Section: series, flatness	Appearance: ivory-white Section: series, flatness
1.2	Appearance: white Section: series, flatness	Appearance: white Section: series, flatness	Appearance: ivory-white Section: series, flatness

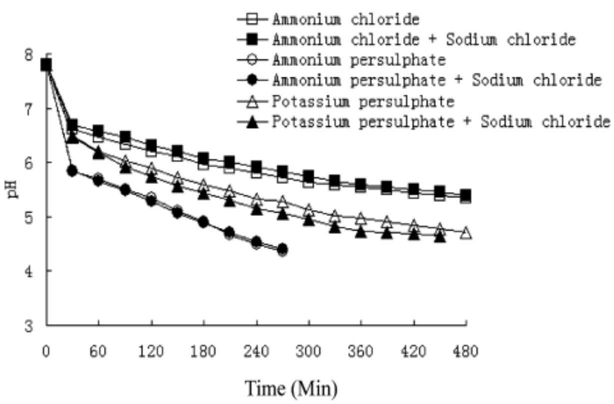

Figure 5. The pH value changes of UF resin with molar ratio of 1.0 using single and composite components as catalysts.

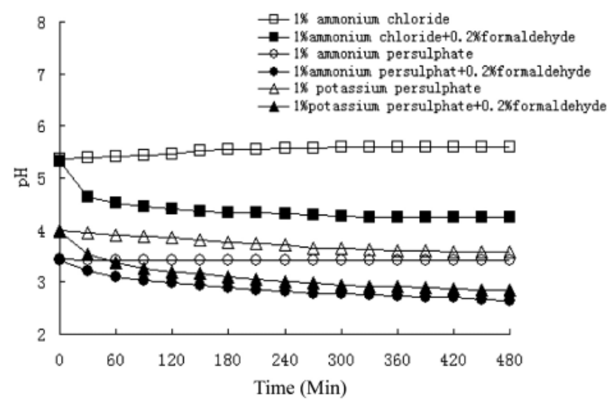

Figure 6. The pH value changes of single component catalyst solution with and without formaldehyde.

measured. The results were shown in Figure 6.

It could be seen that the pH value of 1% ammonium chloride solution did not change greatly, and only varied from 5.53 to 5.59 at room temperature after 480 minutes. Correspondingly, the pH value of ammonium chloride solution which contained 0.2% formaldehyde decreased from 5.53 to 4.24. The pH value of 1% potassium persulphate solution changed from 3.98 to 3.57, after adding 0.2% formaldehyde. Its pH value decreased from 3.98 to 3.43.The pH value of 1% ammonium persulphate solution changed from 3.44 to 3.43, after adding form-aldehyde, and its pH value decreased from 3.44 to 2.67.

The pH values of potassium persulphate solution and ammonium persulphate solution were lower than 4.0, which was enough to make UF resin cure, but the pH value of ammonium chloride solution was maintained at about 5.5 after 480 minutes. Hence LUF resins using different catalysts have great differences in curing rate and pot life (Table 2). After adding formaldehyde, the pH value of ammonium chloride decreased most greatly in three catalysts, reaching 1.29. However, the pH value decreases of potassium persulphate solution and ammonium persulphate solution were 0.56 and 0.77, respectively. Thus, the acidity of UF resin system using ammonium chloride as a catalyst mostly depended on the reaction of catalyst with formaldehyde, but those of UF resins using potassium persulphate and ammonium persulphate as catalysts were derived from two reaction actions mentioned above. Therefore, it is concluded that the free formaldehyde content is not the main factor, affecting curing rate of the LUF resins when potassium persulphate and ammonium persulphate were used as catalysts.

Table 6. Curing temperature parameters of LUF resins with different types of catalysts

F/U ratio	Catalyst	Onset temperature (℃)	Peak temperature (℃)	Endset temperature (℃)
0.8	Ammonium chloride	87.55	97.03	101.05
	Ammonium persulphate	71.03	80.54	89.80
	Potassium persulphate	80.59	88.96	94.54
0.9	Ammonium chloride	89.70	95.74	101.30
	Ammonium persulphate	71.05	80.38	89.62
	Potassium persulphate	80.52	88.89	94.23
1.0	Ammonium chloride	86.12	94.94	99.43
	Ammonium persulphate	70.90	80.24	87.35
	Potassium persulphate	80.73	88.77	92.85
1.1	Ammonium chloride	86.46	92.72	98.82
	Ammonium persulphate	70.85	79.95	83.44
	Potassium persulphate	80.89	88.58	91.02
1.2	Ammonium chloride	84.13	90.99	94.80
	Ammonium persulphate	70.84	79.81	82.63
	Potassium persulphate	80.91	88.46	90.73

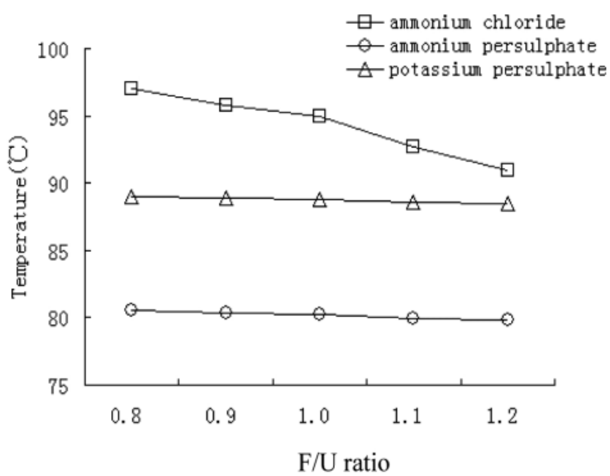

Figure 7. Peak temperature of LUF resins with different types of catalysts.

3.10. Appearances of Cured LUF Resins

In Table 5, it was showed that the appearances of the cured LUF resins with different catalysts were very different. Appearance of UF resin reflects its internal molecular structure. UF resins with different molar ratios catalyzed by different catalysts showed different appearance, which indicated that the chemical structures of cured LUF resins with different catalysts were not the same, and the reason needs further research.

3.11. Thermal Behavior of LUF Resins

In this study, the onset temperature, peak temperature, and endset temperature of LUF resins with different catalysts were measured by DSC to analyze thermal behavior of LUF resins in curing process.

From Table 6 and Figure 7, it could be seen that onset temperature, and endset temperature of LUF resins catalyzed by ammonium persulphate (or potassium persulphate) were hardly influenced by molar ratio. Peak temperatures of LUF resin using different catalysts were different, and peak temperature of LUF resin using ammonium persulphate (or potassium persulphate) as catalyst was lower , while that of ammonium chloride as a catalyst was higher, which indicated slower curing rate. This indirectly illuminates that free formaldehyde content is not the main factor, affecting the curing rate of LUF resins, and both ammonium persulphate and potassium persulphate are significantly more effective than ammonium chloride in accelerating LUF resin's curing.

4. Conclusions

Based on the results in this study, the following conclusions can be arrived at:

1) LUF resins catalyzed by ammonium persulphate (or potassium persulphate) with a molar ratio than 1.0 can

still cure.

2) Free formaldehyde content is not the main factor for affecting LUF resin curing rate, while the LUF resin's molar ratio and the catalyst aqueous solution's pH value influence the curing rate more effectively.

3) Compared with ammonium chloride as a traditional catalyst, persulfate salts markedly accelerated LUF resins curing rate and the pot life of resins was more than 8 hours, which could meet the practical production requirements.

4) Appearances of the cured LUF resins with different catalysts were almost different.

5) Sodium chloride added to catalysts accelerated curing rate and shortened pot life of five LUF resins, but the effects were not remarkable.

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