

Condensation Reaction and Crystallization of Urea-Formaldehyde Resin during the Curing Process

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Urea-formaldehyde (UF) resins were synthesized with different molar ratios and solid contents, and simultaneously they were cured under conditions of different pH values. The curing behaviors of cured UF resins were examined by synchronous thermal analysis (TG-DSC). The crystallinity of cured UF resin was analyzed by X-ray diffractometry. The gel time of cured UF resin was recorded by chemical methods. The results indicate that condensation reactivity leads condensation reaction and crystallization to play various roles during the curing process of UF resin. The condensation reaction and crystallization in the curing process interact to result in different structures of cured resin. A new mechanism for UF resin curing (reaction-crystallization) is thus proposed.

Keywords: Urea-formaldehyde resin; Curing; Condensation reactivity; Condensation reaction; Crystallization; Crystallinity

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INTRODUCTION

Urea-formaldehyde resin (UF resin) is one of the most important adhesives for the assembly of man-made wood-based panels, such as MDF, plywood, and particleboard. Commonly, thermosetting urea-formaldehyde (UF) resin is cured by condensation reaction under acidic conditions.

The curing process of UF resin has been studied by using differential scanning calorimetry (DSC) technology. Szesztay *et al.* (1993, 1996) found that an exothermic peak (condensation reaction) and an endothermic peak (decomposition of methylene-ether linkages) appeared in the DSC curve. In a high pressure DSC cell, the endothermic effect shifted to higher temperature and avoided disturbing the exothermic peak. Xing *et al.* (2005) studied the effect of catalyst content on curing behavior of UF resin under high pressure conditions. The parameters of the exothermic peak showed that the condensation reactivity of resin increased with increment of pH value in the resin system. Pizzi's team (2019) analyzed the effect of initial F/U molar ratio on reaction heat, onset temperature, exothermic and endothermic peak temperatures of the DSC curve. The results showed that the initial molar ration obviously affected physico-mechanical properties of the boards.

The studies also found that cured UF resin has a crystalline state that does not exist in other thermosetting resins such as phenolic resins, epoxy resins, *etc.* (Gupta *et al.* 1985). The crystalline structure of the cured UF resin is inherent in UF resin, especially in the UF resin with low molar ratios of formaldehyde to urea (F/U molar ratio) (Nuryawan *et al.* 2016). The crystallinity of cured resin is affected by molar ratios, temperature of curing process, and curing agents. The crystallinity of the cured UF resin increases as the F/U molar ratio decreases (Park and Causin 2013; Singh *et al.* 2014; Nuryawan *et al.* 2017).

The crystallinity of cured resin was inversely proportional to the degree of branched structure of cured resin (Nuryawan *et al.* 2015; Park and Jeong 2011; Ding and Tian 2017).

Based on the previous studies, there is not only a condensation reaction but also crystallization during the UF resin curing process. The impact of the factors, such as F/U molar ratio and curing agent, *etc.*, on condensation reactivity or crystallinity has been reported. However, the study of the combined effects of condensation reaction and crystallization on curing mechanism of UF resin is very limited.

Therefore, in the present work, the UF resins with different condensation reactivity were obtained by adjusting final F/U molar ratio, solid content, and pH value of curing condition. The gel time, which characterizes the reactivity, as well as the crystallinity of cured resin, which characterizes the structure of resin, were measured under same pH conditions. The TG-DSC curves were obtained under normal pressure. The curing processes of UF resins with different condensation reactivity were studied. The results clarify the variety of curing mechanism of UF resin with different condensation reactivity. Accurate understanding of the curing mechanism of UF resin is beneficial to the development of UF resin with low-formaldehyde release and high-performance.

EXPERIMENTAL

Materials

Reagent-grade formaldehyde (37%), sodium hydroxide, formic acid, and hydrochloric acid were purchased from Shanghai Chemical Reagent Ltd., China. Industrial-grade Urea was provided by ChuzhouJinhe Chemical Industry Ltd., China.

Preparation of UF Resins

All resins were synthesized in the laboratory. The synthesis of all UF resins was a typical three-step procedure (alkaline-acidic-alkaline). First, formaldehyde (F=250 g) was poured into a three-necked flask and adjusted to pH 7.5 to pH 8.0 with 20% sodium hydroxide solution. The first amount of urea ($U_1=94.4$ g) was added to give the F/U molar ratio of 2.0. The mixture was heated to 90 °C and maintained at this temperature for 30 minutes. The condensation reaction took place by adding formic acid (10%) to obtain a pH of 4.6 to 4.8 until endpoint 1 was reached. The pH was adjusted to 5.0 with sodium hydroxide solution, and the second amount of urea ($U_2=23.5$ g) was added to give the F/U molar ratio of 1.60. The temperature was maintained at 85 to 90 °C until the endpoint 2 was reached. The endpoint was determined by the cloudy appearance when the solution mixture was dropped into a beaker of water at certain temperature (endpoint 1: 20 °C, endpoint 2: 40 °C). When endpoint 2 was reached, the pH was adjusted to 7.5 to 8.0 with the sodium hydroxide solution. The third amount of urea (U_3) was added. The reaction mixture was maintained at 70 °C for 30 min. Finally, the mixture was cooled to ambient temperature. The pH was adjusted to 7.5 to 8.0 again. Various amounts of U_3 ($U_3= 0$ g, 16.9 g, 39.4 g, 61.9 g, or 80.8 g) had different final F/U molar ratios (the F/U molar ratio = 1.60, 1.40, 1.20, 1.05, and 0.95, respectively). The UF resin with the F/U molar ratio of 1.60 was dehydrated on vacuum conditions to obtain the resins with different solid contents (50%, 58%, and 67%). The solid content of UF resin was measured according to GB/T14732 (2006).

Preparation of Samples for Measure

Liquid resin with different pH values

The pH values of all resins were adjusted to 7.5, 4.5, 4.0, and 3.0 with sulfuric acid solution (20%).

In other studies, the pH value of UF resin used to be adjusted by ammonium salt, such as NH_4Cl . The pH value was affected by the formaldehyde produced during the UF resin curing process. This meant that the pH value changed with the variety of the amount of formaldehyde during the curing process (Xing *et al.* 2005; Dazmiri *et al.* 2019). To maintain pH values during the UF resin curing process, the sulfuric acid solution was used to adjust the pH values directly.

Powdered cured resin

The resins with different pH values were cured in the oven at 120 °C for 2 h. The cured resins were ground into particles and sieved to obtain particles between 80 mesh and 120-mesh for the XRD test.

Gel Time Measurement

The gel time of the liquid resins with different pH values was measured at 100 °C by a gel time meter (Sunshine 22A, Shanghai, China). An average of three replications was used for each measurement.

TG-DSC Measurement

TG-DSC measurements were carried out with a synchronous thermal analyzer (SDT Q600, TA, City, USA) with the heating rate of 5K/min in dynamic nitrogen atmosphere (100 mL/min). The mass of the samples was 10 to 15 mg. The temperature of samples ranged from 30 °C to 200 °C. The TG-DSC test was carried out with an open crucible. All samples were the same as those in the gel time test.

X-Ray Diffraction (XRD)

An X-ray diffractometer (D8 Advance, Bruker, Karlsruhe, Germany) was used to investigate the crystallinity of cured UF resins. The powdered cured resins were analyzed at ambient temperature using a CuK α -1 X-ray source with a wavelength (λ) of 1.5406 Å. The angle of incidence changed from 10° to 70° by steps of 0.02°/min.

The XRD diffractogram was analyzed by MDI jade5.0 software. The crystallinity of cured UF resin was obtained.

RESULTS AND DISCUSSION

TG-DSC Curves of Urea-Formaldehyde Resin

The UF resin was cured with the F/U molar ratio of 1.60 and solid content of 50% under conditions of pH 7.5 and 3.0, respectively. Figure 1 shows the TG-DSC curves of the UF resins curing. There are two endothermic peaks (peak 1 and peak 2) on every DSC curve, and these peaks are accompanied by significant mass loss appearing on the TG curve.

Under the pH 7.5 condition, the water in initial resin is quickly evaporated with increment of temperature before peak 1. Due to the water loss, the liquid state of resin changes to the gel state between peak 1 and peak 2 (Nuryawan *et al.* 2017). The resistance

of water diffusing from interior to surface of resin in gel state increases, and water evaporation rate decreases. When temperature reaches peak 2, the formaldehyde from decomposition of methylene-ether linkages, as well as small amount of initial water, is evaporated from the resin, accompanying the endothermic effect (Szesztay *et al.* 1993).

The temperatures at peak 1 and endothermic heat at pH 3.0 are lower than those at pH 7.5. This indicates that the condensation reaction has taken place. The condensation reaction is an exothermic reaction. The exothermic heat offsets some endothermic heat. No exothermic peak appears between peaks 1 and 2 on the DSC curve because the exothermic effect is covered by endothermic effect of water evaporation (Siimer *et al.* 2003; Zorba *et al.* 2008). The condensation reaction will increase the degree of cross-linking of resin. A higher degree of cross-linking in the structure leads to higher diffusion resistance. More water (reaction water) and methylene-ether linkages are produced by the condensation reaction. Thus, it is known that there will be greater amounts of water and methylene-ether linkages in the resin. Here, comparing to the TG curves of pH 3.0 and 7.5 between peaks 1 and 2, the evaporation rate of water at pH 3.0 is obviously lower than that at pH 7.5. The mass loss for peak 2 at pH 3.0 is more than that at pH 7.5. This means that more of the initial water, reaction water, and methylene-ether linkages are left in the resin in gel state before peak 2. However, those substances are all quickly evaporated at peak 2 (Siimer *et al.* 2003; Dazmiri *et al.* 2019).

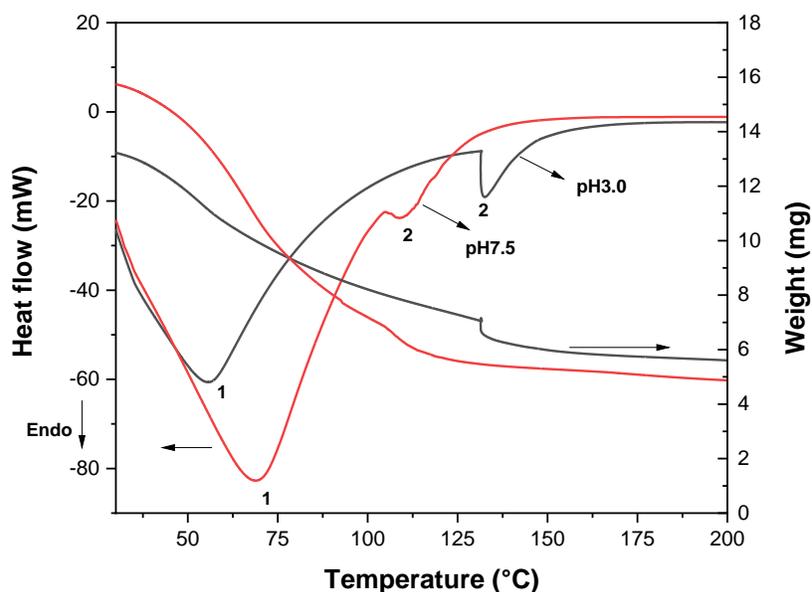


Fig. 1. TG-DSC curves of UF resin with F/U molar ratio of 1.60 and solids content of 50%

Figure 2 shows the TG-DSC curves for when the UF resins with a mole ratio of 1.60 and various solid contents (50%, 58%, and 67%) were cured under the condition of pH 3.0. Figure 3 shows the gel time and mass loss of the resins corresponding to the peak 2. The gel time decreased with the increment of solid contents. This means that the condensation reactivity of the resin increased with the increment of solid contents. Figure 2 also shows that the amount of the evaporated substance at peak 2 (mass loss) increased with the increment of condensation reactivity rather than with the increment of water content of the initial resin. This indicates that the evaporated substance at peak 2 was

mainly derived from the reaction water as well as due to the formaldehyde from the decomposition of methylene-ether linkages.

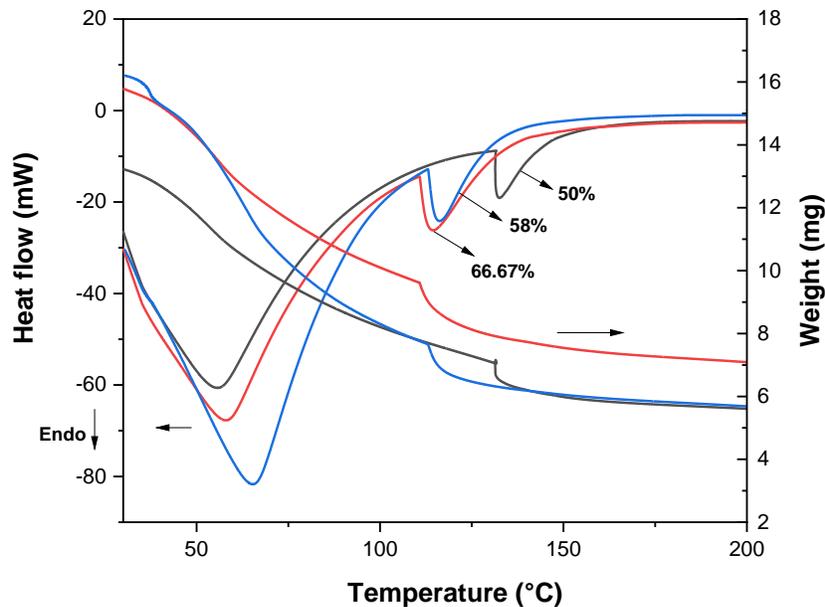


Fig. 2. TG-DSC curves of UF resin with F/U molar ratio of 1.60 and different solids content under pH 3.0 condition

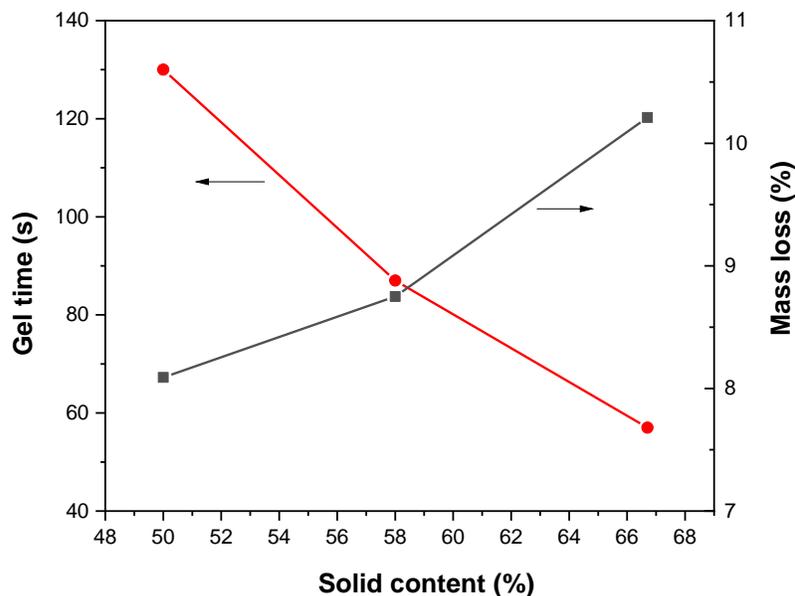


Fig. 3. Gel time and mass loss corresponding to peak 2 of UF resin with F/U molar ratio of 1.60 curing under condition of pH 3.0

Figure 4 shows that the temperature at peak 2 (T_p) increased with the increment of the gel time of the resin under pH 3.0. This means that T_p decreased with the increment of the condensation reactivity of resin. The studies found that, for the UF resin with higher

F/U molar ratios, the increment of condensation reactivity could result in a higher degree of branching of cured resin. The branched network structure facilitated water penetration into the interior of cured resin, which led to more hydrolysis (Park and Jeong 2011; Ding and Tian 2017). In other words, the branched network structure facilitates water and formaldehyde to evaporate from interior of resin in gel state at lower temperature as well (Siimer *et al.* 2003). The value of T_p is inversely proportional to diffusion resistance of substance evaporation in resin. It is reasonable to conclude that T_p is affected by condensation reactivity, the gelling process, and the degree of branched structure of the cured resin.

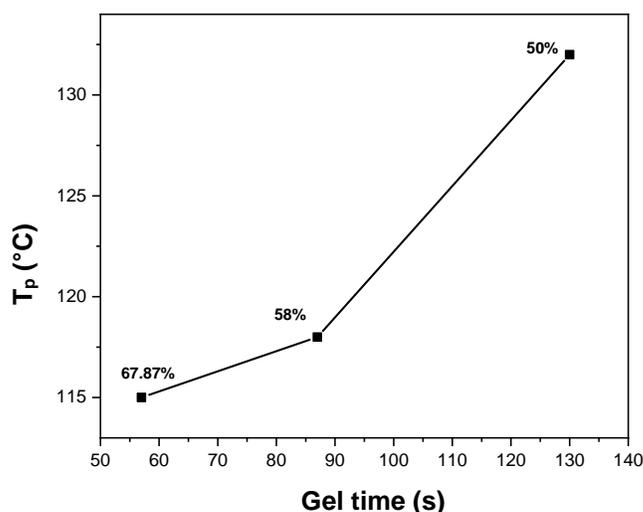


Fig. 4. Gel time and T_p of peak 2 of UF resin with F/U molar ratio of 1.60 curing under condition of pH 3.0

Condensation Reaction and Crystallization of Urea-Formaldehyde Resin during Curing Process under Conditions of Different pH

Figure 5 shows the peak 2 of the DSC curve, when the UF resin with the F/U molar ratio of 1.60 was cured under conditions of pH 3.0, pH 4.0, and pH 4.5, respectively. The T_p value of peak 2 decreased with the decrement of pH values. This means that the water and formaldehyde in resin evaporated more easily with the increment of the condensation reactivity of UF resin. However, Fig. 6 shows that T_p increases with the decrement of the pH value, when the UF resin with the F/U molar ratio of 0.95 was cured under conditions of pH 3.0, pH 4.0, and pH 4.5, respectively. This means that it is difficult to evaporate water and formaldehyde in resin with the increment of the condensation reactivity of UF resin. In summary, there are different impacts of condensation reactivity of UF resins on the structure of cured resin with different F/U molar ratios.

Figure 7 (a) shows that, for UF resin with the F/U molar ratio of 1.60, the structure of cured UF resin was amorphous. Figure 8 shows that the crystallinity of cured UF was near to zero and that it was not affected by the pH value. Only the value of T_p was affected by the pH value. This indicates that the condensation reaction enhanced the degree of branching of cured UF resin and limited the crystallization of the UF resin during the curing process. The condensation reaction played a major role during the curing process for the UF resin with the F/U molar ratio of 1.60.

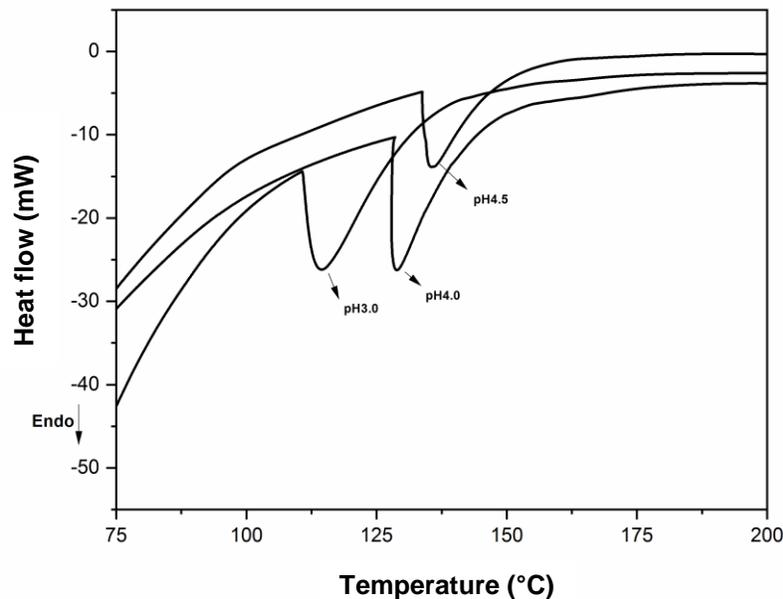


Fig. 5. Peak 2 on DSC curves of UF resin with F/U molar ratio of 1.60 curing with different pH

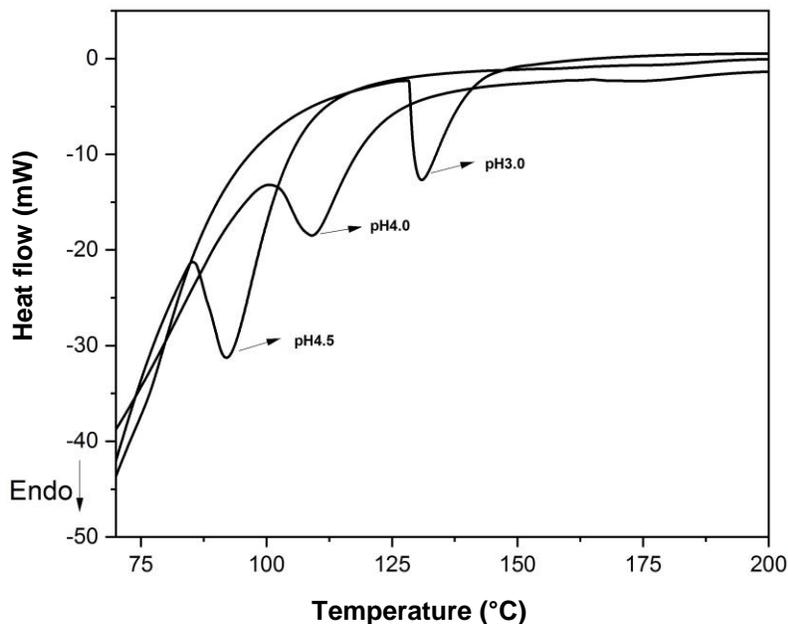


Fig. 6. Peak 2 on DSC curves of UF resin with F/U molar ratio of 0.95 curing with different pH

Figures 7(b) and 8 show that, for the UF resin with the F/U molar ratio of 0.95, the crystallinity of cured resin increased with the decrement of the pH value. This means that the condensation reactivity of the UF resin enhanced the crystallinity and decreased the degree of branched structure of cured resin. As we have known, the condensation reactivity of UF resin with a low molar ratio was lower than that with a high molar ratio (Park *et al.* 2006). When UF resin with the F/U mole ratio of 0.95 was cured, the macromolecular

chains firstly intertwined with each other and arranged themselves in an orderly way because of lower reactivity. The crystal structure was formed in the cured resin (Nuryawan *et al.* 2017). The condensation reaction occurred between adjacent reactive groups in the crystal region. New covalent bonds fastened the molecular chains in the crystal zone and so the crystallinity increased. The agglomeration and crystallization occurred before the condensation reaction. In other words, crystallization played a major role during the curing for UF resin with the F/U mole ratio of 0.95, but the condensation reaction only enhanced the crystallization.

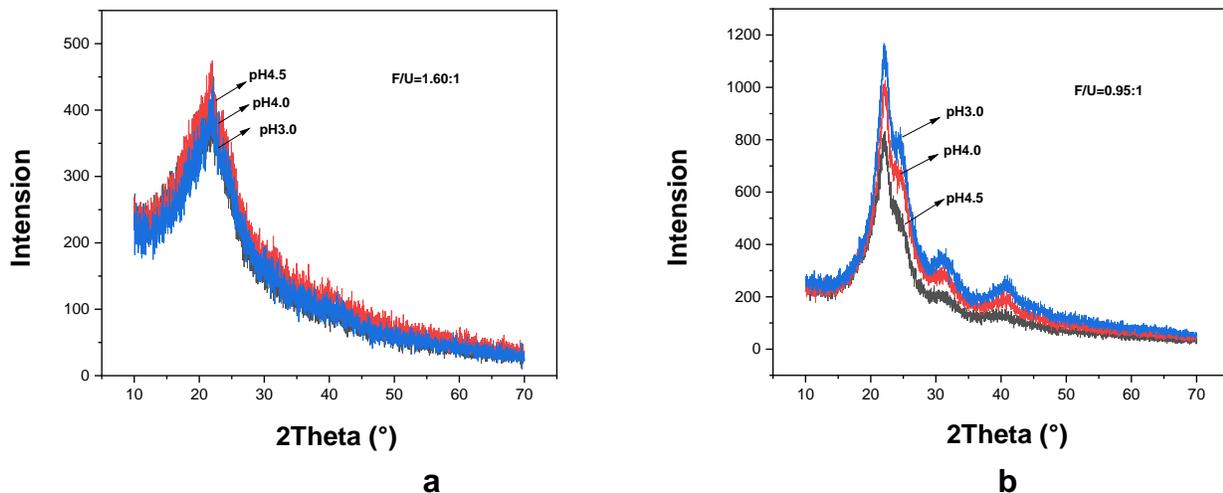


Fig. 7. X-ray diffractograms of cured UF resins with F/U molar ratio of 1.60 and 0.95 under different pH conditions

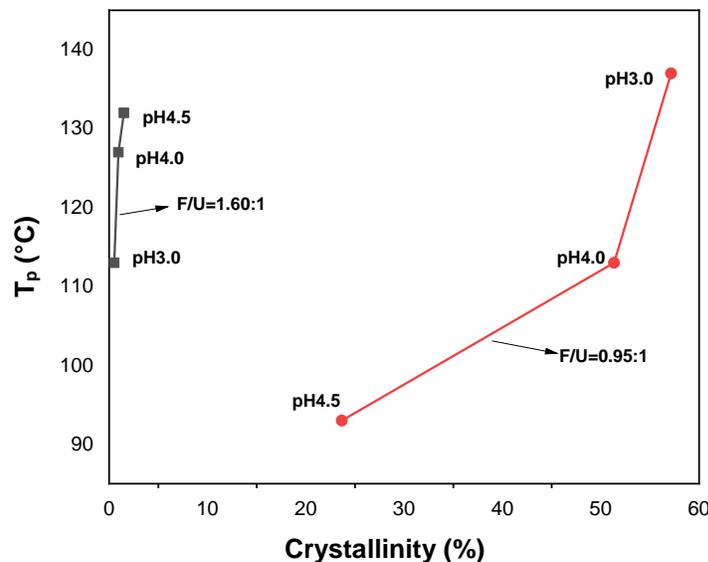


Fig. 8. T_p of Peak 2 and crystallinity of cured resin with F/U molar ratio of 1.60 and 0.95 under different pH conditions

Condensation Reaction and Crystallization of Urea-Formaldehyde Resin with Different Molar Ratio during the Curing Process

Figure 9 shows the peak 2 of DSC curves, when UF resins with different molar ratios (1.60, 1.40, 1.20, and 0.95, respectively) were cured under the condition of pH 3.0. The value of T_p increased when the F/U mole ratio decreased. This means that the evaporation resistance of water and formaldehyde in resin increased with the decrement of F/U molar ratios. Figure 10 shows that the crystallinity of the cured UF resins obviously increased with the decrement of F/U molar ratios. In other words, the degree of branching of the cured UF resin decreased with the decrement of F/U molar ratios. Figure 11 shows that the gel time of the UF resins increased and the mass loss decreased when the F/U molar ratio decreased from 1.60 to 0.95. This indicates that the reactivity and degree of condensation reaction decreased with the downturn of F/U mole ratios during the curing process. In other words, the influence of condensation reaction decreased in the cured resin and that of crystallization increased with the decrement of F/U molar ratios.

Figure 12 shows the T_p at peak 2, when UF resins with different F/U mole ratios were cured under conditions of different pH values. When the F/U mole ratio gradually declined from 1.60 to 0.95, the variations of T_p with the decrement of pH values switched from decrement to increment. When the F/U mole ratio was 1.05, the variation of T_p with pH values was very limited. This result indicates that the turning point of importance of condensation or crystallization during resin curing was around the F/U mole ratio of 1.05. When the F/U molar ratio was higher than 1.05, the condensation reaction played a major role. However, when the F/U molar ratio was lower than 1.05, the crystallization played a major role.

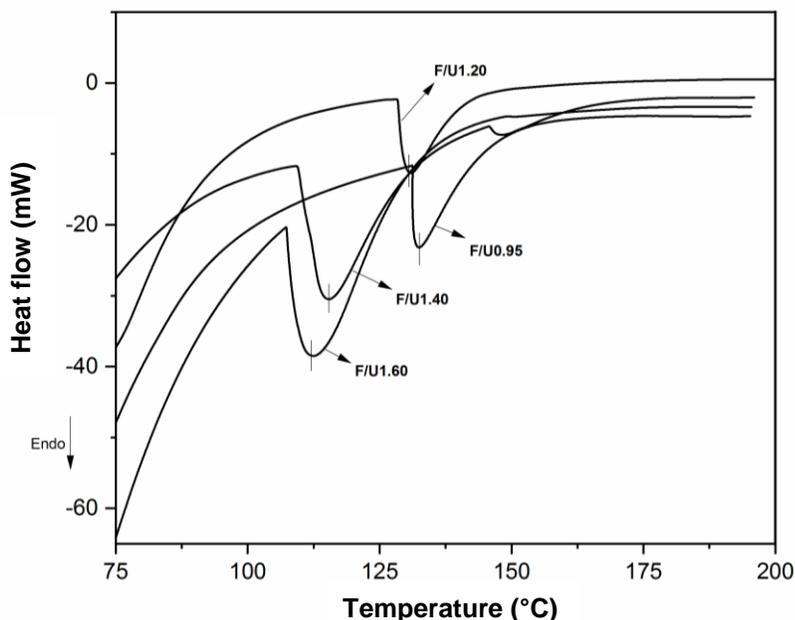


Fig. 9. Peak 2 on DSC curves of UF resin with different F/U molar ratios of curing with pH 3.0

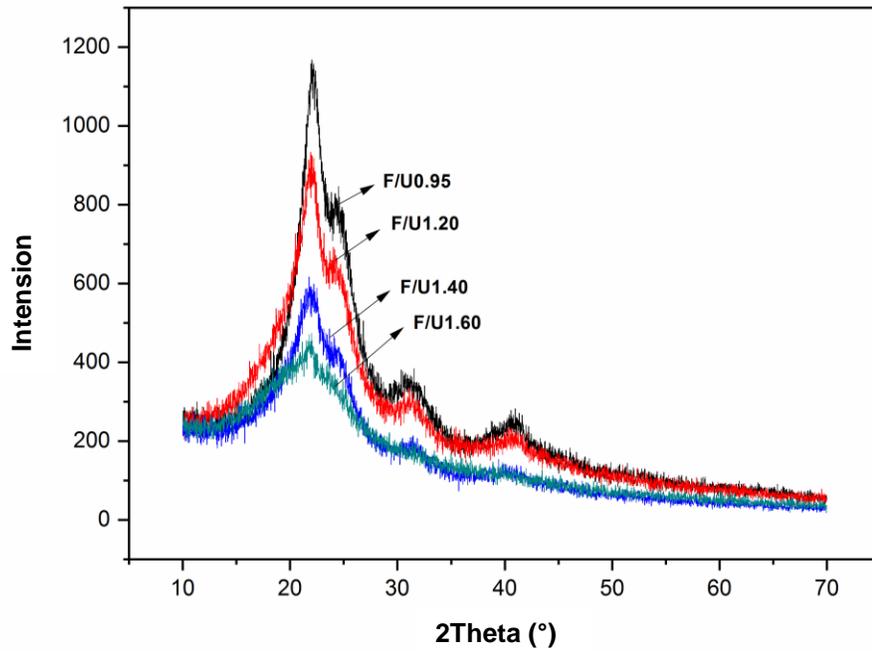


Fig. 10. X-ray diffractograms of cured UF resins with different F/U molar ratios at pH 3.0

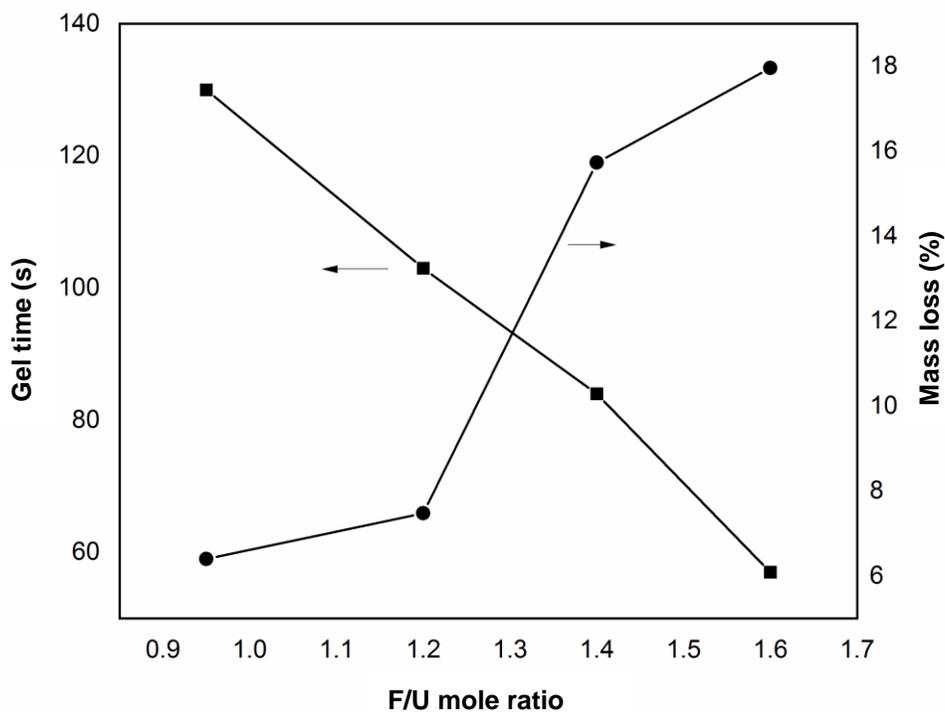


Fig. 11. Gel time and mass loss corresponding to peak 2 of UF resin with different F/U molar ratios curing under condition of pH 3.0

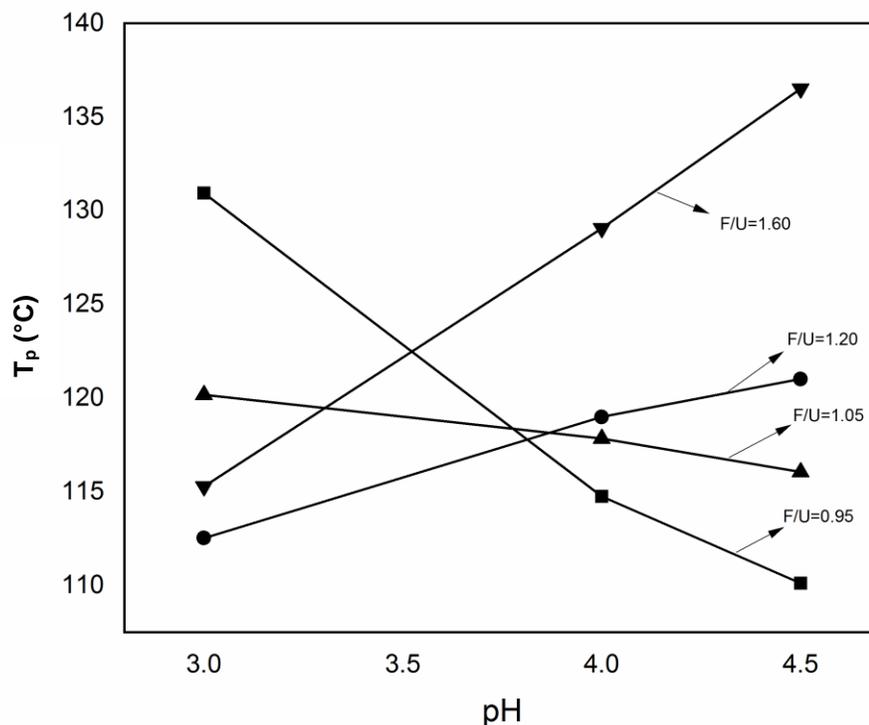


Fig. 12. T_p of peak 2 on DSC curves of UF resin with different F/U molar ratios of curing under condition of different pH

CONCLUSIONS

1. Condensation reaction, and as well as crystallization, takes place during the urea-formaldehyde (UF) resin curing process. When the resin is cured with a higher F/U molar ratio, the condensation reaction happens before the aggregation of macromolecular chains of initial resin. The reaction increases the degree of branching of resin and weakens the crystallization. In contrast, when the resin is cured with a lower molar ratio, the aggregation and crystallization of macromolecular chains take place before the condensation reaction. The reaction enforces the crystallinity of the cured resin.
2. With the decrement of F/U molar ratios, the importance of the condensation reaction and importance of crystallization will gradually convert to each other in the course of the curing process. When the F/U molar ratio is higher than 1.05, the condensation reaction plays a major role. When the F/U molar ratio is lower than 1.05, the crystallization plays a major role. The turning point is around a mole ratio of 1.05.
3. The molar ratio, and as well as the pH condition, will affect the curing process through the condensation reactivity of the initial resin. The impact of the mole ratio on resin curing is larger than the impact of the pH condition. This indicates that the effect of the hardener on the properties of the cured resin is limited.

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