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Hydrolytic stability and crystallinity of cured urea–formaldehyde resin adhesives with different formaldehyde/urea mole ratios[☆]

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ABSTRACT

This study investigated the relationship between the hydrolytic stability and the crystalline regions of cured UF resins with different formaldehyde/urea (F/U) mole ratios to better understand the hydrolysis of cured urea–formaldehyde (UF) resin adhesives responsible for its formaldehyde emission in service. As the F/U mole ratio decreased, the hydrolytic stability of cured UF resins improved, but decreased when the particle size of the resin was reduced. To further understand the improved hydrolytic stability of cured UF resin with lower F/U mole ratios, X-ray diffraction (XRD) was extensively used to examine the crystalline part of cured UF resins, depending on F/U mole ratios, cure temperature and time, hardener type and level. Cured UF resins with higher F/U mole ratios (1.6 and 1.4) showed amorphous structure, while those with lower F/U mole ratios (1.2 and 1.0) showed crystalline regions, which could partially explain the improved hydrolytic stability of the cured UF resin. The crystalline part intensity increased as cure temperature, cure time and hardener content increased. But the 2θ angles of these crystalline regions did not change, depending on cure temperature and time, hardener type and level, suggesting that the crystalline regions of the cured UF resin were inherent. This study indicates that the crystalline regions of cured UF resins with lower F/U mole ratio contribute partially to the improved hydrolytic stability of the cured resin.

1. Introduction

Urea–formaldehyde (UF) resin adhesive is a polymeric condensation product of the chemical reaction of formaldehyde with urea, and considered as one of the most important wood adhesives among melamine–urea–formaldehyde (MUF) resins, melamine–formaldehyde (MF) resins and phenol–formaldehyde (PF) resins. The UF resin adhesive, an amino resin, is most widely used for the manufacture of wood-based composite panel such as plywood, particleboard or medium density fiberboard. Therefore, the wood panel industry is a major consumer of UF resin adhesive.

In spite of some advantages such as fast curing, good performance in the panel, water solubility and lower price, UF resin adhesives also possess a critical disadvantage, formaldehyde emission from the panels. Its lower resistance to water also limits the use of wood-based panels bonded with UF resin adhesives to interior applications. Furthermore, the formaldehyde emission from the panels used for interior applications is known as one of the main factors, causing sick building syndrome in an indoor environment. Therefore, the formaldehyde emission issue has been one of the most important aspects of UF resin research [1–8].

Free formaldehyde present in UF resin and the hydrolysis of UF resin under acidic and moisture conditions are known to be responsible for the formaldehyde emission from wood-based panels [1]. For example, the amount of free formaldehyde present in UF resin proportionately contributed to the emitted formaldehyde from particleboard even after hot-pressing at high temperature [9]. But, it was reported that hydrolysis of cured UF resin was a major factor affecting long-term formaldehyde emission of UF resin-bonded wood panels [1].

Many studies investigated the hydrolysis of UF resins to understand the mechanisms of formaldehyde released from cured UF resin and UF resin-bonded wood panels [10–14]. The susceptibility of hydrolytic degradation of cured UF resin depended on its chemical structure and the degree of cross-linking, and could be accelerated by high temperature and strong acidic conditions [12].

In addition, the presence of crystal structure in UF resin has been reported by several authors [15–19]. Stuligross and Koutsky [15] reported the colloidal character and crystallinity of UF resin when the F/U mole ratio decreased to 1.0, and also showed that the resin formulation did not change the crystal structure but only the percent of crystallinity. In a comparison of chemistry between protein and UF resin, Dunker et al. [20] also reported that UF resin contained colloidal regions of semi-crystalline nature, and ascribed

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the origin of the crystal structure to a high degree of order due to hydrogen bonding. They also mentioned another possibility that the crystalline regions could have arisen from the crystallization of some minority components of UF resin, like urons or other ring structures. Johns and Dunker [16] also reported that a physical association in the UF resin solution was related to the crystalline region in solid form. The crystallinity of the cured UF resins depended on the F/U mole ratio and NH_4Cl hardener content, and the crystalline regions of the UF resin were corresponded to the mixtures of minimum energy configurations in its molecular forms [19].

Pratt et al. [17] extensively investigated the colloidal particles of UF resin, which was believed to be related to its crystalline part. They also postulated that the colloidal particles were covered by double layers of formaldehyde. In a recent study, Despres and Pizzi [21] showed that filament-like colloidal aggregates were initially formed in UF resin, which eventually changed to super-clusters by coalescence during its ageing.

Even though the influence of F/U mole ratio to the hydrolysis of UF resin had been investigated, the relationship between the hydrolytic stability and the crystalline regions of cured UF resins have not been studied so far. Thus, this study investigated any possible relation between the hydrolytic stability and the crystalline regions of cured UF resins.

2. Experimental

2.1. Materials

Technical grade urea and formalin (37%) were used for the synthesis of UF resins. Aqueous solutions of both formic acid (20%) and sodium hydroxide (20%) were used to adjust the pH level during the UF resin synthesis. Aqueous solutions (20%) of ammonium chloride (NH_4Cl), ammonium sulfate ($(NH_4)_2SO_4$) and aluminum sulfate ($Al_2(SO_4)_2$) as hardeners were used. Different levels of the hardeners were added into the synthesized UF resin based on the non-volatile resin solids.

2.2. Experimental methods

2.2.1. Preparation of UF resins

All UF resins used for this study were prepared in the laboratory, following traditional alkaline-acid two-step reaction. The formalin was placed in the reactor and then adjusted to pH 7.8 with aqueous NaOH and then heated up to 45 °C. Subsequently, a certain amount of urea was added equally at 1 min intervals. Then the mixture was heated to 90 °C under reflux for 1 h to allow for methylolation reactions. The second stage of UF resin synthesis consisted of the condensation of the methylolureas. The acidic reaction was brought by adding formic acid (20 %wt solution) to obtain a pH of about 4.6, and the condensation reactions were carried out until it reached a target viscosity of JK, which was measured using a bubble viscometer (VG-9100, Gardner-Holdt Bubble Viscometer, USA). Final F/U mole ratios of UF resins were adjusted by adding different amounts of the second urea. Then, the UF resin was cooled to room temperature, later followed by adjusting the pH to 8.0.

2.2.2. Properties of UF resins

About 1 g of UF resin was poured into a disposable aluminum dish, and then dried in a convective oven at 105 °C for 3 h. The non-volatile solids content was determined by measuring the weight of UF resin before and after drying. An average of three replications was presented.

To compare the reactivity of UF resins synthesized, the gel times of UF resins were measured by adding different hardeners at the 3% level at 100 °C using a gel time meter (Davis Inotek Instrument, Charlotte, NC). The measurements were done with three replications for each UF resin with different hardeners. The viscosity of UF resins at 25 °C was measured using a cone-plate viscometer (DV-II+, Brookfield, US) with No. 2 spindle at 60 rpm.

2.2.3. Model compounds preparation

All model compounds were prepared according to the reported procedures [22]. Dry solid urea was ground into powdered form as a model compound for the XRD scanning. Monomethylol urea was prepared by reacting 30 g urea with 50 g formaldehyde (30% formalin) under 0.5 g of $Ba(OH)_2$ in aqueous solution at room temperature. The formaldehyde was added within 2 h. The solution was neutralized with $NaHCO_3$ and freeze-dried. The crude product was washed several times with ethanol.

Dimethylol urea was prepared by adjusting the pH of 21 g of 30% formaldehyde to 8.0 using the aqueous solution of $Ba(OH)_2$, adding 6 g of urea and 0.08 g monosodium phosphate at −10 °C to the solution, and by precipitating dimethylol urea after reacting the mixtures for 24 h. The precipitate was filtered, and then recrystallized from ethanol.

2.2.4. Hydrolytic stability measurement

2.2.4.1. UF resin hydrolysis. Prepared UF resin was cured at 120 °C for 60 min after adding 3% of NH_4Cl to prepare samples to measure the hydrolytic stability of cured UF resins. After curing, the resins were ground into particles using a grinding mill (MF 10 basic, IKA Werke, Germany) and then sieved using a sieve shaker (CG-211-8, Korea) to obtain 250 or 180 μm size particles. About 2 g of the cured UF resins prepared in powdered form was added to a 250 ml Erlenmeyer flask that contained 200 ml of 0.1 M hydrochloric acid. The mixture was hydrolyzed on a hot-plate with continuous stirring using a magnetic bar at 50 °C for 90 min (2 replications for each sample). The hydrolyzed mixture was separated by filtering to give a solution and a resin particle residue. Then, the hydrolytic stability of cured UF resins was evaluated by determining both the concentration of liberated formaldehyde in the solution, and the mass loss of the cured resin particle residue.

2.2.4.2. Determination of mass loss. In order to determine the mass loss of cured UF resin, the particles of cured resins after the acid hydrolysis were filtered with a filter paper, and then dried at 105 °C for 3 h. After drying, the mass loss of cured resins was determined by weighing the masses of cured resins before and after the hydrolysis.

2.2.4.3. Determination of liberated formaldehyde concentration. Liberated formaldehyde concentration after the hydrolysis was determined by the sulfite method. An aliquot of 50 ml of filtered solution was placed in 250 ml beaker and carefully neutralized by titration with 0.1 N sodium hydrosulfite. Then 50 ml of sodium sulfate was added to the solution. The solution was stirred for 5 min; then the mixture was slowly titrated with the 1 N hydrochloric acid.

2.2.5. X-ray diffraction (XRD)

An X-ray diffractometer (D/Max-2500 Rigaku, Tokyo, Japan) was used to investigate the crystallinity of cured UF resins. Different types and levels of hardeners were mixed with the UF resin of the F/U mole ratio of 1.0, and then cured at the same curing condition as the hydrolytic stability measurement. The milled and powdered samples were analyzed at ambient temperature using a CuK$\alpha-1$ X-ray source with a wavelength (λ) of

1.5405 Å. The angle of incidence was varied from 10° to 60° bysteps of 0.02°/min each.

3. Results and discussion

3.1. Properties of UF resin adhesives with different F/U mole ratios

Properties of UF resin adhesives with different F/U mole ratios are shown in Table 1. As the F/U mole ratio decreases, the non-volatile solids content increases. This could result from the final F/U mole ratio of UF resin adhesive being adjusted by the amount of the second urea added. But, the viscosity of the UF resin adhesive decreases as the F/U mole ratio decreases. As expected, the gelation time increased as the F/U mole ratio decreased. In other words, a decrease in the F/U mole ratio reduced the reactivity of the resin adhesive. This could be due to the free formaldehyde in the UF resin adhesives because less free formaldehyde makes the curing condition less acidic. It was already reported that the amount of free formaldehyde in UF resin decreases with a decrease in the F/U mole ratio [8].

3.2. Hydrolytic stability of cured UF resin with different F/U mole ratios

Fig. 1 shows the hydrolytic stability of cured UF resins prepared at different F/U mole ratios. As the F/U mole ratio decreases, the mass losses of two different cured UF resins with different particle sizes (180 and 250 μm) increased and then decreased (Fig. 1). Smaller particle sizes influenced hydrolytic stability of cured UF resins. This could be due to larger surface areas of the smaller particles than those of the larger particles. A similar trend was also found for the liberated formaldehyde concentration after acid hydrolysis (Fig. 2). It is believed that lower mass loss at the F/U mole ratio of 1.6 could be due to a greater cross-linking density. A decrease in the mass loss and liberated formaldehyde concentration of cured UF resin with an F/U mole ratio of 1.4 could be due to high branched network structure of the resin. But, in general, these results indicate that hydrolytic stability of cured UF resin improved as the F/U mole ratio decreases. In other words, UF resin of lower F/U mole ratio is more resistant to hydrolysis than those of higher F/U mole ratios. These results might be related to the molecular structure of cured UF resin. It is known that UF resin of higher F/U mole ratio is much more branched than those of low F/U mole ratios [23–25]. A greater degree of branch of UF resin has a greater probability of exposing the methylol groups to hydrolysis, which subsequently increases the mass loss and the concentration of liberated formaldehyde [24]. However, it was reported that UF resins of low F/U mole ratio were less branched and more linear in structure [23]. Thus, the linear structure of low mole ratio UF resins has fewer number of methylol groups exposed to hydrolysis, which will consequently improve the hydrolytic resistance.

Table 1
Properties of UF resins of different F/U mole ratios.

F/U mole ratio	Non-volatile solids content (%)	Viscosity (mPa s)	Gelation time (s)
1.6	52.5	327.3	51
1.4	54.1	276.0	72
1.2	54.9	250.7	168
1.0	57.6	248.0	201

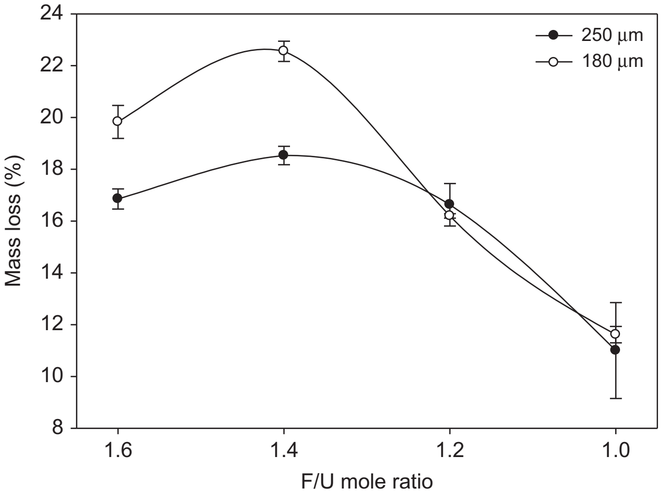

Fig. 1. Mass loss of cured UF resins with different F/U mole ratios.

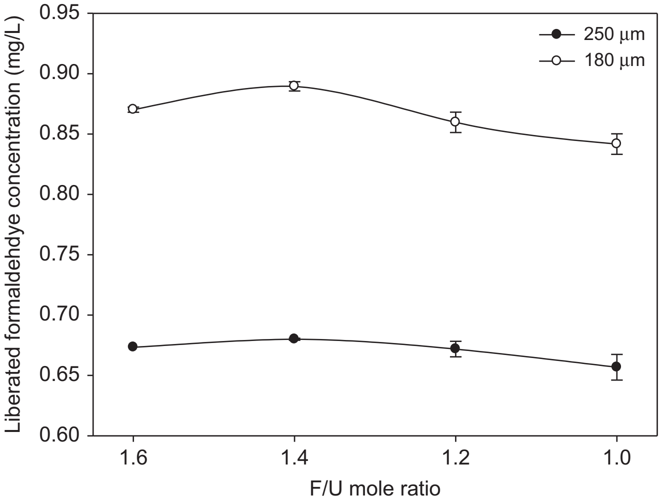

Fig. 2. Liberated formaldehyde concentration of cured UF resins with different F/U mole ratios.

3.3. Crystalline regions of cured UF resin with different F/U mole ratios

Fig. 3 shows the results of X-ray diffractograms of cured UF resins, depending on the F/U mole ratios. As shown, the UF resins with the F/U mole ratios of 1.6 had a single main peak at a 2θ of about 21°. By contrast, that of cured UF resin with an F/U mole ratio of 1.4 showed the same strong peak as well as a weak peak around its shoulder. These results indicate that the cured UF resins with higher F/U mole ratios are of amorphous structure [26]. When the F/U mole ratio further decreased to 1.2 and 1.0, these two peaks became sharper and showed much greater intensity. In addition, two additional peaks that appeared at about 31° and 40° indicate additional crystalline regions for these cured UF resins. Each of the d-spacing was calculated as 2.86 nm and 2.22 nm. These results are consistent with other reported results [15–19]. In other words, UF resins at lower F/U mole ratio from 1.1 to 0.5 show crystal structure while UF resins with higher F/U mole ratio are amorphous polymer. For example, Levendis et al. [19] mentioned that UF resins at lower F/U mole ratio than 1.1 showed crystal structure while UF resins with higher F/U mole ratio than 1.5 were amorphous structure. However, the result of this study shows that UF resin with a lower F/U mole ratio of 1.2 also possess crystalline regions, which was observed for the first time.

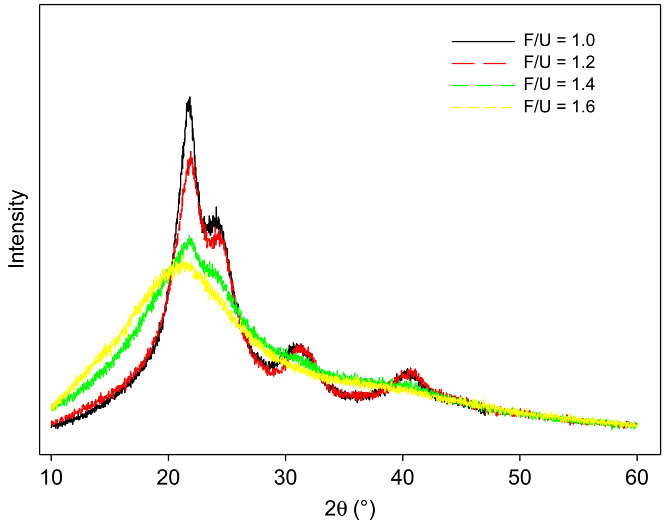

Fig. 3. X-ray diffractograms of cured UF resins with different F/U mole ratios (3% NH_4Cl).

In addition, these results are quite interesting in terms of the hydrolytic stability of cured UF resins at these low F/U mole ratios. In general, cured UF resins at lower F/U mole ratios of 1.2 and 1.0 had a greater hydrolytic stability and these resins showed additional crystalline regions at the same time. These results suggest that an improved hydrolytic stability of cured UF resins with lower F/U mole ratios of 1.2 and 1.0 can be related to the additional crystalline regions of the resins. In other words, the crystalline regions could provide more resistance to the degradation of their hydrolysis process than those of higher F/U mole ratio resins.

3.4. *Crystalline regions of cured UF resin (1.0 F/U mole ratio), depending on curing temperature, time, hardener type and level*

In order to understand whether these crystalline regions of cured UF resin with the F/U mole ratio of 1.0 are inherent, we investigate these crystalline regions of cured UF resin with the F/U mole ratio of 1.0, depending on curing conditions and hardener type, and Fig. 4 shows the X-ray diffractograms of the UF resin of F/U mole ratio of 1.0, which was cured at different curing temperatures. As shown, the intensities of all crystalline regions increased as the curing temperature increased. This result indicates that higher curing temperature causes a greater amount of crystallinity of the UF resin. But the 2θ position of two additional peaks did not change with the curing temperature. This result indicates that cured UF resins with lower F/U mole ratios (1.2 and 1.0) had additional crystalline structures. It was reported that these low F/U mole ratio UF resins were reported to have spherical structures [27]. The authors believed that these additional crystalline peaks could be related to the spherical structures observed at the UF resins of lower F/U mole ratios.

X-ray diffractograms of the UF resins depending on curing time are shown in Fig. 5. As the curing time increases, the peak intensities of the two additional peaks also increase. This result also suggests that higher curing temperature causes a greater amount of crystalline regions in the resin.

Influences of different hardener types and addition levels are also investigated for the UF resin, which are shown in Figs. 6–8. No hardener samples (or 0% NH_4Cl) were prepared by hardening the sample by drying at 120 °C overnight to remove the water content of the resin. As shown in Fig. 6, the intensities of the crystalline regions of the UF resin increased up to 3% hardener

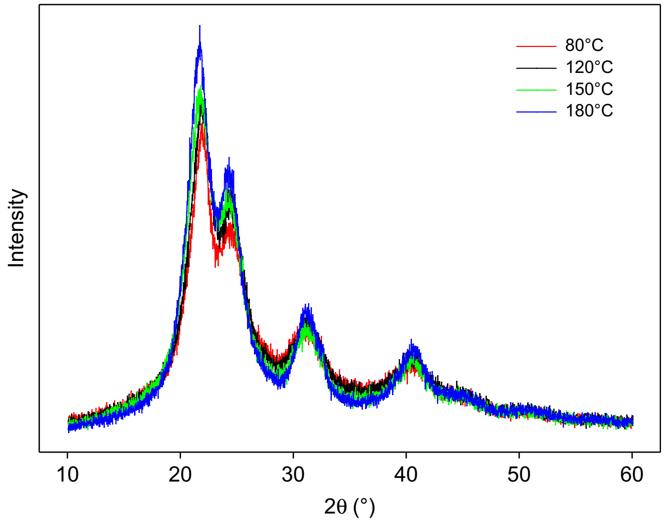

Fig. 4. X-ray diffractograms of cured UF resins with the F/U mole ratio of 1.0 at different curing temperatures (3% NH_4Cl).

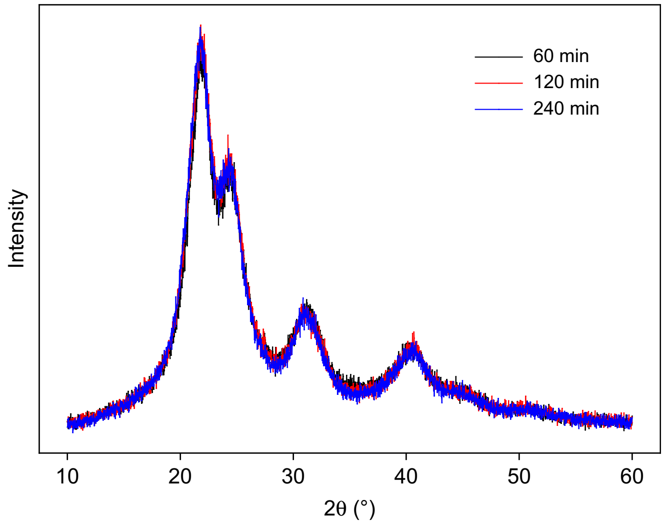

Fig. 5. X-ray diffractograms of cured UF resins with the F/U mole ratio of 1.0 at different curing times (3% NH_4Cl).

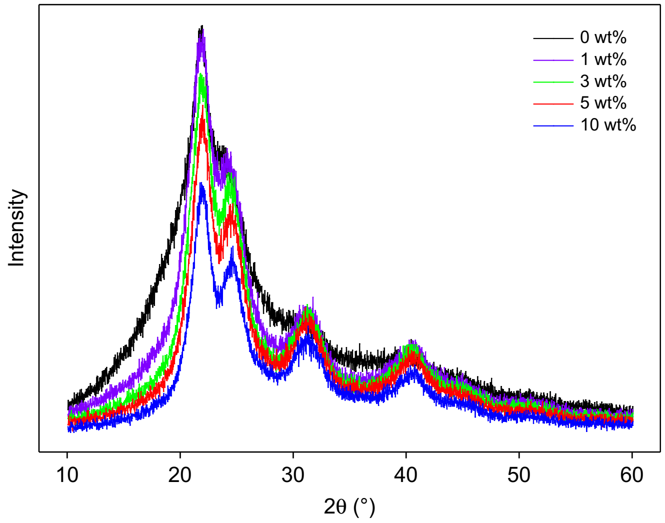

Fig. 6. X-ray diffractograms of cured UF resins with the F/U mole ratio of 1.0 at different NH_4Cl levels (120 °C, 60 min).

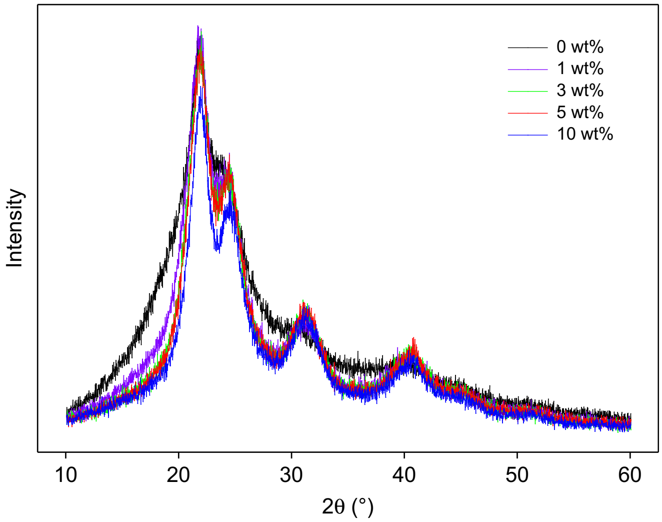

Fig. 7. X-ray diffractograms of cured UF resins with the F/U mole ratio of 1.0 at different $(NH_4)_2SO_4$ levels (120 °C, 60 min).

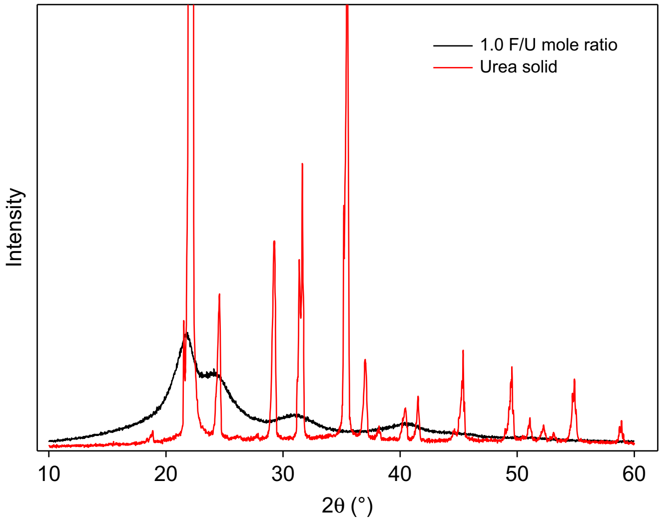

Fig. 9. X-ray diffractograms of solid urea and cured UF resins (1.0 F/U mole ratio) at 120 °C, 60 min and 3% NH_4Cl.

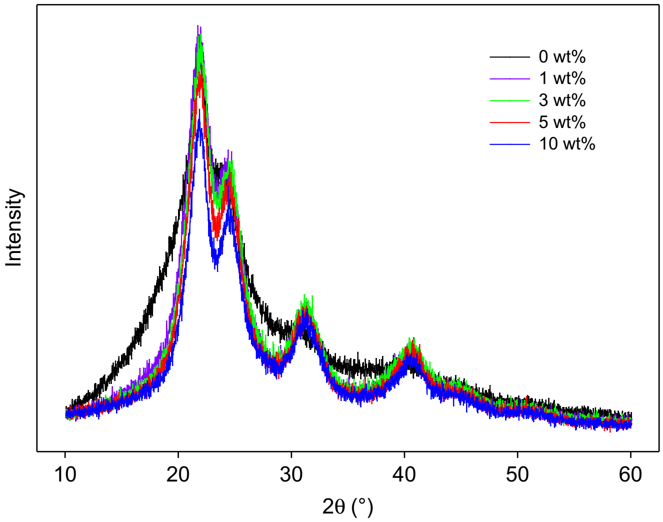

Fig. 8. X-ray diffractograms of cured UF resins with the F/U mole ratio of 1.0 at different $(Al_2)(SO_4)_3$ levels (120 °C, 60 min).

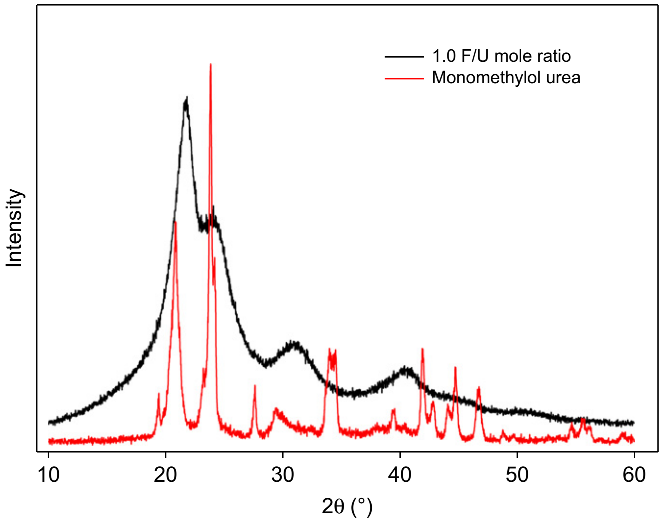

Fig. 10. X-ray diffractograms of monomethylol urea and cured UF resins (1.0 F/U mole ratio) at 120 °C, 60 min and 3% NH_4Cl.

level and then slightly decreased for three hardener types. These results suggest that the addition level of hardener influences the extent of the crystalline regions, and not on the peak position. This result is partially consistent with the reported results that the crystallinity increased with an increase in the NH_4Cl level and curing temperature [19]. However, the types of hardener did not affect the additional crystalline regions of the UF resin. Figs. 7 and 8 show X-ray diffractograms of cured UF resins by adding ammonium sulfate and aluminum sulfate at different levels. Two hardeners also showed a quite similar trend to that of the ammonium chloride. These results indicated that hardener type and its addition level did not change the additional crystalline regions of the UF resin. Even though the curing condition, hardener type and level influenced the intensity of the crystalline regions, the crystalline peak positions did not change, depending on these parameters. This result indicates that the crystalline regions are inherently present for the cured UF resin with the F/U mole ratio of 1.0 [28].

3.5. *Crystalline regions of cured UF resin (1.0 F/U mole ratio) and model compounds*

In order to better understand the additional crystalline regions of the UF resin (1.0 F/U mole ratio), we also tried to compare the crystalline regions of the model compounds such as urea, monomethylol urea and dimethylolureas. Fig. 9 shows X-ray diffractograms of dry solid urea and that of the cured UF resin (1.0 F/U mole ratio). As expected the dry urea solid showed many sharp crystal peaks, owing to its crystal structure. When two diffractograms are compared, the crystal peaks at the 2θ of 31° and 40° of the cured UF resin (1.0 F/U mole ratio) are overlapping with those of the solid urea. These results suggest that the crystal structure of dry urea is partially responsible for the additional crystalline regions of the UF resin.

Figs. 10 and 11 show X-ray diffractograms of monomethylol urea and dimethylol urea as well as that of the cured UF resin with the F/U mole ratio of 1.0. The X-ray diffractogram of the

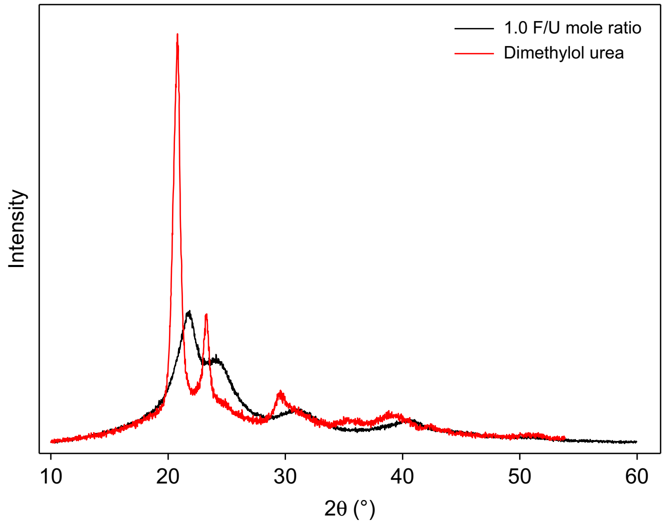

Fig. 11. X-ray diffractograms of dimethylol urea and cured UF resins (1.0 F/U mole ratio) at 120 °C, 60 min and 3% NH_4Cl.

monomethylol urea is quite different from that of the solid urea. And the peaks of additional crystalline regions did not overlap with those of the monomethylol urea. These results indicate that the crystal structure of monomethylol urea does not contribute much as that of the cured UF resin. The X-ray diffractograms of both dimethylol urea and cured UF resin are shown in Fig. 11. The X-ray diffractogram of the dimethylol urea is quite similar to that of the cured UF resin, which suggests that the crystalline regions of the cured UF resin with the F/U mole ratio of 1.0 are mainly influenced by the presence of dimethylol urea. In other words, the crystalline regions of the cured UF resins with the F/U mole ratios of 1.2 and 1.0 could be mainly composed of dimethylolureas.

4. Conclusions

This paper reports on the relation between the hydrolytic stability and the crystalline regions of cured UF resins with different F/U mole ratios to better understand the hydrolysis of cured UF resins that have been known as responsible for the formaldehyde emission of UF resin adhesives used for wood-based composite panels.

1. As the F/U mole ratio decreased, the hydrolytic stability of cured UF resins improved, but decreased when the particle size decreased.
2. Cured UF resins of higher F/U mole ratios (1.6 and 1.4) were mainly amorphous, while those of lower F/U mole ratios (1.2 and 1.0) showed crystalline regions. These crystalline regions of cured UF resin with the F/U mole ratio of 1.0 did not change depending on curing temperature, time, hardener type and level, which suggested that the crystalline regions of the cured UF resin were inherently present.
3. This study indicates that the crystalline regions of cured UF resin with lower F/U mole ratio contribute in part to the improved hydrolytic stability of the resin.

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