Effects of Formaldehyde to Urea Mole Ratio on Thermal Curing Behavior of Urea–Formaldehyde Resin and Properties of Particleboard

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ABSTRACT: As a part of abating the formaldehyde emission (FE) of urea–formaldehyde (UF) resin, this study was conducted to investigate the effects of formaldehyde to urea (F/U) mole ratio on thermal curing behavior of UF resins and properties of PB bonded with them. UF resins synthesized at different F/U mole ratios (i.e., 1.6, 1.4, 1.2, and 1.0) were used for the manufacture of PB. Thermal curing behavior of these UF resins was characterized using differential scanning calorimetry (DSC). As the F/U mole ratio decreases, the gel time, onset and peak temperatures, and heat of reaction (ΔH) increased, while the activation energy (E_a) and rate constant (k) were decreased. The amount of free formaldehyde of UF resin and FE of PB prepared decreased in parallel with decreasing the F/U mole ratio. The internal bond strength, thickness swelling, and water absorption of PB was slightly deteriorated with decreasing the F/U mole ratio of UF resins used. These results indicated that as the F/U mole ratio decreased, the FE of PB was greatly reduced at the expense of the reactivity of UF resin and slight deterioration of performance of PB prepared. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1787–1792, 2006

Key words: formaldehyde to urea mole ratio; urea–formaldehyde resin; thermal behavior; formaldehyde emission; particleboard

INTRODUCTION

Urea–formaldehyde (UF) resin adhesives have been extensively used for the manufacture of wood-based composite panel, particularly particleboard (PB) or medium density fiberboard (MDF) production. Therefore, wood panel industry is a major user of UF resins. For example, the production of formaldehyde-based resin in 2002 was about 470,000 tons, of which 37% of the total production of adhesives in Republic of Korea. The production of UF resin was about 74% (i.e., about 170,000 tons) of the formaldehyde-based resin. The UF resin is a polymeric condensation product of the chemical reaction of formaldehyde with urea, and regarded as one of the most important types of adhesive in the wood-based panel industry.

Compared to other wood adhesives, such as phenol–formaldehyde (PF) resins and diphenylmethane diisocyanate, UF resin possesses some advantages such as fast curing, good performance in the panel, water solubility, and lower price. Disadvantages of using the UF resin are formaldehyde emission (FE)

from the panels and lower resistance to water. Lower resistance to water limits the use of wood-based panels bonded with UF resin to interior applications. However, the FE from the panels used for interior applications was one of the factors, affecting sick building syndrome in indoor environment. Free formaldehyde present in UF resin and hydrolytic degradation of UF resin under moisture condition has been known as responsible for the FE from wood-based panels.[1] In other words, unreacted formaldehyde in UF resin after its synthesis could be emitted from wood panels even after hot-pressing at high temperature. In addition, the reversibility of the aminomethylene link and its susceptibility to hydrolysis also explains lower resistance against the influences of water and moisture and subsequently FE.[2] Therefore, the FE issue has been one of the most important aspects of UF resin in last few decades.[3–8]

Much attention has been paid to reduce or control the FE from UF resin-bonded panels through resin technologies. Until the mid-sixties, most UF resins were synthesized by the two-step reaction procedures: i.e., methylolation and condensation. In other words, the methylolation reaction was done under alkaline condition followed by the condensation reaction under acidic condition.[9] This synthesis method was widely employed for UF resin preparations for a long time. In the early seventies, however, this method

faced the serious problem of the FE. So, lowering the formaldehyde to urea (F/U) mole ratio for the synthesis of UF resin was adopted as one of the approaches to reduce the FE of UF resin-bonded panels.[6] Thus, lower F/U molar ratios from 1.1 to 1.2 started to be used for the resin synthesis.

An excellent literature review on the influence of F/U mole ratio on the FE as well as panel properties has been done by Myers.[10] According to the review, the gel time used as an indicator of resin reactivity increased with decreasing F/U mole ratio. In general, lower F/U mole ratios cause less FE from the panel with a loss of panel properties, particularly internal bond (IB) strength as well as thickness swelling after water immersion for 24 h. Lower F/U molar ratios also reduced modulus of rupture (MOR).[6] In recent year, it was reported that close F/U mole ratios produced quite similar structures and performance in UF resin, leading the conclusion that the most important factor in synthesis of UF resin was the F/U mole ratio.[11]

Different methods of characterizing thermal behavior of UF resin have been employed. For example, thermal analysis includes thermogravimetric (TG) analysis, differential thermal analysis (DTA), differential scanning calorimetry (DSC), etc. The TG method was used to characterize 8 UF resins, and provided linear relationship between peak temperatures of derivative TG curves and sample weight, indicating a close relation with molecular structure of UF resin.[12] Myers and Koutsky (1990) employed DSC to compare the reactivity of UF resins depending on types of hardeners used.[13] The DSC also used to monitor thermal curing behavior of UF resins modified with the addition of amines to lower residual stress once it cured. In recent year, thermal behavior of commercial UF resins was characterized using TG-DTA techniques.[14]

Even though many authors investigated the influence of F/U mole ratio on the FE of wood-based panel products, there is limited data available for thermal curing behavior of UF resins prepared under different F/U mole ratios. Therefore, this study was conducted to investigate the influence of F/U mole ratio on thermal curing behavior of UF resins, using DSC and PB performance including the FE.

MATERIALS AND METHODS

Resin preparation

All UF resins used for this study were prepared in the laboratory, following traditional alkaline-acid two-step reaction. Formaldehyde (37%) was placed in the reactor and heated to 60°C and then adjusted the reaction pH to 7.5 with sodium hydroxide (20 wt %). Subsequently, urea was added in equal parts at 1-min

intervals, and the mixture was heated to 90°C for 1 h. Then, the reaction pH was adjusted to 4.5 with formic acid (20 wt %) for the condensation. The second urea was again placed in the reactor at 40°C before rapid cooling to 25°C terminated the reaction. Different amounts of the first urea were added for the synthesis to obtain the F/U mole ratios of 1.6, 1.4, 1.2, and 1.0. For all resins prepared, final pH was adjusted to 8.0 after cooling.

Gel time measurement

The gel time was measured by adding 3 wt % ammonium chloride (NH_4Cl) (20 wt % solution) as hardener at 100°C, using a gel time meter. The measurements were done using a gel time meter (Sunshine, USA) with three replications for each UF resin with different F/U mole ratios.

Determination of free formaldehyde

Free formaldehyde in the prepared UF resins was determined by a slightly modified sodium sulfite method.[15] The solution of 25 mL $1M$ sodium sulfite mixed with 10 mL HCl was added to 2–3 g of UF resin sample dissolved in 100 mL distilled water. The mixed solution containing about 10 drops of 0.1% thymolphthalein was neutralized with $1N$ sodium hydroxide. The percent of free formaldehyde was determined by the equivalent of the amount of the consumed sodium hydroxide in titration.

DSC measurement

A DSC (TA Q10, TA Instrument, New Castle, DE) with high-pressure cells was used to evaluate curing behaviors of UF resins synthesized with different F/U mole ratios at the heating rate of 10°C/min. About 3~5 mg of the UF resins was weighed in the high-pressure cell prior to scanning with at least two replications per sample. For each sample, the onset temperature, peak temperature (T_p), heat of reaction (ΔH), and activation energy (E_a) was obtained from analyzing two DSC curves, and an average value was presented. A single dynamic scan method (also called as Borchardt-Daniels method) was used to calculate the E_a of UF resins prepared (Borchardt and Daniels, 1957).[16] This method is based on a single-heating run to analyze a curing reaction assuming nth-order kinetics expressed by the following eq. (1):

$$d\alpha/dt = Z \exp\left(-E_a/RT\right)(1-\alpha)^n \qquad (1)$$

The rate of curing reaction ($d\alpha/dt$) is dependent on Z (preexponential factor or Arrhenius frequency factor, s^{-1}), E_a (activation energy, J/mol), R (gas constant,

TABLE I
Hot-pressing Parameter Values for Particleboard Prepared

Parameters	Condition
Board size	$18.0 \times 300 \times 350$ mm^3
Target board density	700 kg/m^3
Wax content	1 wt % (oven dry weight of particle)
Particle moisture content	2% prior to blending
Resin content	8 wt % of oven dry weight of particle

TABLE II
Properties of the UF Resins Prepared

F/U mole ratio	Nonvolatile solid content (%)	Viscosity (cps)	Specific gravity
1.6	50.1	240	1.26
1.4	51.7	248	1.25
1.2	53.3	254	1.25
1.0	54.5	160	1.21

8.314 J/mol K, and T (absolute temperature, K). Taking logarithms of the eq. (1) gives:

$$\ln (d\alpha/dt) = \ln Z - E_a/RT + n \ln (1-\alpha) \qquad (2)$$

The eq. (2) can be solved with a multiple linear regression. Both Z and E_a can be obtained form the intercept and slope of the regression line. This method is attractive because it provides abundant information potentially contained in a single temperature-programmed experiment. However, it is not consistently reliable when used to predict the course of a reaction over wide time-temperature range.[17]

Particleboard manufacture and determination of properties

Commercial wood particles including at least 50% of recycled chips donated from a local particleboard (PB) mill were dried to about 2% moisture content before being blended with UF resins. Liquid UF resins synthesized were sprayed onto the dried particles in a rotary drum blender. The resins were applied at 8 wt % resin solids, based on oven dry weight of the furnish. Before the resin application, an emulsified wax (40 wt % solids) for UF resin were applied at a 1 wt %, based on oven dry weight of the particle onto the furnish in the same blender. A pumping system in conjunction with a pressurized atomizing air stream was used to deliver and atomize the wax and resin, respectively.

The dried particles were felted into a mat of 30×30 cm^2 with a target density of 700 kg/m^3. A single layer mat was prepared, and then were hot-pressed at 180°C for 5 min (Table I). The initial pressure was allowed to increase to 4.5 MPa. The pressure was completely released over the last 30 s.

Mechanical properties of PBs including modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond (IB) strength were determined according to standard procedures. Thickness swelling and water absorption were also measured by soaking six specimens (150×150 mm^2) in cold water (20°C) for 24 h.

RESULTS AND DISCUSSION

The properties of UF resins prepared at different F/U mole ratio were summarized in Table II. The nonvolatile solids contents of UF resins prepared at different F/U mole ratios were ranged from about 50 to 54 wt %. The resin viscosity and specific gravity was not much different for the F/U mole ratios.

The results of gel time measurements of the UF resins prepared at different F/U mole ratio were shown in Figure 1. As shown, the gel time of UF resins increased with decreasing the F/U mole ratio. In particular, the gel time rapidly increased when the F/U mole ratio decreased from 1.4 to 1.2. These results indicate that the curing reactivity of UF resin decreased with decreasing F/U mole ratio. This might be explained by a decrease in the availability of formaldehyde at lower F/U mole ratio. The result is quite compatible with those of onset and peak temperatures as shown in Figure 3.

Figure 2 shows typical DSC curves of UF resins at different F/U mole ratios. All DSC curves obtained at the 10°C/min show an exothermic peak at different temperatures. This exothermic peak could be attributed to the heat released from the polycondensation reaction of primary amino groups of unreacted urea with hydroxymethyl groups (—CH$_2$OH) (Siimer et al. 2003). As the F/U mole ratio decreased, the exother-
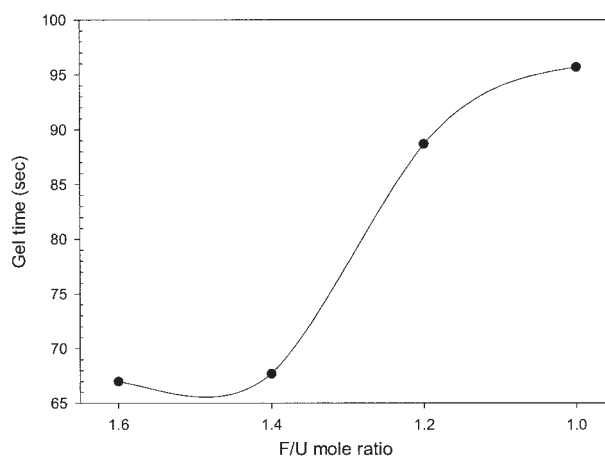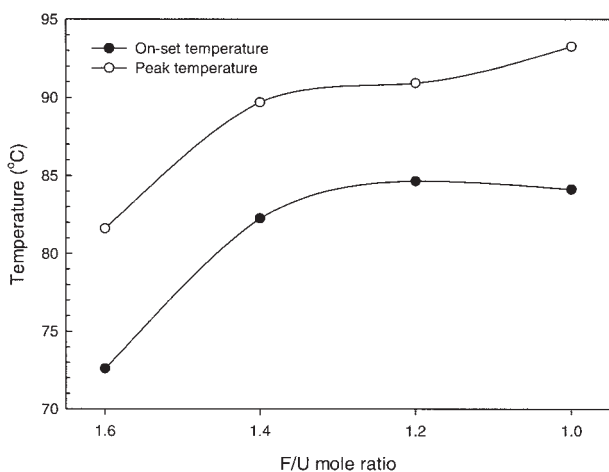

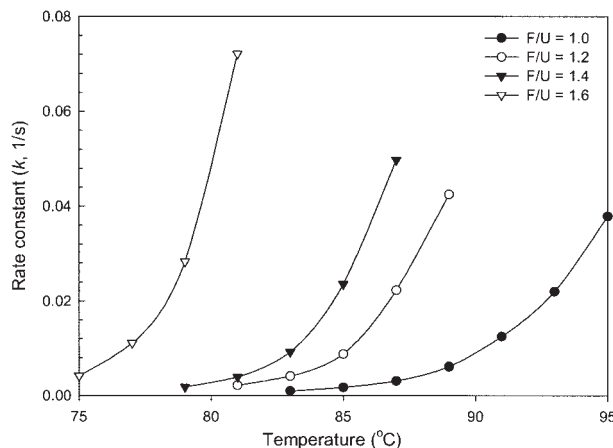**Figure 1** The gel time of UF resins at different F/U mole ratios.
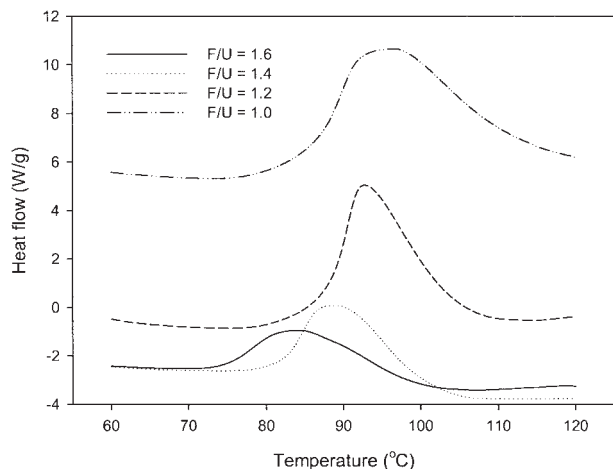
Figure 2 DSC curves of UF resins at 10°C/min at different F/U mole ratios.

Figure 4 Rate constant of UF resins at different F/U mole ratios.

mic peak temperature of UF resins increased, suggesting a decrease in the resin curing reactivity. And levels of heat flow of UF resin were much greater for lower F/U mole ratio. This was quite consistent with the result of heat of reaction (i.e., ΔH) as shown in Figure 5.

Figure 3 shows both the onset and peak temperatures of UF resins at different F/U mole ratios, which were determined using DSC curves. As shown in Figure 2, the onset temperature is defined as a temperature at which the polymerization of UF resin starts under an acidic condition. The onset temperature increased with decreasing the F/U mole ratio, which indicated a decrease in the resin reactivity at lower F/U mole ratio. By contrast, the peak temperature is defined as a temperature at which the polymerization of UF resin reaches the maximum conversion rate. The peak temperature increased as the F/U mole ratio

decreased. This result also suggested that the reactivity of curing reaction of UF resin was declined as the F/U mole ratio decreased.

The gel time, onset and peak temperatures showed a similar trend in the resin reactivity, i.e., the curing reactivity decreased as the F/U mole ratio decreased. In addition, the rate constant (k) of curing reaction was compared for UF resins with different F/U mole ratios (Fig. 4). In general, the rate constant of the curing reaction of UF resin increases as the temperature increases. As expected, the rate constant decreased as the F/U mole ratio decreased. This result was quite compatible with those of the gel time and peak temperature. In other words, a decrease of the rate constant provided a justification of decreases in the gel time and peak temperature, which were regarded as indicators of the curing reactivity of UF resin.

Figure 5 shows the heat of curing reaction (ΔH) of UF resin in the presence of an acid hardener. The ΔH

Figure 3 On-set and peak temperatures of UF resins at different F/U mole ratios.
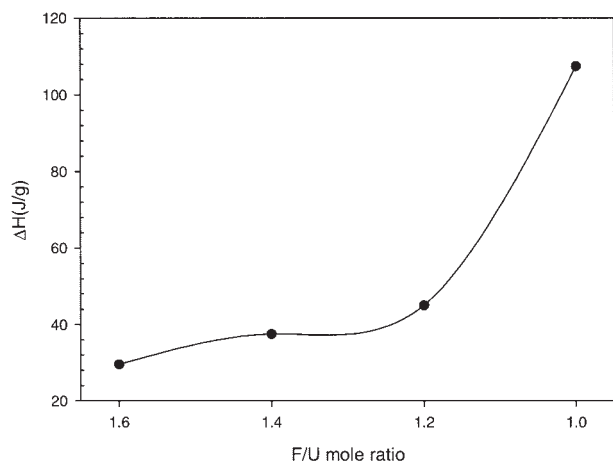
Figure 5 The heat of reaction (ΔH) of UF resins at different F/U mole ratios.
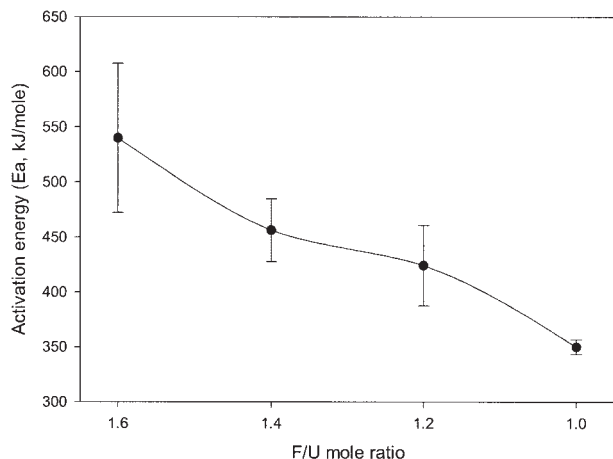
Figure 6 The activation energy (E_a) of UF resins at different F/U mole ratios.

is defined as the area under an exothermic thermogram of a DSC curve The ΔH increased with decreasing the F/U mole ratio. This result was quite reasonable. Since the gel time and peak temperature increased with decreasing the F/U mole ratio, the area under the DSC curve was getting larger with decreasing the F/U mole ratio, which resulted in an increase of the ΔH. These results suggested that more energy was required to complete the cure of UF resin when a lower F/U mole ratio was used.

The activation energy (E_a) based on the eq. (2) of UF resins with different F/U mole ratios was shown in Figure 6. As shown in Figure 6, the E_a decreased with decreasing the F/U mole ratio. This result indicated that UF resin with lower F/U mole ratio requires less energy to spontaneously start the curing reaction than that with higher F/U mole ratio. In general, more branched polymers require greater E_a than those of less branched ones. So, it is believed that UF resin prepared at higher F/U mole ratio has more branched network polymer than that synthesized at lower F/U mole ratio. However, the composition of chemical species such as monomethylolurea, dimethylolurea, trimethylolurea, and tetramethylolurea could provide different levels of branched polymer network after the cure of UF resin. Thus, further research work needs to employ ^{13}C NMR spectroscopy to compare the composition of these chemical species depending on different F/U mole ratios.

Figure 7 shows the results of the amount of free formaldehyde and FE of PB bonded with UF resins at different F/U mole ratios. As shown, the amount of free formaldehyde present in the UF resin decreased with decreasing the F/U mole ratio. This result also makes it possible to explain changes of the gel time and onset temperature as a function of F/U mole ratios. As the UF resin cures under the acidic condition produced by the added hardener (i.e., NH_4Cl), a de-

crease of the free formaldehyde amount with decreasing F/U mole ratio could retard to begin the cure of UF resin, which resulted in a longer gel time and higher onset temperature. In addition, the amount of free formaldehyde in UF resin was closely related with the FE of PB as shown in Figure 7.

In general, the FE of PB was heavily dependent on the amount of free formaldehyde present in UF resin before it was cured. This result was quite compatible with other findings. [10] This result also suggested that the amount of free formaldehyde in UF resin made a great contribution for the FE of PB. The FE of PB bonded with UF resins prepared at different F/U mole ratios rapidly decreased up to the F/U mole ratio of 1.2, and then slightly decreased as the F/U mole ratio decreased to 1.0 (Fig. 7). This result showed that the F/U mole ratio below 1.2 was more effective in reducing the FE of PB. Thus, the F/U mole ratio should be below 1.2, preferably 1.0, in order for UF resin to lower the FE of PB. This result was in a good agreement of other result.[6]

The properties of PB bonded with UF resins of different F/U mole ratios were presented in Table III and Figure 8. As shown in Table III, the moisture content (MC) of PB ranged from about 6% to 7% for all F/U mole ratios. The density of PB was around the target density of 700 kg/m^3 with the exception of PB bonded with the UF resin prepared at the F/U mole ratio of 1.2. Both MOR and MOE were not changed much for all F/U mole ratios.

The IB strengths of PBs bonded with UF resins prepared at the different F/U mole ratios were also shown in Table III. The IB strength gradually decreased with decreasing the F/U mole ratio. This result could be attributed to a decreased reactivity of UF resin with a lower F/U mole ratio as shown by the gel time, peak temperature, and rate constant. But, the variations of IB strength were relatively large when compared with other properties.
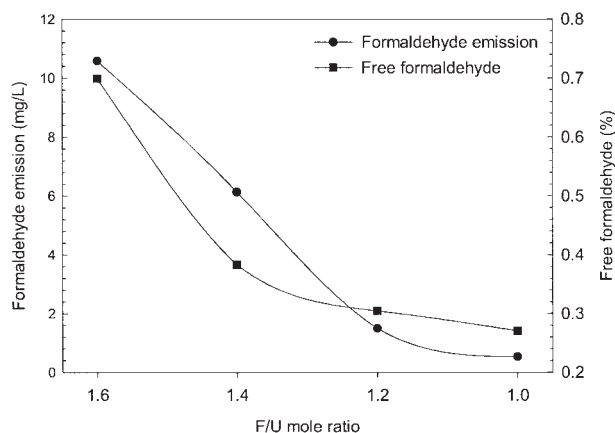
Figure 7 Free formaldehyde in UF resins at different F/U mole ratios and formaldehyde emission of bonded with the UF resins.

F/U ratio	Board MC (%)	Board density (kg/m^3)	MOR (kgf/cm^2)	MOF ($\times 10^3$ kgf/cm^2)	IB strength (kgf/cm^2)
1.0	5.7	694	136.3	23.5	8.8
1.2	5.9	746	185.5	27.6	9.7
1.4	6.9	664	143.2	20.8	9.1
1.6	6.8	684	138.7	25.8	9.9

Figure 8 shows both thickness swelling and water absorption of PB bonded with UF resins at different F/U mole ratios. As expected, the thickness swelling of PB increased with decreasing F/U mole ratio of UF resin. This result was consistent with the IB strength. As the F/U mole ratio decreased, the curing reactivity of UF resin decreased, and consequently resulted in a lower IB strength. Lower IB strength allows more water molecules to penetrate into the board, resulting in a greater thickness swelling. In general, thickness swelling has a negative relationship with IB strength of PB.[6] Water absorption of PB showed different behavior with decreasing F/U mole ratio. But, water absorption increased for lower F/U mole ratio. These results indicated that lowering F/U mole ration of UF resin cause a loss of dimensional stability of PB at the expense of reduced FE.

CONCLUSIONS

This study was undertaken to investigate the effects of F/U mole ratio on thermal curing behavior of UF resins and performance of PB bonded with them. The following conclusions were made from this study.
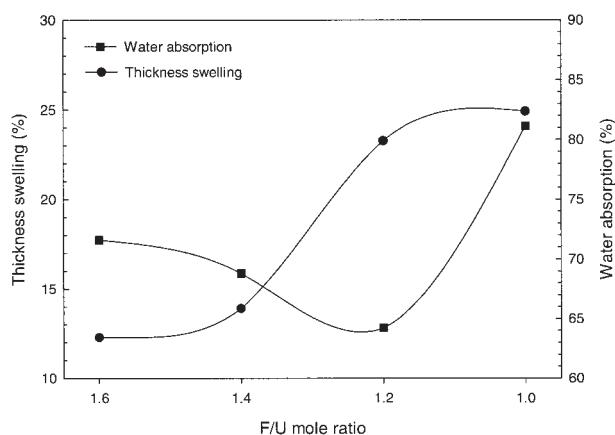
1. Thermal curing reactivity of UF resin decreased with decreasing F/U mole ratio as indicated by an increase in the gel time and peak temperature, and a decrease in the rate constant. As F/U mole ratio decreased, the heat of reaction of UF resin increased, while the activation energy decreased.

2. The amount of free formaldehyde in UF resin and FE from PB proportionally decreased with decreasing F/U mole ratio. A quite close relationship was found between free formaldehyde of UF resin and FE of PB bonded with them.

3. As the F/U mole ratio of UF resin decreased, the adhesive bond strength and dimensional stability of PB were deteriorated because of decreased IB strength, and increased thickness swelling and water absorption.

Figure 8 Thickness swelling and water absorption of PB bonded with UF resins at different F/U mole ratios.

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