

# Influence of Acrylamide Copolymerization of Urea-Formaldehyde Resin Adhesives to Their Chemical Structure and Performance

Zaimatul Aqmar Abdullah, Byung-Dae Park

Department of Wood Science and Technology, Kyungpook National University, Daegu 702-701, Republic of Korea

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**ABSTRACT:** To lower the formaldehyde emission of wood-based composite panels bonded with urea-formaldehyde (UF) resin adhesive, this study investigated the influence of acrylamide copolymerization of UF resin adhesives to their chemical structure and performance such as formaldehyde emission, adhesion strength, and mechanical properties of plywood. The acrylamide-copolymerized UF resin adhesives dramatically reduced the formaldehyde emission of plywood. The  $^{13}\text{C}$ -NMR spectra indicated that the acrylamide has been copolymerized by

reacting with either methylene glycol remained or methylol group of UF resin, which subsequently contributed in lowering the formaldehyde emission. In addition, an optimum level for the acrylamide for the copolymerization of UF resin adhesives was determined as 1%, when the formaldehyde emission and adhesion strength of plywood were taken into consideration. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3181–3186, 2010

**Key words:** copolymerization; resins; thermosets; NMR

## INTRODUCTION

Urea-formaldehyde (UF) resin adhesives have been extensively used for the manufacturing of wood-based composite panels, particularly particleboard or medium density fiberboard production. Therefore, wood panel industry is a major user of UF resins. UF resins possess some advantages, such as fast curing, a good performance in wood panels, high reactivity, water solubility, and lower cost. The disadvantages of using UF resin are the formaldehyde emissions from the panels and a lower resistance to water. The resultant lower resistance to water limits the use of wood-based panels bonded with UF resins to interior applications.<sup>1,2</sup> Furthermore, the lower dimensional stabilities of wood-based panels bonded with UF resin are attributable to its hydrolytic degradation.<sup>3,4</sup> Poor durability and the emission of formaldehyde have been recognized as important drawbacks of UF resins.<sup>5</sup> The free formaldehyde present in UF resin and the hydrolytic degradation of UF resin under humid conditions have been known to be responsible for the formaldehyde emissions from wood-based panels.<sup>6</sup> 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 water, and subsequently the formaldehyde emissions.<sup>7</sup>

However, a large variety of structural elements in UF resins (such as methylene bridges, ether bridges, methylol, amide groups, or even cyclic derivatives like uronic rings) and the large variety of possible reactions make difficult to understand the process of formaldehyde emission of UF resin adhesive. These structural elements in the uncured resins have an obvious influence on their curing rate and structure and subsequent the formaldehyde emission. Indoor air-pollution by formaldehyde emitted from adhesively bonded wood products has been a major concern in the wood panel products industry in recent years. Much attention has been paid to reduce or control the formaldehyde emissions from UF resin-bonded panels through resin technologies. Lowering the formaldehyde to urea (F/U) mole ratio for the synthesis of UF resins was adopted as one of the approaches to reduce the formaldehyde emissions of UF resin-bonded panels. An excellent literature review on the influence of F/U mole ratio on the formaldehyde emissions and on its panel properties has been done.<sup>8</sup> According to the review, the gel time, used as an indicator of resin reactivity, decreased together with a decreasing F/U mole ratio. In general, lower F/U mole ratios cause less formaldehyde emissions from the panel with an

Correspondence to: B.-D. Park (byungdae@knu.ac.kr).

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expense of panel properties, particularly internal bond strength and thickness swelling after water immersion for 24 h.<sup>9</sup>

It was known that UF resin had the least hydrolytic stability among amino resins.<sup>10</sup> As a way of understanding of the formaldehyde emissions of amino resins, many studies attempted to measure hydrolytic stability of amino resin adhesives (UF resin or MUF resin).<sup>5,10–12</sup> These studies suggested that the hydrolysis of UF resin consisted of different reversible reactions to those of the UF resin synthesis. For example, infrared spectra study showed major reduction of the content of methylol groups ( $\text{CH}_2\text{OH}$ ) while it increased tertiary amide.<sup>11</sup> A solid-state  $^{13}\text{C}$ -NMR spectroscopic study on the hydrolytic stability of UF resins also reported that the dimethylene ether linkages, methylol groups attached to tertiary amides, and poly(oxymethylene glycol) were the main formaldehyde emitters.<sup>5</sup>

The hydrolytic stability of the UF resin could be enhanced if the structure of UF resins was modified by incorporating comonomers into the polymer chains or by the use of some suitable modifiers and buffers into the resin that were capable of neutralizing the acid-catalysts used as a curing agents.<sup>13</sup> Modified UF resin with urea-terminated hexamethylenediamine, bis-hexamethylenetriamine, and poly(propylene oxide) resulted in an excellent stability of the UF resin.<sup>13,14</sup> These studies also reported that the resistance of UF resin bonded joints to cyclic stress was substantially improved by modifying the resins. In addition, the UF resin modification by a simple mixing of acrylamide showed that the acrylamide did improve the hydrolytic stability of modified UF resin compared to that of other additives.<sup>15</sup>

However, there are limited studies on UF resin modification by the acrylamide copolymerization to lower the formaldehyde emissions of UF resin bonded-wood panels. So, this study investigated the chemical structure of modified UF resins by the copolymerization of acrylamide at different levels. In addition, the performance of plywood bonded with modified UF resins such as formaldehyde emissions, its adhesion strength, and its mechanical properties were evaluated.

## MATERIALS AND METHODS

### Materials

The acrylamide that has been used in this study was a technical grade reagent (pH 6.6, 71.08  $M_w$ , Yongsan Mitsui Chemicals, purity 50.2 wt %, Korea) was used as received. A commercial granular urea and formaline (37%) was used for UF resin synthesis as received.

### Methods

#### Preparation and modification of UF resin

All UF resins used for this study were prepared in the laboratory, following traditional alkaline-acid two-step reaction. The formaline was placed in the reactor and then adjusted to pH 7.8 with sodium hydroxide (20 wt % solution) and then heated up to 45°C. Subsequently, a certain amount of urea was added equally at 1 min intervals. And then, different levels of acrylamide at (0, 1, 4, and 6 wt %) based on the weight of the first urea was added. 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). The UF resin with the final F/U mole ratio of 1.2 was used for different levels of acrylamide. Then, the UF resin was cooled to room temperature, later followed by adjusting the pH to 8.0. Finally, a 3 wt % of  $\text{NH}_4\text{Cl}$  as hardener was physically mixed with the copolymerized UF resin.

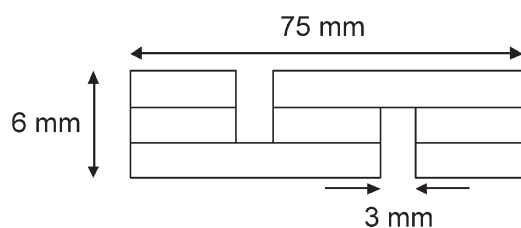
#### Properties of modified UF resins

About 1 g of modified UF resin was poured into a disposable aluminum dish and then dried in a convective oven at 105°C for 3 h. The nonvolatile 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 neat and modified resins were measured, with 3%  $\text{NH}_4\text{Cl}$  (20 wt %) as a hardener, 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 levels of acrylamide. 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.

#### Free formaldehyde measurement

Free formaldehyde of neat and modified UF resins was determined by adding 50 mL of distilled water to 10 g of resin. Then, the mixture was mixed with 50 mL of sodium sulfite. After that the mixture was neutralized with 1N hydrochloride acid. The percent of free formaldehyde was determined by the equivalent amount of the consumed hydrochloride acid in titration.



**Figure 1** The specimen geometry for tensile shear adhesion strength test for 3-ply plywood.

### $^{13}\text{C}$ -NMR spectroscopy

The liquid state  $^{13}\text{C}$ -NMR spectra of the neat and modified UF resin by the copolymerization of acrylamide and pure acrylamide were dissolved in deuterated dimethyl sulfoxide ( $\text{DMSO-}d_6$ ) as an internal standard for  $^{13}\text{C}$ -NMR spectroscopy. The  $^{13}\text{C}$ -NMR spectra were obtained with 9.5 s pulse width (30) and a pulse delay of 10 s, using 500 MHz model (Bruker AMX-R300). By using the gated decoupling method to minimize the nuclear Overhauser effect, about 2000 scans were accumulated to obtain reliable spectra.

### Plywood manufacture and specimen preparation

Veneers (Radiata pine) (350 mm  $\times$  350 mm  $\times$  2.3 mm) were prepared for 3-ply lay-up. Neat and modified UF resins were applied on the veneers with 170 g/m<sup>2</sup> glue spread per surface. After the glue spreading process, the veneers were laid-up and then prepressed at 980 kPa for 8 min at ambient temperature. This was to obtain even spread of adhesive with the plies. After that the board was shifted to hot-pressing at 130°C for 4 min to obtain 3-ply plywood with a target thickness of 6.3 mm.

Twelve panels with a size of 350 (L)  $\times$  350 (W)  $\times$  6.3 (T) mm were prepared using each of four UF resins with different acrylamide levels (0, 1, 4, and 6 wt %). Three replicates for each acrylamide level were prepared. The plywood was manufactured in the laboratory. A total of twelve 3-ply plywood panels were produced in this study. At least 10 test specimens were taken randomly from each board. Specimens for static bending (206 mm  $\times$  50 mm  $\times$  6.3 mm), tensile shear adhesion strength (75 mm  $\times$  25 mm  $\times$  6.3 mm), and formaldehyde emission test (150 mm  $\times$  50 mm  $\times$  6.3 mm) were prepared. Figure 1 shows the specimen geometry for tensile shear adhesion test according to the standard procedure.<sup>16</sup>

### Determination of formaldehyde emission

The formaldehyde emission of plywood was measured by the 24 h desiccators method.<sup>17</sup> Ten specimens of each sample in two replicates were placed in the desiccators contains dish holding 300 mL dis-

tilled water. After being closed, the desiccators were allowed to stand at  $20 \pm 2^\circ\text{C}$  for 24 h so that the formaldehyde released from each test piece is absorbed by the water. The dish was then removed, and the water was analyzed for formaldehyde content. The results were expressed as mg/L of formaldehyde in water.

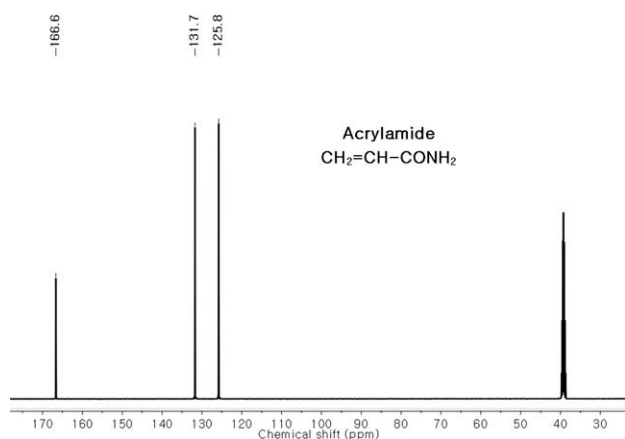
The formaldehyde concentration in distilled water was determined by acetylacetone analysis procedures for all tests. The formaldehyde solution was mixed with the equal amount of reagent composed of 150 g ammonium acetate, 3 mL acetic acid, and 2 mL acetylacetone in 1 L aqueous solution. The resultant mixture was heated in a water bath circulator for 10 min at  $65 \pm 2^\circ\text{C}$  and then put it into dark place for 1 h before UV test was carried out. The absorbance was measured in a standard quartz cell (path length 10 mm) at 412 nm using a UV spectrophotometer (Optizen 3320UV, Mecasys Incorp., Korea) against a similarly treated blank.

## RESULTS AND DISCUSSION

As shown in Table I, the nonvolatile solids contents of neat and modified UF resins were ranged from 55 to 64%. As expected, it increased as the acrylamide content increased. The viscosity of neat UF resin was lower than those of the copolymerized. And the viscosity of the copolymerized UF resins slightly increased when the acrylamide increased up to 6% level. This result suggests that the molecular weights of the resins also follow a similar change. So, an increased viscosity of modified UF resins indicates a possible copolymerization of the acrylamide. The free formaldehyde content of modified UF resins was below the level of neat UF resin and 1% level gave the lowest value. These results suggest that the acrylamide reduces the free formaldehyde in the UF resin. The gel time of modified UF resins dramatically decreased when the acrylamide was added, but it slightly increased with an increase in the acrylamide content. These results indicate that the reactivity of UF resin is improved with added acrylamide and decreases with an increase in the acrylamide content.

**TABLE I**  
Properties of Modified UF Resins at Different Levels of Acrylamide

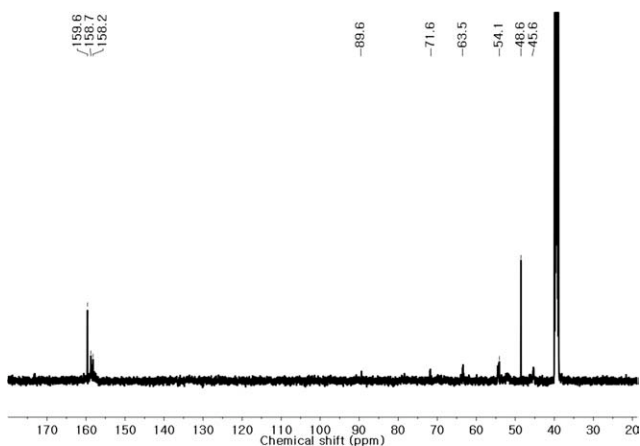
Acrylamide level (wt %)	Nonvolatile solid content (wt %)	Viscosity (25°C, mPa s)	Free HCHO (%)	Gel time (s)
0	55.20	225.0	1.27	234
1	62.05	268.0	1.11	120
4	62.10	263.0	1.15	135
6	63.91	278.0	1.16	140



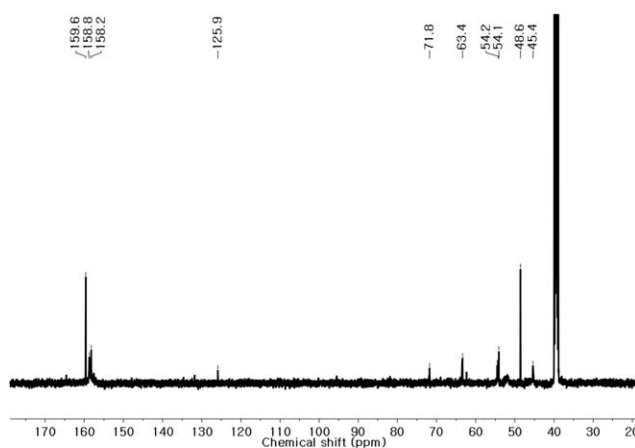
**Figure 2**  $^{13}\text{C}$ -NMR spectrum of pure acrylamide.

To understand chemical structures of copolymerized UF resins,  $^{13}\text{C}$  NMR spectroscopy was used, and the results were shown in Figures 2–5. As shown in Figure 2, two peaks at 125.7 and 131.7 ppm belonged to the pure acrylamide. And the peak at 89.5 ppm of control UF resin (Fig. 3) belonged to the methylene glycol, indicating the presence of unreacted formaldehyde in the neat UF resin. After adding 1% acrylamide, two peaks at 89.5 and 131.7 ppm were disappeared (Fig. 4). And it is believed that the terminal amino group linked to carbonyl group via C=C bond of acrylamide reacted with either the methylene glycol or the methanol group. However, when the acrylamide increased to the 6% level, the peak at 131.7 ppm appeared again (Fig. 5). It is believed this peak comes from the excess of the C=C linkages of acrylamide that are not reacted with the methylene glycol or the methanol groups.

Figure 6 showed the formaldehyde emission of plywood panels manufactured with copolymerized UF resin with acrylamide. All modified UF resins with different levels of the acrylamide release less formaldehyde emission than that of neat UF resin.



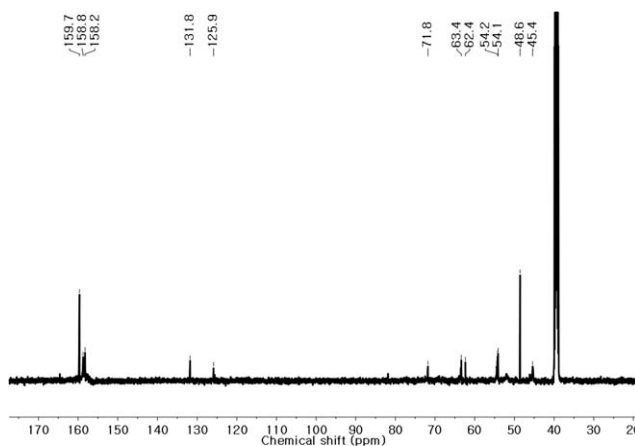
**Figure 3**  $^{13}\text{C}$ -NMR spectrum of the neat UF resin.



**Figure 4**  $^{13}\text{C}$ -NMR spectrum of modified UF resin with 1% acrylamide.

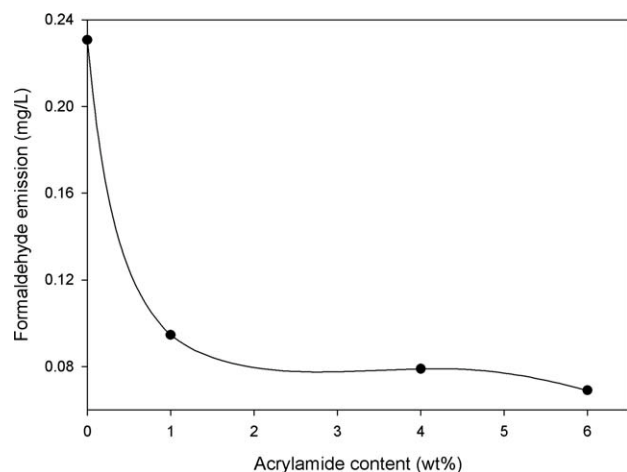
This could be due to that the free formaldehyde content of the modified UF resin adhesive decreased with an increase of acrylamide level. Another reason might be that the acrylamide reacts with methylene glycol in UF resin adhesive during the copolymerization (Figs. 4 and 5). The copolymerization of UF resin could reduce the number of terminal methylol groups that were supposed to be converted into methylene linkages by liberating formaldehyde during its curing.<sup>11</sup> Therefore, the acrylamide copolymerization lowers the formaldehyde emission of plywood bonded with the modified UF resin adhesives.

As a measure of adhesion performance, tensile shear strengths of plywood bonded with modified UF resin adhesives by different levels of acrylamide are given in Figure 7. As the acrylamide content increased, the tensile shear strength initially increased and then decreased. The best adhesion strength was obtained for the modified UF resin with 1% acrylamide. Although there are many factors affecting the adhesion strength of plywood, some of the parameters that have contributed to an



**Figure 5**  $^{13}\text{C}$ -NMR spectrum of modified UF resin with 6% acrylamide.

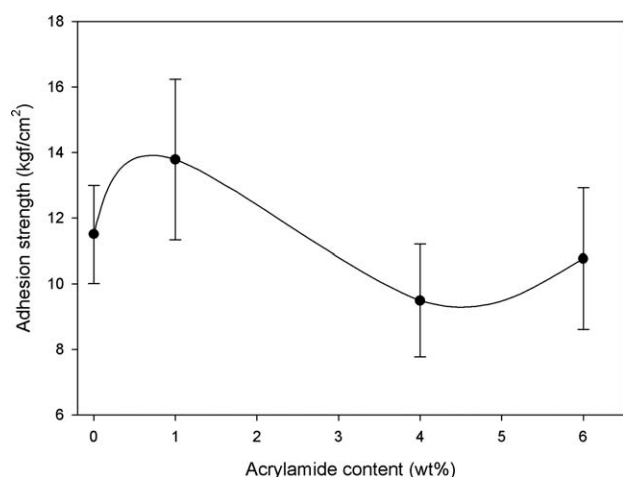




**Figure 6** Formaldehyde emission of plywood's bonded with modified UF resins with different levels of acrylamide.

increased adhesion strength of plywood at 1% acrylamide addition could be a shorter gel time of the modified UF resin by adding 1% acrylamide (see Table I). In other words, a faster gel time of the modified UF resin by adding 1% acrylamide produces more crosslinks during the hot pressing compared to those of the other modified UF resins, which eventually increases cohesive strength of the adhesive.<sup>18</sup>

The average values of modulus of rupture (MOR) and modulus of elasticity (MOE) of plywood depending on different levels of acrylamide are given in Table II. Compared to that of the control sample, MOR and MOE values of plywood bonded with the copolymerized-UF resin adhesives slightly decreased. This result could be ascribed to an increased viscosity of the copolymerized-UF resin adhesives as shown in Table I. In other words, an increase in the viscosity of the modified UF resin adhesives might have influenced the adhesive penetration into the veneers dur-



**Figure 7** Tensile shear strength of plywood bonded with copolymerized UF resins with different levels of acrylamide.

**TABLE II**  
MOR and MOE Values of Plywood Bonded with Modified UF Resins at Different Levels of Acrylamide

Acrylamide level (wt %)	MOR (MPa) <sup>a</sup>	MOE (GPa) <sup>a</sup>
0	22.3 ± 3.4	2.25 ± 0.229
1	19.5 ± 3.0	2.11 ± 0.143
4	15.0 ± 1.0	1.72 ± 0.167
6	19.6 ± 3.1	2.34 ± 0.282

<sup>a</sup> MOR and MOE values show an average value with standard deviation.

ing the manufacture of plywood. A slight penetration of the adhesives into the veneer could result in less stress transfer from veneer to the glue lines in plywood. However, it is believed that MOR and MOE of plywood might be affected by other factors as well, which is beyond the scope of this study. In general, it is believed that the addition of 1% acrylamide is an optimum level when the formaldehyde emission and tensile shear strength were taken into consideration.

## CONCLUSIONS

This study was undertaken to investigate the copolymerization effects of different acrylamide levels on the chemical structures of modified UF resins, and the copolymerized adhesive performance such as formaldehyde emission, adhesion strength, and mechanical properties of plywood bonded with them. The following conclusions were drawn:

1. The liquid <sup>13</sup>C-NMR spectra of neat and modified UF resin revealed that the methylene glycol or methylol groups in modified UF resin had reacted with acrylamide.
2. The formaldehyde emissions of plywood bonded with modified UF resins by the copolymerization decreased with an increase in the acrylamide levels.
3. Modified UF resin with 1% acrylamide was found as the optimum level, based on the both FE and adhesion strength of plywood.

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