

Effects of Reaction pH and Hardener Type on Reactivity, Properties, and Performance of Urea-Formaldehyde (UF) Resin

Byung-Dae Park*^{2†}, Yoon Soo Kim*², Won Tek So*², and Kie Pyo Lim*²

ABSTRACT

This study was conducted to investigate the effects of reaction pH conditions and hardener types on the reactivity, chemical structure and adhesion performance of UF resins. Three different reaction pH conditions, such as traditional alkaline-acid (7.5 → 4.5), weak acid (4.5), and strong acid (1.0), were used to synthesize UF resins which were cured by adding three different hardeners (ammonium chloride, ammonium citrate, and zinc nitrate) to measure adhesion strength. Fourier transform infrared (FT-IR) and carbon-13 nuclear magnetic resonance (¹³C-NMR) spectroscopies were employed to study chemical structure of the resin prepared under three different reaction pH conditions. Adhesion strength of the resins cured with three different hardeners was determined with lap shear specimens in tension. The gel time of UF resins decreased with an increasing in the amount of both ammonium chloride and ammonium citrate added in the resins. However, the gel time increased for zinc nitrate. Both FT-IR and ¹³C-NMR spectroscopies showed that the strong reaction pH condition produce uronic structures in UF resin, while both alkaline-acid and weak acid conditions produce quite similar chemical species in the resins. The maximum adhesion strength was occurred with the resin prepared under strong acid pH condition. However, this study indicated that the weak acid reaction condition provide a balance between increasing resin reactivity and improving adhesion strength of UF resin. The measurement of formaldehyde emission from the panels bonded with the UF resins prepared is planned for future work.

Keywords: UF resin, reaction pH, gel time, FT-IR, C¹³-NMR, hardener types, shear adhesion strength.

1. INTRODUCTION

To a large extent, aminoresin adhesives or aminoplastic adhesives include urea-formaldehyde (UF), melamine-formaldehyde (MF) resin, melamine-urea-formaldehyde (MUF) resin,

melamine-fortified UF resin, and melamine-urea-phenol-formaldehyde condensation (MUPF) resin. The world wide production of UF resins in 1998 was estimated to be approximately 6 billion tons per year based on 66% resin solids by mass (Dunky, 1998).

*1 Received on February 28, 2001; accepted on February 6, 2002

This work was supported by the Korea Research Foundation Grant (KRF-2000-GA0019) to B. D. Park.

*2 Dept. of Wood Sci. & Eng., Chonnam National University, Gwangju 500-757, Republic of Korea

† Corresponding author : Byung-Dae Park (byungdae@foa.go.kr)

Wood-based composite panel industry is a major consumer of UF resins. For example, the consumption of amino resin, including UF resins, MF resins and MUF resins in North America was about 59% of wood-based adhesives in 1997 (Sellers, Jr., 1999). Among these aminoplastic resins, UF resin is a polymeric condensation product of the chemical reaction of formaldehyde with urea. UF resin is the most important type of adhesive in the wood-based panel industry, such as particle-board (PB), medium density fiberboard (MDF), and partly oriented strandboard (OSB), plywood, and some other types of boards.

Compared to other wood adhesives, such as phenol-formaldehyde (PF) resins and diphenylmethane diisocyanate (MDI), 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 lower resistance to water and its formaldehyde emission from the panels. Lower resistance to water limits UF resin-bonded panels to interior applications. Formaldehyde emission was one of the most important aspects of UF resin in last few decades (Myers 1986). The reversibility of the aminomethylene link and hence the susceptibility to hydrolysis explains lower resistance against the influences of water and moisture, and subsequently formaldehyde emission (Dunky, 1998). Thus, the use of UF resin bonded wood-based composite panels is limited only to non-structural applications due to the lack of water resistance.

Thus, much attention has been paid to reduce or control the formaldehyde emission from UF resin-bonded panels. The presence of free formaldehyde in the UF resins prepared is one of the reasons for formaldehyde emission (Pizzi, 1983). One of the approaches of reducing formaldehyde emission was to lower F/U molar ratio of the resin synthesized (Marutzky, 1986).

In addition, the number of urea additions also influences the properties of prepared UF resin (Steiner, 1973). However, lower F/U molar ratio reduced formaldehyde emission at the expense of poor mechanical properties such as internal bond (IB) strength and modulus of rupture (MOR) (Marutzky, 1986). In order to overcome this problem, many attempts have been made to modify the resin synthesis methods, hardener types, additives, etc (Dunky, 1998).

Until the mid-sixties, most UF resins were synthesized by the two-step reaction procedure, i.e., methylation and condensation. In other words, the methylation reaction was done under alkaline condition followed by the condensation reaction under acidic condition (Hse *et al.*, 1994). This synthesis method was widely employed for UF resin preparations for a long time. In early the seventies, however, this method faced the serious problem of formaldehyde emission. Thus, lower F/U molar ratios from 1.1 to 1.2 started to be used in preparing resin. Obviously, these lower F/U molar ratio resins produced poor IB strength of the panel.

In addition to lowering the F/U molar ratio, a number of studies have focused on modifying UF resin properties by manipulating resin synthesis parameters, such as reaction pH condition (Tomita and Hatono, 1978; Gu *et al.*, 1995; Tohmura, 2000; Hse *et al.*, 1994), introduction of second urea addition (Tomita and Hatono, 1978), and the use of additives (Dutkiewicz, 1984; Pizzi, 1994). In particular, a Japanese group (Tomita and Hatono, 1978; Gu *et al.*, 1995; Tohmura, 2000) and Hse *et al.* (1994) have studied the change of chemical structure of UF resins prepared under different reaction pH conditions. One of the common findings of these studies was the detection of uronic structures in the UF resin prepared under a strong acid condition. Furthermore, Hse *et al.*

(1994) suggested weak acid reaction pH condition as a compromise between lower formaldehyde emission and poor mechanical properties of panel. Even though many authors investigated the chemical structure of UF resins prepared under different reaction pH conditions, the work done to study the influence hardener types on the curing behavior and adhesion strength of the resins has been limited. Therefore, this study was conducted to investigate the influence of reaction pH condition on the reactivity, hardener types, and chemical structures of the UF resins using FT-IR and ^{13}C -NMR spectroscopies.

2. CHEMICAL REACTIONS in UF RESIN

The use of different conditions of reaction and preparation could produce a broad variety of UF resins. Basically, the reaction of urea and formaldehyde is a two-step process: usually alkaline methylation followed by an acid condensation. The combination of these two chemicals results in both linear and branched as well as tridimensional network in the cured resin. This is due to the functionality of 4 in urea (due to the four replaceable hydrogen atoms), and that of 2 in formaldehyde. The most important factors determining the properties of the reaction products are: 1) the relative molar proportion of urea and formaldehyde, 2) the reaction temperature and time, and 3) the various pH values at which the condensation takes place (Pizzi, 1983).

Fig. 1 shows the methylation and condensation reactions in UF resin. The alkaline condensation (i.e., methylation) refers to the addition of up to three (four in theory) molecules of the bifunctional formaldehyde to one molecule of urea to give the so-called methylolureas. The molecular species of the

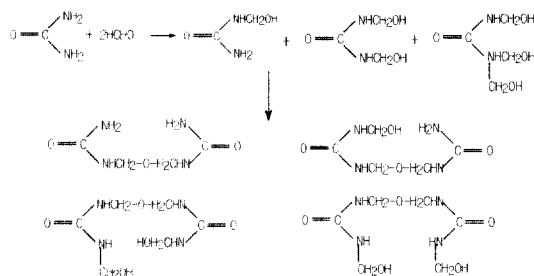


Fig. 1. The Chemical reactions in UF resins (methylation above and condensation below).

methylation are mono-, di-, and trimethylolureas as shown in Fig. 1. It is known that tetramethylolurea has never been isolated (Pizzi, 1983).

Low temperature and weak acidic pH favors the formation of methylene ether bridges (-CH₂-O-CH₂-) over methylation (Pizzi, 1994). Each methylation step has its own rate constant (k), with different k values for the forward and backward reactions. The reversibility of this reaction is one of the most important aspects of UF resins. This feature is responsible for both the low resistance against hydrolysis and the subsequent formaldehyde emission. An acid condition for UF resin synthesis is known to produce varieties of uronic derivatives as shown in Fig. 2 (Pizzi, 1994). The presence of some of these species was detected by many other studies (Gu *et al.*, 1995; Soulard *et al.*, 1998; Tohmura *et al.*, 2000; Tomita and Hatono, 1978).

3. MATERIALS and METHODS

3.1. Resin preparation

All UF resins used for this study were prepared in the laboratory. Three different procedures were used according to three reaction pH conditions, i.e., traditional alkaline-acid, weak acid and strong acid conditions. For

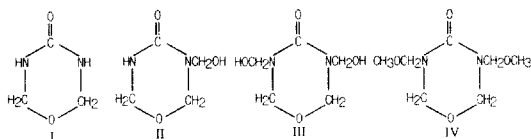


Fig. 2. Various derivatives of uronic structures.

the alkali-acid reaction, UF resins were synthesized according to traditional two-step procedure. 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 one hour. 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 the reaction was terminated by rapid cooling to 25°C. For weak acid condition, the initial reaction pH was adjusted to 4.5 with formic acid. The mixture was heated to 70°C and followed by the addition of the second urea into the reactor at 40°C. For the strong acid condition, the initial pH was adjusted to 1.0 with concentrated sulfuric acid. The reaction was kept at 70°C for one hour, and kept until the end reaction point. The initial F/U molar ratios were 2.2 for alkali-acid and weak acid condition while the strong acid condition was 3.0. For all resins prepared, both final F/U molar ratio and final pH were adjusted to 1.15, and 8.0, respectively.

Three hardeners used were ammonium chloride, ammonium citrate, and zinc nitrate. These hardeners were dissolved to 20% by weight in water. The gel time measurement was made using different hardeners as well as at different levels at 120°C, which was higher than the normal temperature (100°C). The aim was to reduce the measuring time of gel times because the UF resins prepared for this study were relatively less condensed and lower in viscosi-

ties. The gel time was measured with three replications for each hardener type and level.

3.2. Free formaldehyde determination

Free formaldehyde in the prepared UF resins was determined by a slightly modified sodium sulfite method (McCaffery, 1970). The solution of 25 mL 1 M sodium sulfite mixed with 10 ml HCl was added to 2~3 gram of UF resin sample dissolved in 100 ml distilled water. The mixed solution containing about 10 drops of 0.1% thymol phthalein 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.

3.3. FT-IR and ¹³C-NMR spectroscopy

The prepared UF resins were freeze-dried without further pH adjustment, ground to a fine powder, and thoroughly oven-dried at 60°C overnight. A KBr pellet mixed with the powder UF resin (0.5% concentration) was used to obtain infrared spectra with FT-IR spectroscopy (Nicolet 520P, Nicolet Instrument). The powder UF resins were also dissolved in deuterated dimethyl sulfoxide (DMSO-*d*₆) as an internal standard (~5% concentration) for ¹³C-NMR spectroscopy. ¹³C-NMR spectra were obtained using 300 MHz model (Bruker AMX-R300) with a 9.5 s pulse width (30) and a pulse delay of 1 second. By using the gated decoupling method to minimize the nuclear overhauser effect, about 20,000 scans were accumulated to obtain reliable spectra.

Table 1. The physical and chemical properties of the prepared UF resins.

Reaction pH	Non-volatile solid content (%)	Initial F/U molar ratio	Viscosity (cps)	Free HCHO (%)	Final pH
7.5	48.5	2.2	58	0.45	8.0
4.5	52.1	2.2	135	0.69	8.0
1.0	49.8	3.0	66	0.55	8.0

3.4. Shear adhesion strength measurement

In order to compare the adhesion strength of UF resins prepared by three different methods, a lap shear test was done according to the procedure of Korean Standard (KSM 3720, 1987). Ten specimens (8 mm thick \times 25 mm wide \times 80 mm long) for tensile shear test were cut from commercial softwood plywood for each reaction condition and hardener type. The prepared UF resins were sprayed on one surface only at a glue spray level of 300 g/m² including 5% ammonium chloride to the resin solids. The other specimen without glue spray was assembled with the glued one into a shear test sample. The assembled specimens were tightly kept in metal clamps at room temperature for twenty four hours before the metal clamps were removed. These samples were tested in tensile load and the average breaking strength of ten replications was reported.

4. RESULTS and DISCUSSION

The properties of UF resins prepared under three different reaction conditions are summarized in Table 1. The resin prepared under weak acid condition showed relatively greater viscosity and higher free formaldehyde compared with other two resins prepared.

The gel times of the UF resins prepared under three different reaction pH conditions are shown in Figs. 3~5. As shown in Fig. 3, the gel time of all UF resins decreased with

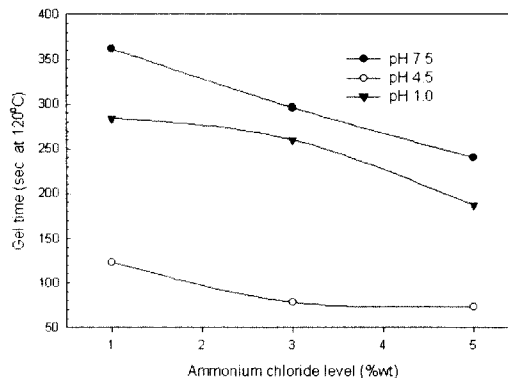


Fig. 3. Gel time of UF resins synthesized under different reaction pH conditions as a function of ammonium chloride level.

increasing ammonium chloride level. In spite of this, the UF resins synthesized under traditional alkaline-acid reaction condition showed the longest gel time at all hardener levels, followed by the strong acid and weak acid condition. However, the gel time of UF resins synthesized under weak acid condition was much shorter than that of the resins prepared under both alkaline-acid and strong acid conditions. This result indicates that the weak acid reaction condition provide a better reactivity with UF resin compared with other reaction conditions. It is interesting that the gel time was not proportionately decreased when the hardener level was increased from 3% to 5%.

The result of the gel time measurement of UF resins as a function of ammonium citrate level is shown in Fig. 4. As expected, the gel time decreased with increasing the hardener level. However, the resin prepared under the

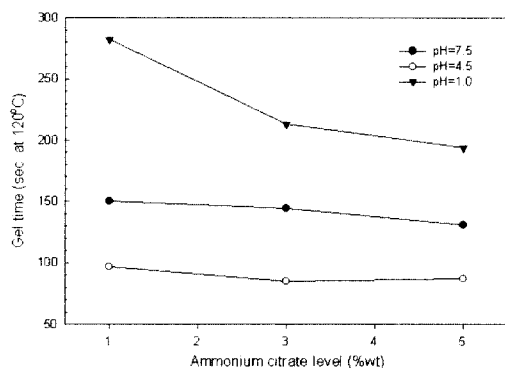


Fig. 4. Gel time of UF resins synthesized under different reaction pH conditions as a function of ammonium citrate level.

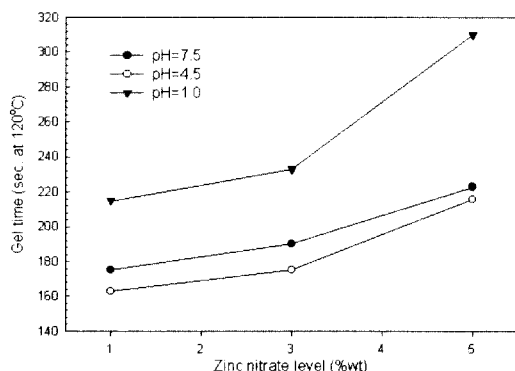


Fig. 5. Gel time of UF resins synthesized under different reaction pH conditions as a function of zinc nitrate level.

strong acid condition produced the longest gel time, followed by the alkaline-acid and then weak acid condition. The result indicates that the resin prepared under weak acid condition had the reactivity when ammonium citrate was used. As a hardener, zinc nitrate was also used for the resins prepared under different reaction pH conditions. The gel time of the resins increased as the zinc nitrate level increased (Fig. 5). In other words, zinc nitrate was not effective for UF resin as a hardener. Nevertheless, the reactivity of UF resins for zinc nitrate was similar to that for ammonium citrate.

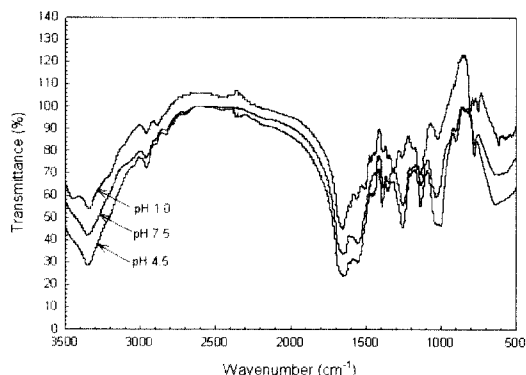


Fig. 6. FT-IR spectra of UF resins prepared three different reaction pH conditions.

Again, the resin synthesized under weak acid condition showed the best reactivity as for ammonium citrate.

In terms of the reactivity of UF resin for three different reaction conditions, the weak acid reaction condition produced much faster reactivity compared to alkaline-acid and strong acid reaction conditions. Among three hardeners used, traditional ammonium chloride gave much shorter gel time than other hardeners used. Thus, the weak acid reaction condition would be a possible solution to accelerate the reactivity of UF resin.

The above results indicated that the reactivity of UF resin depend on the reaction pH condition employed during its synthesis. Determination of chemical structures of UF resins prepared under three different reaction conditions will provide further understanding of the results. Both FT-IR and ¹³C-NMR spectroscopies were employed in this study. Both FT-IR and ¹³C-NMR spectra of three UF resins were shown in Fig. 6 and 7, respectively. Also, the assignments of chemical structures from both FT-IR and ¹³C-NMR spectra are summarized in Tables 2 and 3.

The infrared spectrum of the resin prepared under traditional alkaline-acid reaction condition

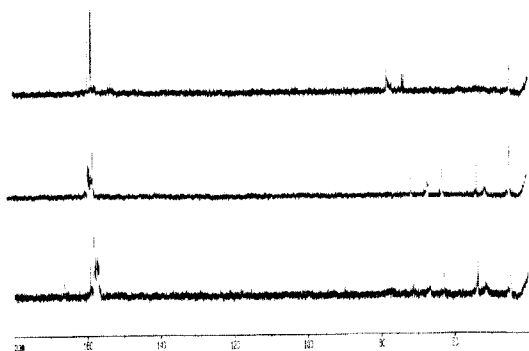


Fig. 7. ^{13}C -NMR spectra of UF resins prepared under three different reaction pH conditions (top: pH 7.5; middle: pH 4.5; bottom: pH 1.0).

showed a typical infrared spectrum of UF resin (Myers, 1981). The absorption band at $3,340\sim 3,350\text{ cm}^{-1}$ was assigned to the N-H stretching of primary aliphatic amines (Socrates, 1994). This absorption band was present for all infrared spectra from three resins. Also, the band at about $2,960\text{ cm}^{-1}$ assigned to the C-H stretching of aliphatic ether group showed the

same result. One of the dominant band occurred at about $1,650\text{ cm}^{-1}$, which was assigned to the C=O stretching of primary amides. Myers (1981) used this band for quantifying infrared spectra.

The band at about $1,560\text{ cm}^{-1}$ was assigned to the C-N stretching of secondary amides (Myers, 1981; Socrates 1994). This band might have arisen from methylene linkages of UF resin. The band at $1,465\text{ cm}^{-1}$ was only detected for the UF resin prepared under the strong acid reaction condition. This might have resulted from the presence of uronic derivatives in the resin as supported by the result of ^{13}C -NMR spectrum of the same resin (Table 3). And, this result was also compatible with the occurrence of $1,320\text{ cm}^{-1}$ band assigned to =C-N or -CH-N structure, as reported by Myers (1981). The region from $1,260$ to $1,250\text{ cm}^{-1}$ was assigned to C-H and N-H stretching combined with tertiary amides (Myers, 1981). The region from $1,130\sim 1,150\text{ cm}^{-1}$ with strong peaks was assigned to the C-O stretching of aliphatic ether

Table 2. Absorption band assignment of FT-IR spectra of UF resins synthesized under different reaction pH conditions.

Known bands (cm^{-1})	Chemical structure assignment	Observed band (cm^{-1})			Ref.
		alkaline	-acid weak acid	strong acid	
3350-3340	NH stretching of primary aliphatic amines	3,340	3,349	3,349	18
2962-2960	-O-CH ₃ , aliphatic ethers	2,962	2,959	2,962	18
1654-1646	C=O stretching of primary amide	1,653	1,646	1,654	9, 18
1560-1550	C-N stretching of secondary amines	1,559	1,560	1,560	9, 18
1465-1440	C-H bending in NCH ₂ N, CH ₂ O, OCH ₃	-	-	1,465	9, 18
1400-1380	C-H mode in CH ₂ and CH ₃	1,387	1,391	1,390	9, 18
1380-1330	C-N stretching of CH ₂ -N	1,349	1,354	-	9, 18
1320-1300	=C-N or =CH-N of tertiary cyclic amides	-	-	1,319	9
1260-1250	C-N and N-H stretching of tertiary amides	1,253	1,256	1,259	9, 18
1150-1130	C-O stretching of aliphatic ether	1,133	1,134	1,133	9, 18
1050-1030	C-N or CN stretching of methylene linkages (NCH ₂ N)	1,032	-	1,024	9
1020-1000	C-O stretching of methylol group	-	1,001	-	9
900-650	N-H bending of primary aliphatic amines	776	780	805	18
750-700	N-H bending of secondary aliphatic amines (R ₁ -CH ₂ -NH-CH ₂ -R ₂)	-	-	752	18

Table 3. Chemical shift assignment of ^{13}C -NMR spectra of UF resins synthesized under different reaction pH conditions.

Chemical shift (ppm)	Chemical structure	Observed chemical shift (ppm)			Reference
		alkai-acid	weak acid	strong acid	
44-45	$\text{NH}-\underline{\text{C}}\text{H}_2-\text{NH}$	44.9	44.8	45.2	4, 19
53-54	$\text{N}(\text{CH}_2-\underline{\text{C}}\text{H}_2\text{N}(\text{CH}_2)-)$	53.6 - 54.1	53.7	-	4, 19, 21, 22
62.9	$\text{NH}-\underline{\text{C}}\text{H}_2\text{OH}$	62.9	62.9	-	19
67.0	$-\text{NH}-\underline{\text{C}}\text{H}_2-\text{O}-\underline{\text{C}}\text{H}_2-\text{NH}-$	-	67.0	-	19
71.7	$\text{N}(\text{CH}_2-\underline{\text{C}}\text{H}_2\text{OH})$	71.3	71.3	-	19, 22
73.5-75.2	uron $-\underline{\text{C}}\text{H}_2-\text{O}-\underline{\text{C}}\text{H}_2-$	-	-	74.0	19
78.8	$-\text{N}(\underline{\text{C}}\text{H}_2-\text{O})\text{CH}_3$	-	-	78.4	19
153.9	$\begin{array}{c} \text{HO}_2\text{HCN}-\underline{\text{C}}\text{O}-\text{NCH}_2\text{OH} \\ \qquad \qquad \\ \text{H}_2\text{C}-\text{O}-\text{CH}_2 \end{array}$	-	-	153.3	4
155.1	$\begin{array}{c} \text{HN}-\underline{\text{C}}\text{O}-\text{NH} \\ \qquad \qquad \\ \text{H}_2\text{C}-\text{O}-\text{CH}_2 \end{array}$	-	-	156.0	4, 5
157.2-157.7	$-\text{HN}-\underline{\text{C}}\text{O}-\text{NH}-$	157.1-157.9	157.0-157.9	157.9	4, 19
161	$-\text{NH}-\underline{\text{C}}\text{O}-\text{NH}_2-$	158.2	158.2	158.6	4, 19, 21
159-163	$\text{HOCH}_2\text{NH}\underline{\text{C}}\text{ON}(\text{CH}_2\text{OH})_2$	159.2	159.2	159.7	4, 19
166.3	$\text{H}\underline{\text{C}}\text{OOH}$	166.3	-	-	19

group in the resins. An absorption band at $1,133 \sim 1,134 \text{ cm}^{-1}$ occurred for all three resins. Thus, this result indicates that all three reaction pH conditions produce ether linkages in the resins. The spectra of both resins from alkaline-acid and from strong acid reaction conditions showed strong bands at $1,032 \text{ cm}^{-1}$ and $1,024 \text{ cm}^{-1}$, respectively. The band from $1,030$ to $1,050 \text{ cm}^{-1}$ could be assigned to C-N stretching from C-N or C-N₂, of amides in the resins (Myers, 1981). So, these bands could result from the methylolated ureas or methylene ureas. However, this region was relatively weak for the resin prepared under weak acid condition. Instead the resin from weak acid condition showed $1,001 \text{ cm}^{-1}$ band, which was assigned to the C-O stretching of methylol groups (Myers, 1981). This result suggests that methylolated and methylene ureas are present for all the resins from three different reaction conditions.

But, the infrared spectra suggest that types of these chemical species present in the resins were quite different from each other.

The region below $1,000 \text{ cm}^{-1}$ wave number was assigned to primary or secondary amines. The absorption band from 900 cm^{-1} to 650 cm^{-1} may have resulted from the N-H bending of primary amines (Socrates, 1994). The absorption bands ranging from 776 cm^{-1} to 805 cm^{-1} were present for all three resins. The band from 700 cm^{-1} to 750 cm^{-1} assigned to N-H bending of secondary amines occurred for the resin prepared under strong acid reaction condition. This absorption band also support the presence of uronic structures in the resin synthesized under the strong acid condition.

The infrared spectra and band assignments to chemical structures produced useful information on the resins synthesized under different reaction pH conditions. The C=O stretching of

primary amides was most dominant absorption band of infrared spectra of UF resin which occurred at $1,650\text{ cm}^{-1}$. Two bands at $1,465\text{ cm}^{-1}$ and $1,320\text{ cm}^{-1}$ supported the presence of uronic derivatives in the UF resin prepared under strong acid reaction condition.

The spectra of ^{13}C -NMR spectroscopy are shown in Fig. 7. The structural assignments of chemical shift are also summarized in Table 3. In general, the spectra of two UF resins synthesized under weak acid and alkaline-acid reaction conditions were similar to each other while the spectrum of the resin prepared under strong acid reaction condition was different.

Both UF resins produced under alkaline-acid and weak acid reaction conditions showed a peak at 44 ppm while the resin synthesized under strong acid reaction condition had a peak at 45 ppm. The chemical shift from 44 to 45 ppm was assigned to the carbon of methylene linkages, according to published information (Gu *et al.*, 1995; Hse *et al.*, 1994; Kim 1999; Soulard *et al.*, 1998; Tohmura, 2000; Tomita, 1978). The chemical shift from 53 to 54 ppm might be attributed to various methylene carbons such as dimethylene urea, trimethylene tetraurea, or tetramethylene pentaurea (Tomita and Hatono, 1978). But, these methylene linkages were not detected for the resin prepared under strong acid condition.

The chemical shift at 62~63 ppm was assigned to various methylol carbons of the resins prepared under alkaline-acid and weak acid conditions. This peak for the resin synthesized under strong acid condition was relatively weak compared to other two reaction conditions. The methyl ether carbon occurred at 67 ppm for the weak acid resin. This peak was fairly weak for the resin from both alkaline-acid and strong acid conditions. The chemical shift of 71.3 ppm from the spectra of both alkaline-acid and weak acid reaction pH resins was

assigned to substituted methylol carbons, according to Tomita and Hatono (1978), and Soulard *et al.* (1998). However, Gu *et al.* (1995) and Tohmura *et al.* (2000) assigned the substituted methylol carbons to 72 ppm, which was shifted to downfield compared with 71 ppm.

The chemical shift of 74 ppm from the spectrum of the strong acid resin might be assigned to methylene carbons of uron structure. As mentioned, uronic structures were found for the resin prepared under strong acid condition (Tomita and Hatono, 1978; Gu *et al.*, 1995; Tohmura, 2000; Hse, 1994). Hence, this assignment is in a good agreement with the published results. Other carbons from uronic structures were also detected 153.3 ppm for the strong acid reaction resin. These chemical shifts were also assigned to the carbonyl group of the uronic structure (Gu *et al.*, 1995; Soulard *et al.*, 1998). The chemical shift of 78.4 ppm was also strongly detected for the strong acid resin, and was assigned to methyl ether of methylol group (Tomita and Hatono, 1978).

Three peaks at 157, 158, and 159 ppm were appeared prominently for all three resins. The peak at around 157 ppm was assigned to the carbons of carbonyl group of urea (Gu *et al.*, 1995; Soulard *et al.*, 1998). The chemical shift of 158 ppm was assigned to the carbons of substituted carbonyl groups (Gu *et al.*, 1995; Soulard *et al.*, 1998; Tohmura *et al.*, 2000). The peak at 159 ppm was assigned to the carbons of carbonyl group of various urea residues (Gu *et al.*, 1995). The chemical shift of 166 ppm was supposed to be due to formic acid used for the pH control during resin synthesis (Soulard *et al.*, 1998).

Fig. 8 shows shear adhesion strengths of the resins prepared under three different reaction pH conditions, and cured with three different hardener types. For the resins prepared under alkaline-acid condition, the adhesion strength

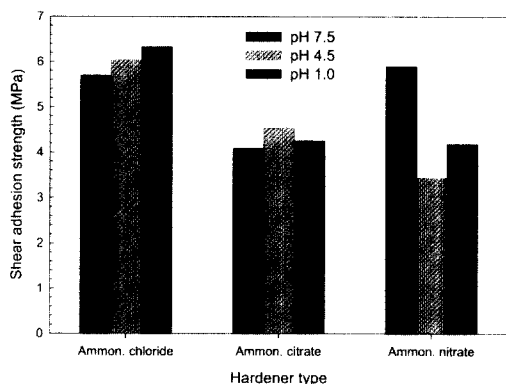


Fig. 8. Shear adhesion strength of UF resins synthesized under three different pH conditions, and cured with different hardener types.

was quite close to each other when hardened with ammonium chloride and zinc nitrate, but the poorest adhesion strength under the alkali-acid condition was found when the resin was hardened with ammonium citrate. For weak-acid and strong acid reaction condition, the adhesion strength was in order of ammonium chloride, ammonium citrate, and zinc nitrate. In other words, the strongest adhesion strength was found when the resin prepared under strong acid condition was hardened with ammonium chloride. This result was quite interesting in terms of the chemical species present in the resin prepared under strong acid reaction condition. Soulard *et al.* (1998) reported that internal bond strength of particleboard increased to an maximum and then decreased as the amount of uron in the resin increased from 0% to 75%. Thus, it was believed that the strongest adhesion strength of the resin prepared under the strong acid condition is responsible for the presence of uronic structures in the resin.

5. CONCLUSION

This study was undertaken to investigate the effects of reaction pH and hardener types on the

chemical structure and adhesion performance of UF resins. Three different reaction pH conditions were used to synthesize UF resins that were cured by adding three different hardeners (ammonium chloride, ammonium citrate, and zinc nitrate) to measure adhesion strength. Following important conclusions were drawn from this study. The gel time of UF resins decreased with an increase in the amount of both ammonium chloride and ammonium citrate added to the resins. However, the gel time increased for zinc nitrate. Both FT-IR and ^{13}C -NMR spectroscopies showed that the strong reaction pH condition produce uronic structures in UF resin while both alkaline-acid and weak acid conditions produced similar chemical structures in the resins. The maximum adhesion strength determined with shear specimens in tension occurred with the resin prepared under strong acid pH condition and cured with ammonium chloride.

ACKNOWLEDGEMENT

The author (B. D. Park) greatly appreciates critical reading and English correction of the manuscript for Dr. Adya P. Singh at the Department of Wood Science and Engineering, Chonnam National University.

REFERENCES

1. Dunky, M. 1998. Urea-formaldehyde (UF) adhesive resins for wood. *Int. J. Adhesion & Adhesives*, 18: 95-107.
2. Dunky, M. 1999. Adhesives for new types and applications of wood-based panels. Proc. of 2nd European Wood-Based Panel Symposium. Hanover, Germany. pp: 1-11.
3. Dutkiewicz, J. 1984. Preparation of cured urea-formaldehyde resins of low formaldehyde emission. *J. Appl. Polym. Sci.*, 29: 45-55.
4. Gu, J.-Y., M. Higuchi, M. Morita, and C.-Y.

- Hse. 1995. Synthetic conditions and chemical structures of urea-formaldehyde resins I. Properties of the resins synthesized by three different procedures. *Mokkuzai Gakkaishi*. 41(12): 1115-1121.
5. Hse, C.-Y., Z.-Y. Xia, and B. Tomita. 1994. Effects of reaction pH on properties and performance of urea-formaldehyde resins. *Holzforschung*. 48: 527-532.
 6. Kim, M. G. 1999. Examination of selected synthesis parameters for typical wood adhesive-type urea-formaldehyde resins by ¹³C-NMR spectroscopy. I. *J. Appl. Polym. Sci.: Part A. Polym. Chem.* 37: 995-1007.
 7. Marutzky, R. 1986. Release of formaldehyde by wood products. In: *Wood Adhesives: Chemistry and Technology*, Vol. 2. Ed. by A. Pizzi. pp: 307-387.
 8. McCaffery, M. 1970. *Laboratory Preparations for Macromolecular Chemistry*. McGraw Hill, New York, USA. p. 61.
 9. Myers, G. 1981. Investigation of urea-formaldehyde polymer cure by infrared. *J. Appl. Polym. Sci.*, 26: 747-764.
 10. Myers, G. E. 1983. Use of acid scavengers to improve durability of acid-catalyzed adhesive wood bonds. *For. Prod. J.*, 33(4): 49-57.
 11. Myers, G. E. 1984. How mole ratio of UF resin affects formaldehyde emission and other properties: A literature critique. *For. Prod. J.* 34(5): 35-41.
 12. Myers, G. E. 1986. Mechanisms of formaldehyde release from bonded wood products. In: *Formaldehyde Release from Wood Products*, Ed. B. Meyer. B. A. K. Andrews, R. M. Reinhardt. American Chemical Society, pp: 8-14.
 13. Myers, G. E. and J. A. Koutsy. 1987. Procedure for measuring formaldehyde liberation from formaldehyde-based resins. *For. Prod. J.* 37(9): 56-60.
 14. Myers, G. E. 1990. Formaldehyde liberation and cure behavior of urea-formaldehyde resins. *Holzforschung*. 44: 117-126.
 15. Pizzi, A. 1983. *Wood Adhesives: Chemistry and Technology*. Marcel Dekker Inc. New York. pp: 59-104.
 16. Pizzi, A., L. Lipschitz, and J. Valenzuela. 1994. Theory and practices of the preparation of low formaldehyde emission UF adhesives. *Holzforschung*. 48: 254-261.
 17. Pizzi, A. 1994. *Advanced Wood Adhesives Technology*. Marcel Dekker Inc., New York. pp: 19-66.
 18. Socrates, G. 1994. *Infrared Characteristic Group Frequencies*. 2nd Edition. John Wiley & Sons, New York.
 19. Soulard, C., C. Kamoun, and A. Pizzi. 1998. Uron and uron-urea-formaldehyde interior wood adhesives. *Holzforschung Holzverwertung*. 50(5): 89-94.
 20. Steiner, P. R. 1973. Durability of urea-formaldehyde adhesives: Effects of molar ratio, second urea, and filler. *For. Prod. J.* 23(12): 32-38.
 21. Tohmura, S., C.-Y. Hse, and M. Higuchi. 2000. Formaldehyde emission and high-temperature stability of cured urea-formaldehyde resins. *J. Wood Sci.* 46: 303-309.
 22. Tomita, B. and S. Hatono. 1978. Urea-formaldehyde resins. III. Constitutional characterization by ¹³C fourier transform NMR spectroscopy. *J. Appl. Polym. Sci.* 16: 2509-2525.