

Reactivity, Chemical Structure, and Molecular Mobility of Urea–Formaldehyde Adhesives Synthesized Under Different Conditions Using FTIR and Solid-State ^{13}C CP/MAS NMR Spectroscopy

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ABSTRACT: This study was conducted to investigate the effects of reaction pH condition and hardener type on the reactivity, chemical structure, and molecular mobility of urea–formaldehyde (UF) resins. Three different reaction pH conditions, such as alkaline (7.5), weak acid (4.5), and strong acid (1.0), were used to synthesize UF resins, which were cured by adding four different hardeners (ammonium chloride, ammonium sulfate, ammonium citrate, and zinc nitrate) to measure gel time as the reactivity. FTIR and ^{13}C -NMR spectroscopies were used to study the chemical structure of the resin prepared under three different reaction pH conditions. The gel time of UF resins decreased with an increase in the amount of ammonium chloride, ammonium sulfate, and ammonium citrate added in the resins, whereas

the gel time increased when zinc nitrate was added. Both FTIR and ^{13}C -NMR spectroscopies showed that the strong reaction pH condition produced ionic structures in UF resin, whereas both alkaline and weak-acid conditions produced quite similar chemical species in the resins. The proton rotating-frame spin–lattice relaxation time ($T_{1\rho\text{H}}$) decreased with a decrease in the reaction pH of UF resin. This result indicates that the molecular mobility of UF resin increases with a decrease in the reaction pH used during its synthesis. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2677–2687, 2003

Key words: resins; NMR; solid-state structure; molecular dynamics; adhesives

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 (MUPF) condensation resin. The worldwide production of UF resins in 1998 was estimated to be approximately 6 billion tons per year based on 66% resin solids by mass.¹ The 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 1997.² 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 particleboard (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.^{3–8} 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.⁹ Thus, the use of UF resin–bonded wood-based composite panels is limited only to non-structural applications attributed 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 prepared UF resins is one of the reasons for formaldehyde emission.¹⁰ One of the approaches of reducing formaldehyde emission was to lower the F/U molar ratio of the synthesized resin.¹¹ In addition, the number of urea additions also influences the properties of prepared UF resin.¹² However, lower F/U mo-

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lar ratio reduced formaldehyde emission at the expense of poor mechanical properties such as internal bond (IB) strength and modulus of rupture (MOR).¹¹ To overcome this problem, many attempts have been made to modify the resin synthesis methods, hardener types, additives, and so forth.⁹

Until the mid-1960s, most UF resins were synthesized by the two-step reaction procedures, methylation and condensation. In other words, the methylation reaction was done under alkaline conditions followed by the condensation reaction under acidic conditions.¹³ This synthesis method was widely employed for UF resin preparations for quite some time. In the early 1970s, 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,^{13–15} introduction of a second urea addition,¹⁶ and the use of additives.^{17–18} In particular, Hse et al.¹³ and a Japanese group^{14–16} studied the change of chemical structure of UF resins prepared under different reaction pH conditions using the ¹³C-NMR technique. 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.¹³ suggested a weak-acid reaction pH condition as a compromise between lower formaldehyde emission and poor mechanical properties of the panel.

Because of limitations in solubility of cured UF resin, solid-state ¹³C-NMR spectroscopy has been used to study the chemical structure of cured UF resins.¹⁹ In recent years, the use of this technique was extended to study formaldehyde emission mechanisms and formation of uron structures in UF resin.^{14,20} This technique also provides an opportunity to directly probe the network structure of the cured resin under nondestructive conditions. In addition, structural information can be obtained from the solid-state spectra, whereas relative molecular mobilities can be determined by measuring the proton rotating-frame spin–lattice relaxation time ($T_{1\rho H}$). $T_{1\rho H}$ measurements have been made for PF resole resins.^{21,22} However, the ¹³C-NMR with cross-polarization (CP) and magic angle spinning (MAS) method was not previously used to monitor the structural characterization of UF resins prepared under different reaction pH conditions.

Even though many investigators studied the chemical structure of UF resins prepared under different reaction pH conditions, the work done to study the influence of hardener types on the reactivity and molecular mobility based on chemical structure of the

resins has been limited. Therefore, this study was conducted to investigate the influence of reaction pH conditions on the reactivity, chemical structures, and molecular mobility of the UF resins using FTIR and solid-state ¹³C-NMR spectroscopies.

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 networks in the cured resin. This is attributed 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 as follows: (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.¹⁰

UF resin is produced through two reactions, methylation and condensation. The methylation in alkaline condition 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 produced molecular species from the methylation include mono-, di-, and trimethylolureas. It is known that tetramethylolurea has never been isolated.¹⁰ Low temperature and weak acidic pH favor the formation of methylene ether bridges ($-\text{CH}_2-\text{O}-\text{CH}_2-$) over methylation.¹⁸ 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 was known to produce varieties of uronic derivatives.¹⁸ The presence of some of these species was detected by many other studies.^{14–16,20} The condensation reaction in the acid condition refers to the reaction of methylolated ureas into methylene ureas with water as a by-product.

EXPERIMENTAL

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, alkaline, weak-acid, and strong-acid conditions. For the alkaline reaction, UF resins were synthesized according to the traditional two-step procedure. Formaldehyde

(37%) was placed in the reactor and heated to 60°C, after which the reaction pH was adjusted 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 the reaction was terminated by rapid cooling to 25°C. For the 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 1 h, and maintained until the end reaction point. The initial F/U molar ratios were 2.2 for the alkali-acid and weak-acid conditions, whereas the strong-acid condition was 3.0. For all resins prepared, both the final F/U molar ratio and the final pH were adjusted to 1.15 and 8.0, respectively.

Four hardeners—ammonium chloride, ammonium sulfate, ammonium citrate, and zinc nitrate—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 viscosity. The gel time was measured with three replications for each hardener type and level.

Free formaldehyde determination

Free formaldehyde in the prepared UF resins was determined by a slightly modified sodium sulfite method.²³ A 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% thymol phthalein was neutralized with 1N sodium hydroxide. The percentage of free formaldehyde was determined by the equivalent of the amount of the consumed sodium hydroxide in titration.

FTIR and liquid- and solid-state 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 FTIR spectroscopy (Nicolet 520P; Nicolet Analytical Instruments, Madison, WI). The powder UF resins were also dissolved in deuterated dimethyl sulfoxide (DMSO-*d*₆) as an internal standard (~ 5% concentration) for

¹³C-NMR spectroscopy. The ¹³C-NMR spectra were obtained using a 300-MHz model (Bruker AMX-R300; Bruker Instruments, Billerica, MA) with 9.5-s pulse width (30°), and a pulse delay of 1 s. By using the gated decoupling method to minimize the nuclear Overhauser effect, about 20,000 scans were accumulated to obtain reliable spectra.

Solid-state cross-polarization/magic angle spinning (CP/MAS) NMR (DSX 400 MHz; Bruker) analysis, at the Korea Basic Science Institute, was used to obtain the carbon spectrum of uncured UF resins at a spin rate of 6.8 kHz. Part of the sample used for liquid ¹³C-NMR spectroscopy was also used for the solid-state ¹³C CP/MAS NMR analysis. The carbon spectra were obtained at 75.45 MHz. The Hartmann–Hahn match was done by tuning ¹H and ¹³C channels with adamantane. The cured PF resin powder was packed into a 7-mm zirconium oxide rotor sealed with Kel-F cap. The rotor was spun at a MAS speed of 6.8 kHz, contact time of 1 ms, and recycle delay of 4 s for spectra acquisitions. A standard cross-polarization pulse with variable contact times at room temperature was used to obtain the proton spin-lattice rotating frame-relaxation times (*T*_{1ρH}). Both *T*_{1ρH} and *T*_{CH} were determined by nonlinear curve fitting of the signal intensities and delay times to the two-component equation that describes the rise and fall of signal intensity as a function of variable contact time.²⁴ The equation is expressed as

$$I(\tau) = I^* \left(\frac{T_{1\rho H}}{T_{1\rho H} - T_{CH}} \right) (\exp^{\tau/T_{1\rho H}} - \exp^{\tau/T_{CH}}) \quad (1)$$

where *I*(τ) is the peak intensity at a given contact time (τ) and *I*^{*} is the corrected intensity. The variable contact times ranged from 0.1 to 6 ms.

RESULTS AND DISCUSSION

The properties of UF resins prepared under three different reaction conditions are summarized in Table I. The resin prepared under weak-acid condition showed relatively greater viscosity and higher free formaldehyde compared with those of the other two resins prepared. The nonvolatile solids content of UF resins prepared under three different reaction conditions were about 50% by weight. The results of gel time measurements of the UF resins prepared under three different reaction conditions are shown in Figures 1–4. As shown in Figure 1, the gel time of all UF resins decreased with increasing ammonium chloride level. In spite of this, the UF resins synthesized under the alkaline-reaction condition showed the longest gel time at all hardener levels, followed by the strong-acid condition and the weak-acid condition. However, the gel time of UF resins synthesized under the weak-acid

TABLE I
Physical and Chemical Properties of the Prepared UF Resins

Reaction pH	Nonvolatile solid content (%)	Initial F/U molar ratio	Final F/U molar ratio	Viscosity (cps)	Free HCHO (%)	Final pH
7.5	48.5	2.2	1.15	58	0.45	8.0
4.5	52.1	2.2	1.15	135	0.69	8.0
1.0	49.8	3.0	1.15	66	0.55	8.0

condition was much shorter than that of the resins prepared under either the alkaline or the strong-acid condition. This result indicated that the weak-acid reaction condition, compared with other reaction conditions, provides a better reactivity with UF resin. It is interesting that the gel time was not proportionately decreased when the hardener level was increased from 3 to 5%.

Figure 2 shows the results of the gel time measurements of UF resins as a function of ammonium sulfate level. The gel time of two UF resins prepared under alkaline and weak-acid conditions decreased with an increase in the hardener level. The gel time of the UF resin prepared under the strong-acid condition increased with an increase in the hardener level, reaching a maximum at 3% ammonium sulfate level. Among three UF resins, the UF resin prepared under the weak-acid condition showed the shortest gel time, indicating that the combination of weak-acid condition with ammonium sulfate could provide an accelerated cure of UF resin.

Results of the gel time measurements of UF resins as a function of ammonium citrate level are shown in Figure 3. As expected, the gel time decreased with an increase in the hardener level. However, the resin

prepared under the strong-acid condition produced the longest gel time, followed by the alkaline and then weak-acid condition. The results indicate that the resin prepared under the 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. 4). In other words, zinc nitrate was not effective for UF resin as a hardener. The resin synthesized under the weak-acid condition showed the shortest gel time when ammonium sulfate was used as hardener.

In terms of the reactivity of UF resin for three different reaction conditions, the weak-acid reaction condition produced much faster reactivity compared to that of alkaline and strong-acid reaction conditions. Among four hardeners used, the ammonium sulfate gave much shorter gel time than other hardeners used. This result might be attributable to the extent of the acidic nature of hardeners used. The more acidic the hardener, the faster the cure of UF resin at the same temperature. Thus, the weak-acid reaction condition would be a possible solution to accelerate the reactivity of UF resin.

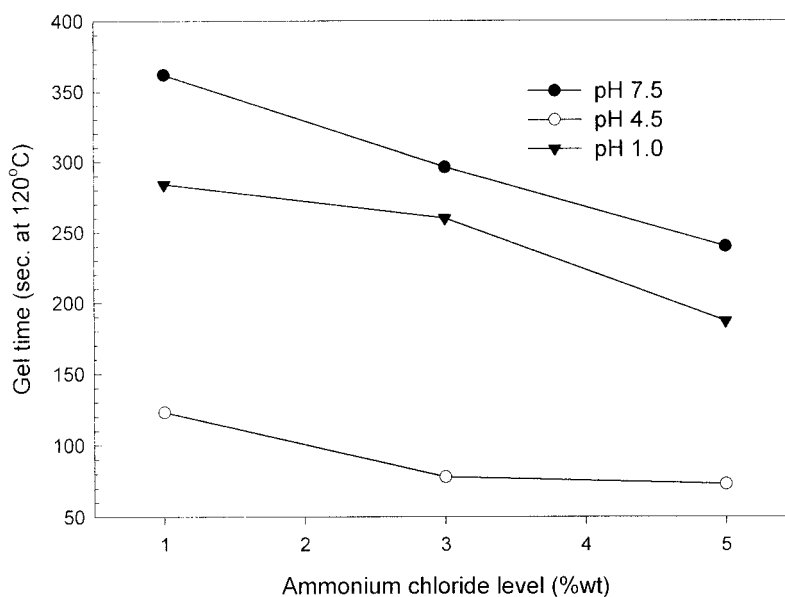


Figure 1 Gel time of UF resins synthesized under three different reaction pH conditions as a function of ammonium chloride level.

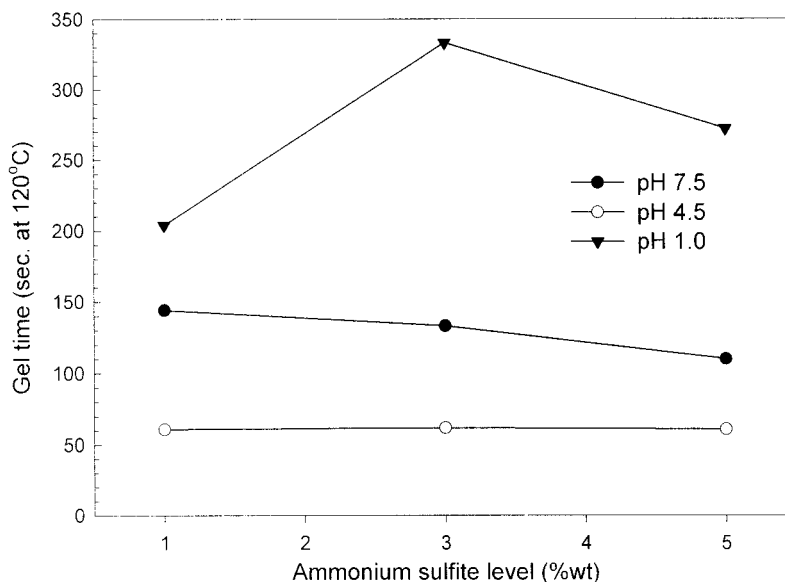


Figure 2 Gel time of UF resins synthesized under three different reaction pH conditions as a function of ammonium sulfate level.

The above results indicate that the reactivity of UF resin depends 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 FTIR and liquid-phase ^{13}C -NMR spectra of three UF resins prepared in this study are shown in Figures 5 and 6, respectively. Also, the assignments of chemical structures from both FTIR and liquid-state ^{13}C -NMR spectra are summarized in Tables II and III.

The band at 1465 cm^{-1} was detected only for the UF resin prepared under the strong-acid reaction condi-

tion. This might have resulted from the presence of uronic derivatives in the resin, as supported by the result of the ^{13}C -NMR spectrum of the same resin (Table III). Moreover, this result was also compatible with the occurrence of the 1320 cm^{-1} band assigned to $=\text{C}-\text{N}$ or $-\text{CH}-\text{N}$ structure as reported.²⁵ The spectra of both resins from alkaline and strong-acid reaction conditions showed strong bands at 1032 and 1024 cm^{-1} , respectively. The band from 1030 to 1050 cm^{-1} could be assigned to $\text{C}-\text{N}$ stretching from $\text{C}-\text{N}$ or $\text{C}-\text{N}_2$ of amides in the resins.²⁵ Thus, these bands could result from the methylolated ureas or methylene ureas. However, this region was relatively weak for

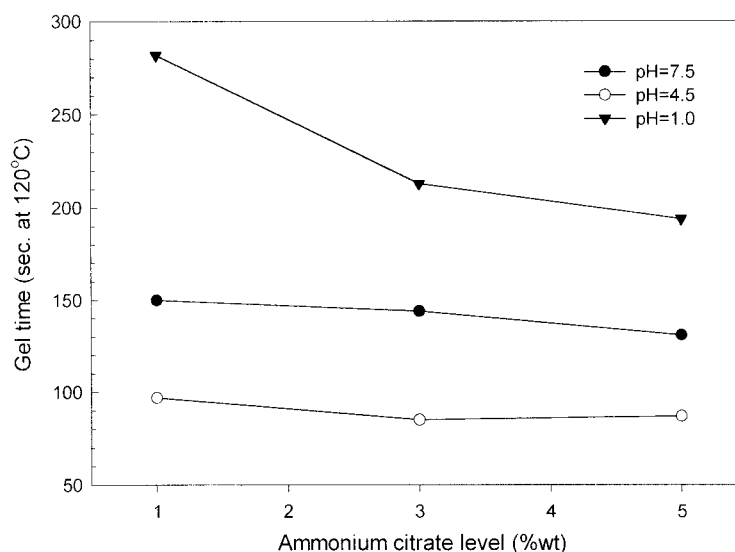


Figure 3 Gel time of UF resins synthesized under three different reaction pH conditions as a function of ammonium citrate level.

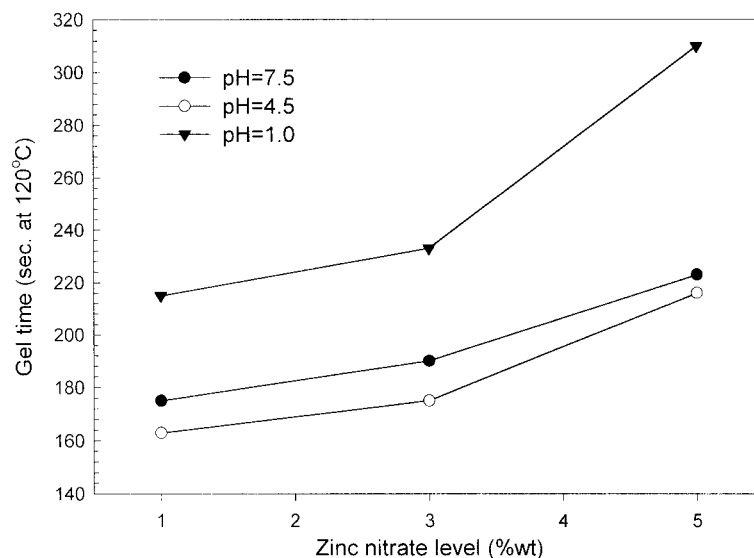


Figure 4 Gel time of UF resins synthesized under three different reaction pH conditions as a function of zinc nitrate level.

the resin prepared under the weak-acid condition. Instead, the resin prepared under the weak-acid condition showed a 1001 cm^{-1} band, which was assigned to the C—O stretching of methylol groups.²⁶ This result suggests that methylolated and methylene ureas are present for all the resins from three different reaction conditions. However, the infrared spectra suggest that types of these chemical species present in the resins were quite different from each other.

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 the most dominant absorption band of infrared spectra of

UF resin, which occurred at 1650 cm^{-1} . Two bands at 1465 and 1320 cm^{-1} supported the presence of uronic derivatives in the UF resin prepared under the strong-acid reaction condition.

The spectra of ^{13}C -NMR spectroscopy are shown in Figure 6. The structural assignments of chemical shifts are also summarized in Table III. In general, the spectra of two UF resins synthesized under the weak-acid and alkaline-reaction conditions were similar to each other, whereas the spectrum of the resin prepared under the strong-acid reaction condition was different. Both UF resins produced under alkaline and weak-acid reaction conditions showed a peak at 44 ppm, whereas the resin synthesized under the strong-acid

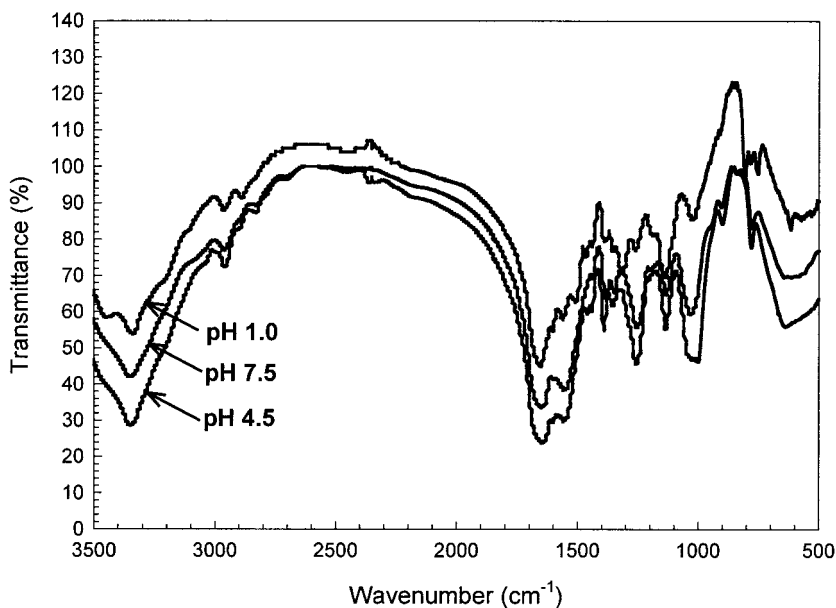


Figure 5 FTIR spectra of UF resins prepared under three different reaction pH conditions.

TABLE II
Absorption Band Assignment of FTIR Spectra of UF Resins Synthesized Under Different Reaction pH Conditions

Absorption band (cm ⁻¹)	Chemical structure assignment	Observed band (cm ⁻¹)			Ref.
		pH 7.5	pH 4.5	pH 1.0	
3350–3340	NH stretching of primary aliphatic amines	3340	3349	3349	26
2962–2960	–O–CH ₃ , aliphatic ethers	2962	2959	2962	26
1654–1646	C=O stretching of primary amide	1653	1646	1654	25, 26
1560–1550	C–N stretching of secondary amines	1559	1560	1560	25, 26
1465–1440	C–H bending in NCH ₂ N, CH ₂ O, OCH ₃	—	—	1465	25, 26
1400–1380	C–H mode in CH ₂ and CH ₃	1387	1391	1390	25, 26
1380–1330	C–N stretching of CH ₂ –N	1349	1354	—	25, 26
1320–1300	=C–N or =CH–N of tertiary cyclic amides	—	—	1319	25
1260–1250	C–N and N–H stretching of tertiary amides	1253	1256	1259	25, 26
1150–1130	C–O stretching of aliphatic ether	1133	1134	1133	25, 26
1050–1030	C–N or NCN stretching of methylene linkages (NCH ₂ N)	1032	—	1024	25
1020–1000	C–O stretching of methylol group	—	1001	—	25
900–650	N–H bending of primary aliphatic amines	776	780	805	26
750–700	N–H bending of secondary aliphatic amines (R1–CH–NH–CH ₂ –R2)	—	—	752	26

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.^{13–16,20,27} The chemical shift from 53 to 54 ppm might be attributable to various methylene carbons such as dimethylene urea, trimethylene tetraurea, or tetramethylene pentaurea.¹⁶ However, these methylene linkages detected were extremely small for the resin prepared under the strong-acid condition.

The chemical shift at 62–63 ppm was assigned to various methylol carbons of the resins prepared under alkaline and weak-acid conditions. This peak for the resin synthesized under the strong-acid condition was relatively weak compared to that of the 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 prepared under either the alkaline or strong-acid condition. The chemical shift of 71.3

TABLE III
Chemical Shift Assignment of ¹³C-NMR Spectra of UF Resins Synthesized Under Different Reaction pH Conditions

Chemical shift (ppm)	Chemical structure	Observed chemical shift (ppm)			Ref.
		pH 7.5	pH 4.5	pH 1.0	
44–45	NH–CH ₂ –NH	44.9	44.8	45.2	14, 20
53–54	N(CH ₂ –)CH ₂ N(CH ₂ –)–	53.6–54.1	53.7	—	14–16, 20
62.9	NH–CH ₂ OH	62.9	62.9	—	20
67.0	–NH–CH ₂ –O–CH ₂ –NH–	—	67.0	—	20
71.7	N(CH ₂ –)CH ₂ OH	71.3	71.3	—	16, 20
73.5–75.2	uron–CH ₂ –O–CH ₂ –uron	—	—	74.0	20
78.8	HN–CO–NH	—	—	78.4	20
153.9	$\begin{array}{c} \quad \\ \text{H}_2\text{C} - \text{O} - \text{CH}_2 \\ \quad \\ \text{HO}_2\text{HCN} - \text{CO} - \text{NCH}_2\text{OH} \\ \quad \\ \text{H}_2\text{C} - \text{O} - \text{CH}_2 \end{array}$	—	—	153.3	14
155.1	$\begin{array}{c} \quad \\ \text{HN} - \text{CO} - \text{NH} \\ \quad \\ \text{H}_2\text{C} - \text{O} - \text{CH}_2 \end{array}$	—	—	156.0	13, 14
157.2–157.7	–HN–CO–NH–	157.1–157.9	157.0–157.9	157.9	14, 20
161	–NH–CO–NH ₂ –	158.2	158.2	158.6	14, 15, 20
159–163	HOCH ₂ NHCON(CH ₂ OH) ₂	159.2	159.2	159.7	14, 20
166.3	HCOOH	166.3	—	—	20

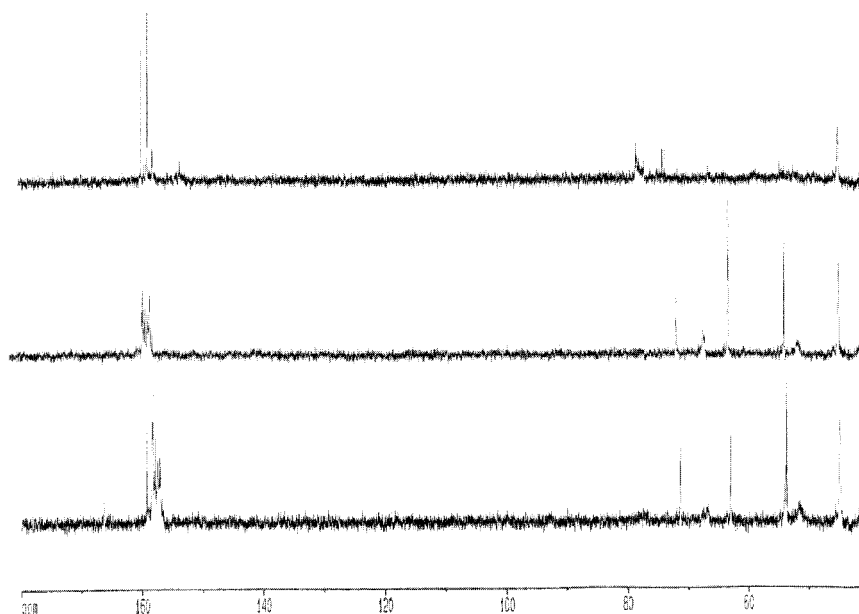


Figure 6 ^{13}C -NMR spectra of UF resins prepared under three different reaction pH conditions (top, pH 1.0; middle, pH 4.5; bottom, pH 7.5).

ppm from the spectra of both alkaline and weak-acid reaction pH resins was assigned to substituted methylol carbons.^{16,20} However, Gu et al.¹⁴ and Tohmura et al.¹⁵ assigned the substituted methylol carbons to 72 ppm, which was shifted to downfield compared with 71 ppm. These results explain why the UF resin synthesized under the strong-acid condition had a longer gel time than that of either alkaline or weak-acid resins.

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 the strong-acid condition.^{13–16} Hence, this assignment is in

good agreement with the published results. Other carbons from uronic structures were also detected at 153.3 ppm for the strong-acid reaction resin. These chemical shifts were also assigned to the carbonyl group of the uronic structure.^{14,20} The chemical shift of 78.4 ppm was also strongly detected for the strong-acid resin, and was assigned to methyl ether of the methylol group.¹⁶

Three peaks at 157, 158, and 159 ppm appeared prominently for all three resins. The peak at around 157 ppm was assigned to the carbons of the carbonyl group of urea.^{14,20} The chemical shift of 158 ppm was assigned to the carbons of the substituted carbonyl

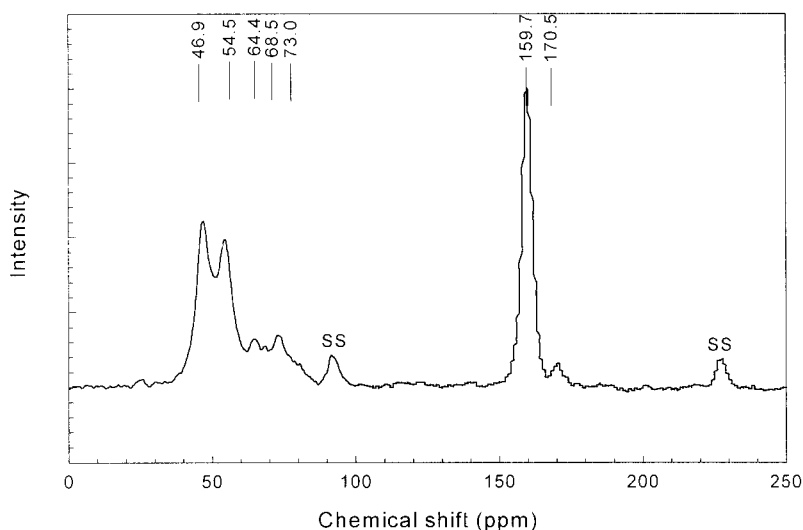


Figure 7 ^{13}C CP/MAS NMR spectrum of UF resin prepared under the alkaline-reaction condition (pH 7.5). SS, spinning side peak.

TABLE IV
Chemical Shift Assignment of Solid-State ^{13}C CP/MAS NMR Spectra of UF Resins
Synthesized Under Different Reaction pH Conditions

Chemical shift (ppm)	Chemical structure	Observed chemical shift (ppm)			Ref.
		pH 7.5	pH 4.5	pH 1.0	
44–45	$\text{NH}-\text{CH}_2-\text{NH}$	46.9	46.9	46.4	15, 20
53–54	$\text{N}(\text{CH}_2-)\text{CH}_2\text{N}(\text{CH}_2-)-$	54.5	54.5	55.1	15, 20
62.9	$\text{NH}-\text{CH}_2\text{OH}$	64.4	64.9	—	15, 20
67.0	$-\text{NH}-\text{CH}_2-\text{O}-\text{CH}_2\text{NH}-$	68.5	—	—	15, 20
71.7	$\text{N}(\text{CH}_2-)\text{CH}_2\text{OH}$	73.0	72.1	—	15, 20
78.8	Uron $\text{CH}_2-\text{O}-\text{CH}_2$	—	—	78.3	20
155.1	$\text{HN}-\text{C}(=\text{O})-\text{NH}$ $\text{H}_2\text{C}-\text{O}-\text{CH}_2$	—	—	155.9	20
159–163	$\text{HOCH}_2\text{NHCON}(\text{CH}_2\text{OH})_2$	159.7	159.9	160.6	20

groups.^{14,15,20} The peak at 159 ppm was assigned to the carbons of the carbonyl group of various urea residues.¹⁴ The chemical shift of 166 ppm was supposed to be attributed to formic acid used for the pH control during resin synthesis.²⁰

Figures 7–9 show the spectra of solid-state ^{13}C CP/MAS NMR spectroscopy for UF resins prepared under alkaline, weak-acid, and strong-acid reaction conditions, respectively. The peak assignments for those spectra are summarized in Table IV. Three UF resins synthesized under three different conditions had a peak in common at 46 ppm, which indicates the presence of methylene linkages ($-\text{CH}_2-$) in UF resin.

The peaks from 54 to 55 ppm, assigned to methylene linkages, were also present for all three spectra of the UF resins. This result was in agreement with other published works.^{15,19} However, the intensity of this peak was relatively large compared with that from the liquid ^{13}C -NMR spectrum of the UF resin prepared under the strong-acid condition. This might be the

solvent effect for liquid ^{13}C -NMR technique. The chemical shift of 64 ppm was assigned to methylene carbon of methylolated ureas. The peak was not strong for the UF resin from the strong-acid reaction condition, which was similar to the liquid ^{13}C -NMR spectrum. This result again indicates that the strong-acid reaction condition is not favorable to methylol groups (CH_2OH) in the UF resin.

The spectra from UF resins prepared under either the alkaline or weak-acid condition did not show the peak at 78 ppm, indicating that uronic structures were not present in either resin (Figs. 7 and 8). One of the distinctive peaks from the UF resin synthesized under the strong-acid condition was the peak at 78 ppm, which was assigned to the carbons of CH_2 groups of uronic derivatives (Fig. 9). Soulard et al.²⁰ reported that the presence of uronic structures improves the adhesion strength of UF resins. This result is also compatible with other published results.^{15,16} Thus, this result suggested that the strong-acid condition might

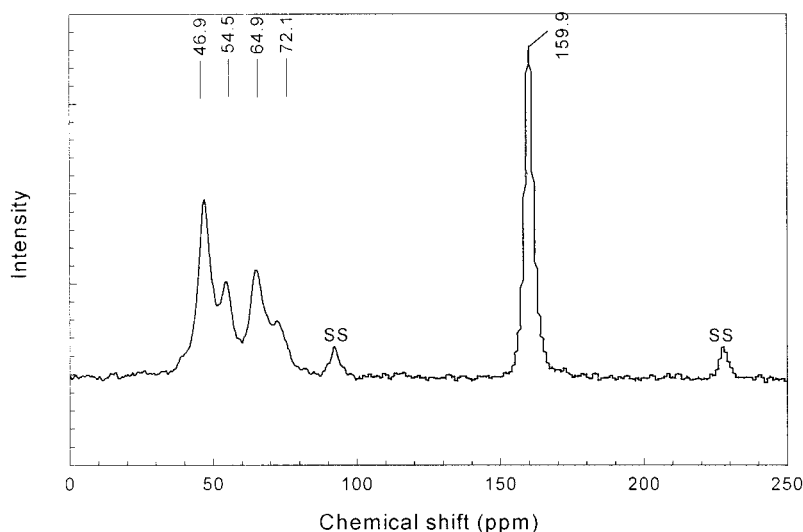


Figure 8 ^{13}C CP/MAS NMR spectrum of UF resin prepared under the weak-acid reaction condition (pH 4.5). SS, spinning side peak.

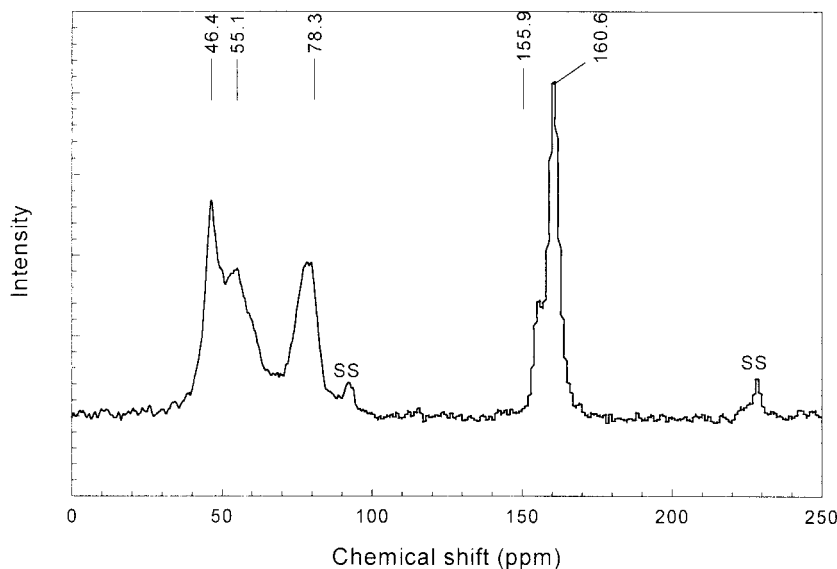


Figure 9 ^{13}C CP/MAS NMR spectrum of UF resin prepared under the strong-acid reaction condition (pH 1.0). SS, spinning side peak.

improve the adhesion strength of UF resin. Moreover, the peak at 155 ppm was also assigned to the carbonyl group of uron.^{16,20} The peak at 159–160 ppm was assigned to the carbonyl group of urea as well as methylolated ureas.

The results of the proton spin–lattice rotating frame relaxation times ($T_{1\rho\text{H}}$) are summarized in Table V. The $T_{1\rho\text{H}}$ value of the peak at 46 ppm assigned to methylene linkages decreased for the weak-acid (pH 4.5) condition and then slightly increased for the strong-acid (pH 1.0) condition. Traditional UF resin synthesis includes methylation at alkaline condition, usually at the pH range from 5.0 to 8.0, and then condensation at the acid condition at the pH range from 3.0 to 5.0. It is known that more branched polymers are formed in methylation reaction, whereas methylene linkages are formed in condensation reaction.¹⁸ In other words, the alkaline condition produces short and sterically hindered polymers, whereas the acid condition produces fewer crosslinked and pliable polymers. Thus, the results of $T_{1\rho\text{H}}$ measurement indicate that a greater relaxation time of the UF resin synthesized under the alkaline condition gives rigid

structures that do not easily relax. By contrast, a smaller relaxation time of the UF resin synthesized under the strong-acid condition indicate a greater mobility of chemical structure. In general, the $T_{1\rho\text{H}}$ value decreased with a decrease in the reaction pH for UF resin synthesis. This result indicates that molecular mobility of UF resin increases with a decrease in the reaction pH used during its synthesis.

CONCLUSIONS

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 four different hardeners (ammonium chloride, ammonium sulfate, ammonium citrate, and zinc nitrate) to measure the gel time. The following important conclusions were drawn from this study. The gel time of UF resins decreased with an increase in the amount of either ammonium chloride, ammonium sulfate, or ammonium citrate added to the resins; however, the gel time increased for zinc nitrate. Both FTIR and ^{13}C -NMR spectroscopies showed that the strong-acid reaction pH condition produced uronic structures in UF resin, whereas both alkaline and weak-acid conditions produced similar chemical structures in the resins. However, the solid-state ^{13}C -NMR spectrum showed that the uronic structures were detected for the UF resin prepared under the strong-acid condition. In general, the $T_{1\rho\text{H}}$ value decreased with a decrease in the reaction pH for UF resin synthesis. This result indicates that the molecular mobility of UF resin increases with

TABLE V
Proton Spin–Lattice Rotating Frame Relaxation Time ($T_{1\rho\text{H}}$) of UF Resins Prepared Under Three Different Reaction pH Conditions Using ^{13}C CP/MAS NMR Spectroscopy

Peak (ppm)	$T_{1\rho\text{H}}$ (ms)		
	pH 7.5	pH 4.5	pH 1.0
160	27.7	15.3	14.3
54	15.4	6.8	5.9
46	14.6	9.9	13.1

a decrease in the reaction pH used during its synthesis.

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