ORIGINAL ARTICLE

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Formaldehyde emission and high-temperature stability of cured urea-formaldehyde resins

Abstract A test method for measuring formaldehyde from urea-formaldehyde (UF) resins at high temperature was developed and used to assess the influence of the reaction pH on the formaldehyde emission and heat stability of the cured resins. Additionally, solid-state ^{13}C CP/MAS nuclear magnetic resonance (NMR) techniques were used to investigate the structure of cured UF resins before and after high temperature heating. Formaldehyde emissions during the cure were related to the UF resins' methylol group content. The heat stability of cured UF resins synthesized under strongly acidic conditions was much higher than that of the other resins, which were prepared in weakly acidic and alkaline media. Solid-state ^{13}C CP/MAS NMR spectra showed that formaldehyde emission from cured UF resins after heating is mainly ascribable to decreased methylol groups and dimethylene ether linkages. Significantly, it was revealed that uron structures characteristically found in the cured UF resin synthesized under strongly acidic medium indicated high heat stability.

Keywords Urea-formaldehyde resin · Formaldehyde-emission · Solid-state ^{13}C CP/MAS NMR · Heat stability

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Introduction

Low cost and proven performance have made urea-formaldehyde (UF) resins the most important wood adhesives for interior applications. However, the formaldehyde emission from UF-bonded wood products has been recognized as a potential source of indoor air pollution leading to inhabitant discomfort and possible health problems. The practical concern over formaldehyde emissions has elicited a great deal of research since the 1970s. Recent studies[1,2] indicate these major sources of formaldehyde emission from UF-bonded wood products are (1) unreacted formaldehyde in the UF resins; (2) released formaldehyde during the condensation reaction between methylol groups; and (3) emitted formaldehyde from the hydrolytic degradation of the cured resin.

Over the past two decades, great progress has been made[3,4] in improving the formaldehyde emission from such wood products as particleboard, hardwood plywood, and medium-density fiberboard. Beneficial steps have included reducing the formaldehyde/urea (F/U) molar ratio,[5] synthesizing UF resin with acidic catalysts without first using an alkaline catalyst,[6] impregnating the wood furnish with a formaldehyde scavenger,[7] and treating boards with formaldehyde scavengers or a barrier coating (or both) after manufacture.[8]

Despite this practical progress, the effect of the UF resin hydrolysis on formaldehyde emission from boards is not a trivial one. Over the past 40 years investigators have extensively examined the structure of low-molecular-weight UF compounds and the physical chemistry of their formation and degradation in aqueous systems. Earlier deJong and deJonge,[9–11] Lanqvist,[12,13] and others[14–16] used classical solution techniques to study the kinetics and equilibria of formation and hydrolysis. Subsequently, chromatographic[17–19] and nuclear magnetic resonance (NMR)[20–25] techniques were applied. It is now generally agreed that the hydrolysis of cured UF resins is responsible for the major portion of liberated formaldehyde from bonded-wood materials.[26] Thus, in principle, the board would retain the potential to

emit formaldehyde during its useful life, and efforts to minimize emissions must be directed toward resin stabilization. Nevertheless, there is little reported in the literature on the chemical stability of the cured wood adhesive, probably because most investigators have focused on the hydrolytic effects on UF-bonded products rather than on cured neat resins. The lack of a database in the literature on the hydrolytic stability of cured neat resin undoubtedly hampered development of more stable UF wood adhesives to minimize formaldehyde emission. This study developed a new method for the measurement of formaldehyde emissions in neat resins and investigated the heat stability of the cured UF resin in relation to the structure of UF resin and curing conditions. To eliminate the effect of free formaldehyde already existing in the resins on formaldehyde emission, freeze-dried UF resins were used in this study.

Experimental methods

Resin preparation

All UF resins (F/U 1.5) were prepared in the laboratory. Each resin preparation was replicated once. To prepare each resin, formaldehyde (37%) was placed in a reaction kettle and the pH adjusted with sulfuric acid or sodium hydroxide (or both). According to the literature,[27] UF resins synthesized with strong acid and weak acid can be used to make low formaldehyde-emission board. Therefore, three reaction pHs during resin preparation were chosen:

Strongly acidic: pH 1.0 adjusted to pH 6.5
Weakly acidic: pH 4.5
Alkaline: pH 8.0

For the resins prepared under weakly acidic (pH 4.5) and alkaline (pH 8.0) catalysis conditions, urea was added in equal parts at 1-min intervals, and the mixture was heated and maintained at 40°C for 4h. Thereafter, the reaction was terminated by rapid cooling. For the resin prepared with strong acid (pH 1.0), the F/U molar ratio was adjusted initially to 3.0 and reacted at 70°C for 30 min. Then additional urea was added to adjust the F/U molar ratio to 1.5, and it was reacted at pH 6.5 and 60°C for 10 min. To clarify the relation between the amount of formaldehyde produced during cure and the resin structure, especially the methylol group, all the resins were prepared to contain less condensation structure than is in ordinary resins.

These resins were freeze-dried without further pH adjustment, ground to a fine powder (60 mesh), and dried again thoroughly. The resins were found to contain no free formaldehyde or methylene glycol structure by solution ^{13}C NMR spectroscopy.

Cure procedure

Figure 1 outlines the system used to cure and collect the emitted formaldehyde. The powdered samples (0.5 g) were
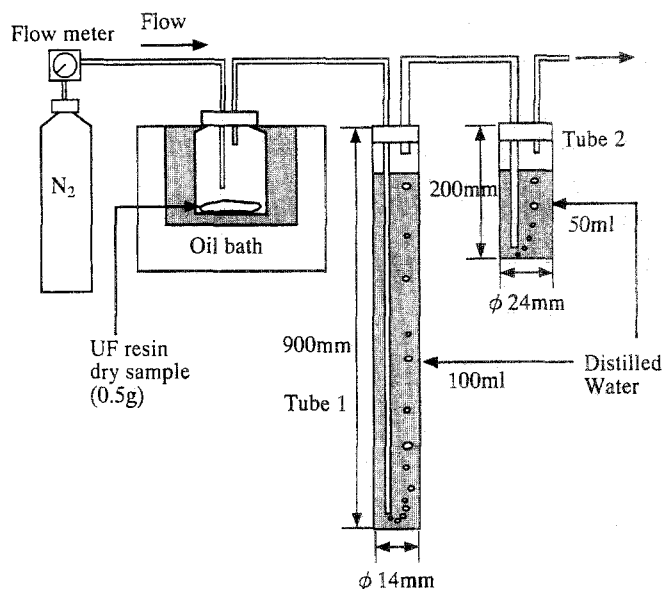

Fig. 1. System used to cure and collect emitted formaldehyde

placed in a crimp-cup vial with a rubber septum. Two needles connected with 316 stainless tubes were inserted into the bottle. A nitrogen gas stream was used to purge the vial continuously. Exhaust nitrogen gas first bubbled through a glass tube scrubber filled with 100-ml distilled water, where the emitted formaldehyde in the air stream was collected. The air stream was then bubbled through a scrubber consisting of a 20-cm test tube with 100 ml distilled water to catch any formaldehyde that might pass the primary collector. From the results of the preliminary experiment, it was shown that the size of the primary tube (14 mm diameter, 900 mm length) and the volume of water (100 ml) were enough to collect all the formaldehyde in this study because no formaldehyde was detected in the secondary tube.

Formaldehyde determination

The determination of formaldehyde absorbed in the distilled water was based on the specific reaction of formaldehyde with chromotropic acid–sulfuric acid solution, forming a purple monocationic chromogen. A 4-ml aliquot of formaldehyde-absorbed water was pipetted into a test tube with a screw cap. Chromotropic acid reagent (1%) was added to the test tube, and the tube was shaken to mix the contents. Next, 6 ml of concentrated sulfuric acid was pipetted into the tube and mixed slowly. The color of the solution turned from light yellow to purple. The capped tube then was placed in a boiling waterbath for 20 min. After cooling, the absorption of the purple solution was measured using a spectrophotometer set at 580 nm.

^{13}C NMR spectroscopy

Solution ^{13}C NMR spectra were obtained with a Bruker WM-250 spectrometer (62.89 MHz) using DMSO-d_6 as the

solvent. Chemical shifts were determined using internal DMSO-d_6 at 39.5 ppm. Quantitative analyses were based on the signal intensities of the total carbonyl groups of the urea residue.[28]

High-resolution solid-state ^{13}C cross polarization magic angle sprinning (CP/MAS) NMR spectra were obtained with a Chemagnetics CMX300 spectrometer. Most spectra were obtained with a 3-ms contact time, 10-s pulse delay, 35 μs decoupling delay, 4.5-μs H 90 pulse, 10-μs C 180 pulse, and 3.0-kHz MAS speed with two large and two small spinning sidebands placed at 40-ppm intervals outside the center band of the carbonyl at 159 ppm. Chemical shifts were determined using a standard reference of the methyl group (17.17 ppm) in hexamethylbenzene.

Results and discussion

Chemical structure of UF resin and the amount of released formaldehyde during cure

Before freeze-drying the resins, the effects of the initial reaction pH during resin synthesis on resin structure were investigated by solution ^{13}C NMR spectroscopy. Table 1 shows the integral ratios of various carbons to the total carbonyl carbon in the urea residue. The resin samples were prepared in a manner different from an ordinal resin preparation followed a condensation reaction acidic conditions

because one objective of this study was to measure the amount of formaldehyde produced during the curing reaction; the resin samples contain many more methylol groups than ordinary resins. Therefore, the main structure is the methylol group in all resins. The total methylol group was most abundant in the resin prepared at pH 8.0. The content of the methylol group increased with increased reaction pH. The amount of methylene linkage was low in the two resins prepared at pH 4.5 and 8.0, which means that the addition reaction of formaldehyde to urea (methylolation) is the main reaction in these two resins. The resin prepared at pH 1.0 contained methylene linkages because of the condensation under strongly acidic conditions and the higher reaction temperature than for the other two resins. It was noted that the free formaldehyde content in the resin prepared at pH 1.0 was markedly lower than that in the other resins. The peaks at 155 ppm are assigned to the carbonyl carbon in the uron, which is the ring ether of urea, and a characteristic structure in the resin prepared at pH 1.0.[28,29] The amount of total ether linkage was slightly higher in the resin prepared at pH 1.0 because of the included uronic ethers. Based on these results, the molecular weights of all resins were small, and methylol urea monomers were the main compound.

Figure 2 shows the amount of formaldehyde released during the cure of UF resins at 120°C and 160°C for 30 min. As the curing temperature and reaction pH at resin synthesis increased, so did the amount of emitted formaldehyde.

Table 1. Solution ^{13}C NMR spectroscopic integral ratios of various carbons to total carbonyl carbon of urea residue.

Structure	NMR signal (Figs. 5, 7)	Chemical shift (ppm)	Reaction pH					
			pH 1		pH 4.5		pH 8	
Total methylene			0.34	(23.1)	0.01	(0.7)	0	(0)
-NH-CH₂-NH-	a	47	0.2		0.01		0	
-N(CH₂)-CH₂-NH-	b	54	0.14		0		0	
-N(CH₂)-CH₂-N(CH₂-)-	c	60	0		0		0	
Total methylol			0.62	(42.2)	0.91	(61.0)	1.05	(72.4)
-NH-CH₂OH	d	65	0.46		0.78		0.86	
-N(CH₂-)CH₂OH	f	72	0.16		0.13		0.19	
Total methyl ether			0.23	(15.6)	0.01	(0.7)	0	(0)
-NHCH₂OCH₃	g	74	0.23		0.01		0	
Total dimethylene ether			0.16	(10.9)	0.1	(6.7)	0.11	(7.6)
-NHCH₂OCH₂-NH-	e	69	0.13		0.1		0.11	
-N(CH₂-)CH₂OCH₂NH-	h	76	0.01		0		0	
Uron-N-CO-N- CH₂-O-CH₂	i	79	0.02		0		0	
Total free formaldehyde			0.12	(8.2)	0.46	(30.9)	0.29	(20.0)
HOCH₂OH		83	0.02		0.09		0.04	
HOCH₂OCH₃		91	0.02		0.02		0	
H(OCH₂)ₙOCH₂OCH₃		95	0.08		0.35		0.25	
Total carbonyl carbon			1		1		1	
Uron-N-CO-N- CH₂-O-CH₂		155	0.03		0		0	
=NCONH-, -NHCONH-		160	0.52		0.32		0.32	
-NHCONH₂		161	0.36		0.56		0.56	
NH₂CONH₂		163	0.09		0.12		0.12	
Total formaldehyde			1.47	(100)	1.49	(100)	1.45	(100)
Combined formaldehyde			1.35	(91.8)	1.03	(69.1)	1.16	(80.0)

Amount of formaldehyde is based on its molar ratio with urea residue (F/U)
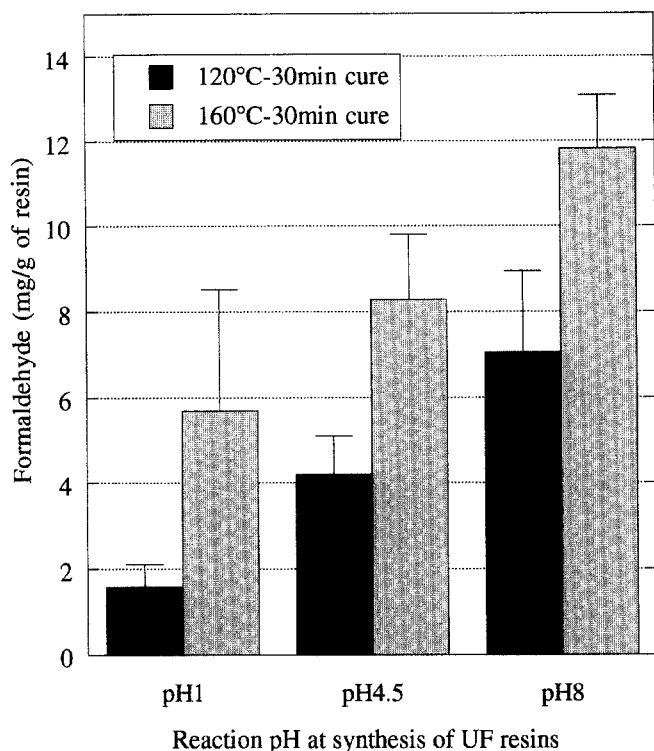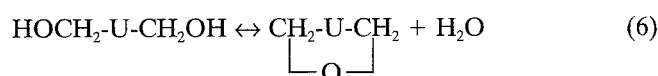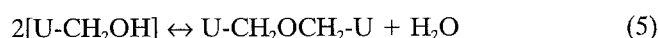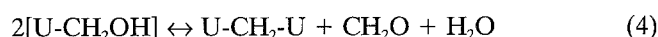Values in parentheses are percentages of total formaldehyde

Fig. 2. Effect of reaction pH while synthesizing UF resins on released fromaldehyde during cure

Fig. 3. Relation between the square of the content of the methylol group in the UF resins and formaldehyde released during cure

The curing reaction of UF resin is believed to occur through some combination of the following reactions:

$$U + HOCH_2OH \leftrightarrow U\text{-}CH_2OH + H_2O \qquad (1)$$

$$U\text{-}CH_2(OCH_2)_nOH + HOCH_2OH \leftrightarrow \\ U\text{-}CH_2(OCH_2)_{n+1}OH + H_2O \qquad (2)$$

$$U\text{-}CH_2OH + U \leftrightarrow U\text{-}CH_2\text{-}U + H_2O \qquad (3)$$

$$2[U\text{-}CH_2OH] \leftrightarrow U\text{-}CH_2\text{-}U + CH_2O + H_2O \qquad (4)$$

$$2[U\text{-}CH_2OH] \leftrightarrow U\text{-}CH_2OCH_2\text{-}U + H_2O \qquad (5)$$

$$HOCH_2\text{-}U\text{-}CH_2OH \leftrightarrow CH_2\text{-}U\text{-}CH_2 + H_2O \qquad (6) \\ \underset{O}{\underline{\qquad}}$$

All resin samples used in this study were freeze-dried before heating to remove free formaldehyde and moisture. Therefore, the formaldehyde collected during the cure must be formed because of the condensation reaction between two methylol groups [reaction (4)] or the hydrolysis reaction of methylol urea [the reverse of reactions (1) and (2)] or both. Because the curing reaction was performed under dry conditions, as described above, reaction (4) is considered to contribute predominantly to formaldehyde release. Reaction (4) is kinetically expressed as second order with respect to the concentration of methylol groups. The linear relation between the square of the methylol group contents in the resins and the amount of formaldehyde released during the cure is plotted in Fig. 3. Therefore, the amount of formaldehyde released during cure is related to the amount of methylol groups in the uncured UF resin. Practically,
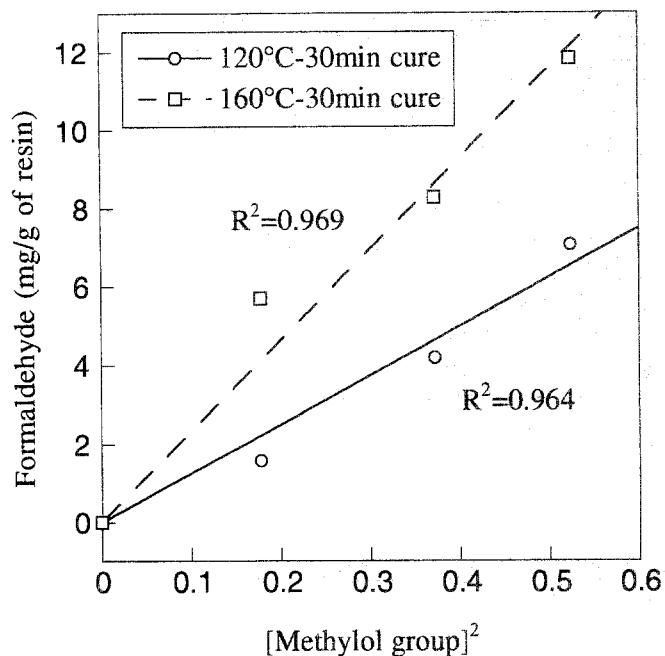
however, the formaldehyde generated during the cure would likely be absorbed on the wood components and released gradually. The absorbed formaldehyde might directly affect the formaldehyde emission from the UF-bonded wood products long after their manufacture.

Chemical structure of cured UF resin and the amount of released formaldehyde at high temperature

After cooling the 12 cured resin samples (at 120°C for 30 min), each set of four cured resin samples were again heated to one of three high temperatures (120°, 150°, 180°C) for 30 min. Figure 4 shows the effect of the reaction pH and postheating temperature on formaldehyde emission in the resins cured at 120°C for 30 min. In general, as the temperature and reaction pH increased, the amount of emitted formaldehyde increased. The most interesting results in the study, however, were the remarkable high-heat stability of the resin prepared at pH 1.0. Even at a postheating temperature of 180°C, the formaldehyde emission was only 0.7 mg/g of resin sample compared to 2.1 and 2.65 mg/g with the resins at pH 4.5 and pH 8.0, respectively.

The cured-resin structure was investigated with solid-state ^{13}C CP/MAS NMR spectroscopy. Figure 5 shows the comparison of ^{13}C CP/MAS NMR spectra of the resins cured at 120°C for 30 min with those of the resins after heating at 180°C for 30 min. Chemical shifts[29–31] and remarks in Fig. 5 are similar to those in Table 1. Although a small peak assigned to the spinning side band of carbonyl carbon seems to be overlapped at 79 ppm on all spectra, the spectra of the resin prepared at pH 1.0 indicated an obviously larger intensity at 79 ppm compared to the other resins. This
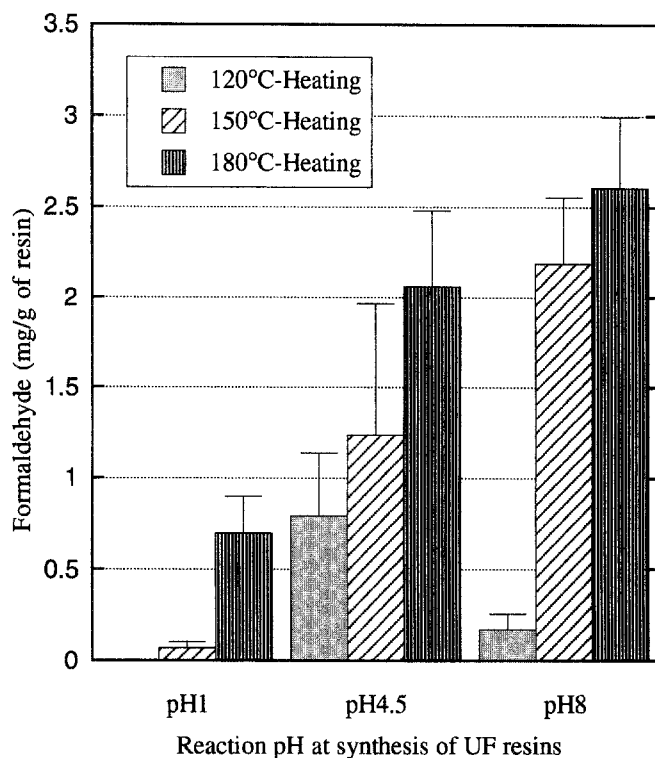
Fig. 4. Effect of the reaction pH and postheating temperature on formaldehyde emission from the UF resins cured at 120°C for 30 min

Fig. 5. Comparison of ^{13}C CP/MAS nuclear magnetic resonance (NMR) spectra of 120°C, 30-min cured UF resins with those of the resins after 180°C, 30 min after heating

greater peak intensity at 79 ppm in the spectra proved that the uronic structure existed in the cured resin prepared at pH 1.0. It is also interesting to note that in the spectra of the 120°C, 30-min cured-UF resins there is more linear methylene linkage (peak a) and less branched methylene linkage (peaks b and c) for the resins prepared at pH 4.5 and pH 8.0, whereas a large amount of branched methylene linkage and less linear methylene linkage was observed in the spectrum of the resin prepared at pH 1.0.

Figure 5 also shows that the methylol group (peaks d and f) and dimethylene ether group (peaks e and h) decreased and the branched methylene bonds (b and c) increased in all resins after heating at 180°C for 30 min. These results supported the evidence that the condensation reactions between methylol groups (reaction 4) and the degradation of dimethylene ether groups (reaction 5) caused the release of formaldehyde. The differences in the peak intensities of the methylol group and dimethylene ether group in the spectra before and after heating for the resins were in the order of pH 8.0 > pH 4.5 > pH 1.0, which was in good agreement with the results of the formaldehyde emission in Fig. 4. These results indicate that the curing condition of 120°C for 30 min is not sufficient for a complete cure, and the cured resins retain a potential for further crosslinking. Incidentally, the characteristic uron structure that existed in the resin prepared at pH 1.0 also was revealed to be stable toward a high temperature postheating.

Figure 6 shows the effect of the initial reaction pH and postheating temperature on formaldehyde emission of the resins cured at 160°C for 30 min. Contrary to the case
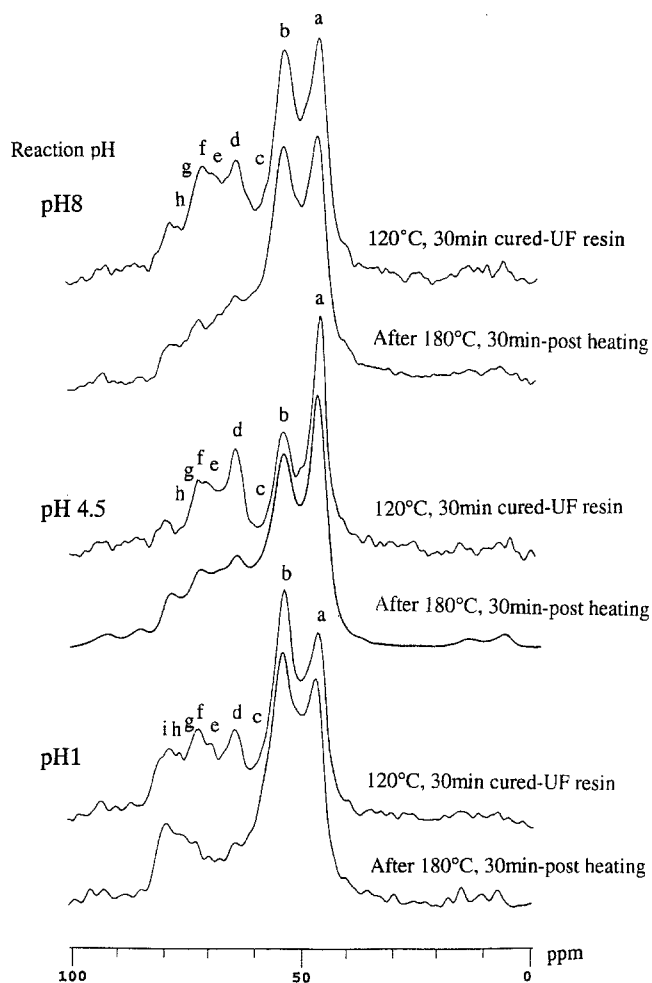
of 120°C cured resins, all samples cured at 160°C for 30 min indicated almost no formaldehyde emission during postheating at 120°, 150°, and 180°C. In particular, the cured resins from resins prepared at pH 1.0 and 4.5 indicated excellent stability toward high temperature heating. This result suggests that the cure at 160°C for 30 min is sufficient for a complete resin cure.

Figure 7 shows the ^{13}C CP/MAS NMR spectra of the resin cured at 160°C for 30 min and those of the resins after heating at 180°C for 30 min. Based on a comparison of Fig. 7 with Fig. 5 it can be said that the resins cured at 160°C for 30 min contain smaller amounts of methylol groups and dimethylene ether linkages than the resins cured at 120°C for 30 min. Moreover, as shown in Fig. 7, there is little change in the spectra before and after heating at 180°C.

Conclusions

A novel method for measuring formaldehyde released during curing and high temperature heating was developed.
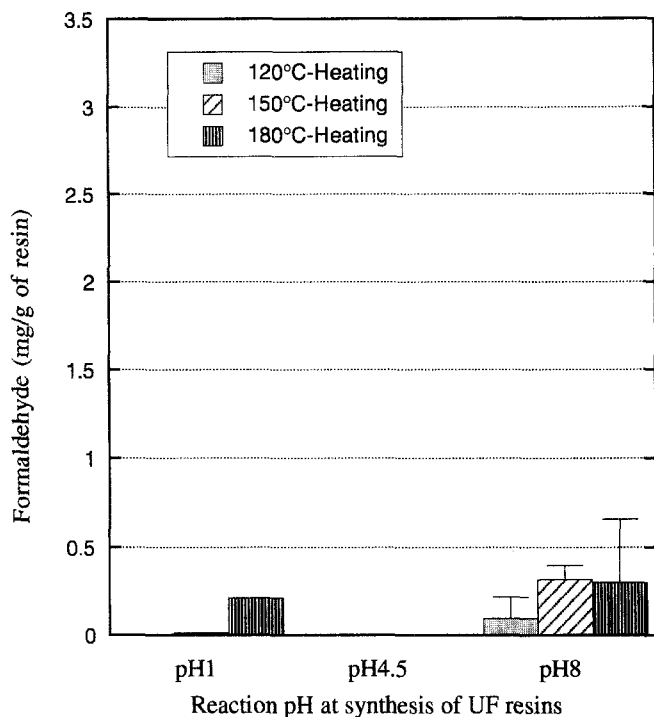
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Fig. 6. Effect of the reaction pH and postheating temperature on formaldehyde emission from the UF resins cured at 160°C for 30min

The amount of formaldehyde released during cure was correlated to the content of methylol groups in the UF resin. The cured resin synthesized with a strongly acidic catalyst was more stable toward high temperatures than the resins synthesized under weakly acidic and alkaline conditions. The uron structure of the resin formulated with a strongly acidic catalyst has shown excellent stability toward high-temperature heating treatment.

Fig. 7. Comparison of ^{13}C CP/MAS NMR spectra of 160°C, 30-min cured UF resins with those of the resins after 180°C, 30min after heating

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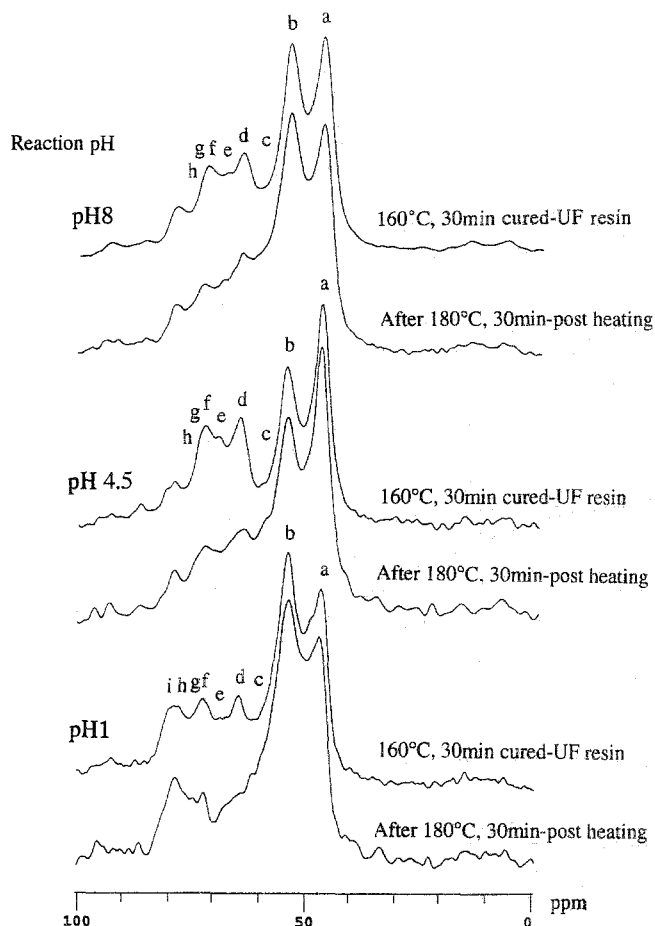
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