

Heat Stability of Cured Urea-Formaldehyde Resins by Measuring Formaldehyde Emission

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Abstract

A test method for measuring formaldehyde from urea-formaldehyde (UF) resins at high temperatures was developed and used to assess the influence of the reaction pH at synthesis on the formaldehyde emission during cure and heat stability of the cured resins without water. Additionally, ^{13}C -CP/MAS solid-state nuclear magnetic resonance (NMR) techniques were used to investigate the structure of cured UF resins before and after high-temperature heating. Formaldehyde emissions during cure were related to the UF resins' methylol group content. Heat stability of cured UF resin increased as the reaction pH at resin synthesis increased. Solid-state NMR spectra show formaldehyde emission from cured UF resins after heating is mainly ascribable to decreases of methylol group

and dimethylene ether linkage. Significantly, it was revealed that the uron **structure characteristically** found in the cured UF resin synthesized under strong acid media indicated high heat stability.

Introduction

Low cost and proven performance have made urea-formaldehyde resins (UF) the most important wood adhesive 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 possibly to health problems. The practical concern over the formaldehyde emission has elicited a great deal of research since the 1970s. Recent studies (12,30) indicate these major sources of formaldehyde emission from **UF-bonded** wood products are:

- unreacted formaldehyde in the UF resins;
- released formaldehyde during the condensation reaction between **methylol** groups; and
- emitted formaldehyde from the hydrolytic **degradation** of the cured resin.

Over the past two decades or so, great progress has been made (19,26) in improving the formaldehyde emission from wood products such as particleboard, hardwood plywood, and medium density fi-

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berboard. **Beneficial** steps have included reducing the formaldehyde-to-urea (F/U) mole ratio (20), synthesizing UF resin with acidic catalysts without first using an alkaline catalyst (11), impregnating the wood furnish with a formaldehyde **scavenger** (21), and treating boards with formaldehyde scavengers and/or a barrier coating after manufacture (23).

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 work by de Jong and de Jonge (4–6), Lanqvist (15,16), and others (3,8,27) used classical solution techniques to study the kinetics and equilibria of formation and hydrolysis. Subsequently, chromatographic (7,14,17) and nuclear magnetic resonance (9,13,22,24,25,28) 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 those materials (31). Thus, in principle, the board would retain the potential to emit **formaldehyde during** its useful life, and the efforts to minimize emission must be directed toward resin stabilization. Nevertheless, there is little reported in the literature on the hydrolytic 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 resin. 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.

Experimental

Resin preparation

All UF resins (F/U = 1.5) were prepared in the laboratory. Each resin preparation was replicated once. To prepare each resin, all formaldehyde (37%) was placed in a reaction kettle, and the pH was adjusted with sulfuric acid and sodium hy-

droxide, respectively. In the resins prepared under weak acid (pH 4.5) and alkaline (pH 8.0) catalysis, urea was added in equal parts at 1-minute intervals to adjust the F/U mole ratio of 1.5, and the mixture was heated and maintained at 40°C for 4 hours. Thereafter, the reaction was stopped by rapidly cooling. The resin prepared under strong acid (pH 1.0) was cooked with F/U mole ratio of 3.0 at 70°C for 30 minutes initially, then the pH was adjusted to 6.5 and urea was gradually added until the F/U mole ratio was 1.5. The reaction was kept at 60°C for 10 minutes and stopped in the same manner. These resins were freeze-dried, ground to a fine powder (60 mesh), and dried again thoroughly. The variables for the reaction pH during resin preparation were:

- strong acid—pH 1.0 and adjusted to pH 6.5;
- weak acid—pH 4.5; and
- alkaline—pH 8.0.

Cure procedure

Figure 1 is a diagram of the system used to cure and collect the emitted formaldehyde. The powdered samples (0.5 g) were placed in a crimp-cup vial with a rubber septum. Two needles connected with 3 16 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 is collected. The air stream was then bubbled through a scrubber consisting of a 20-cm test tube with 50 ml of distilled water to catch any formaldehyde that might pass through the primary collector. From the result of the preliminary experiment, it was shown that the size of the primary tube (14 mm in diameter and 900 mm in length) and the volume of water (100 ml) were enough to collect the maximum formaldehyde in this study because no formaldehyde was found 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. Four milliliters of formaldehyde-absorbed water was **pipetted** into a test tube with a

screw cap. One percent chromotropic acid reagent was added to the test tube and the tube was shaken to mix. Six milliliters concentrated sulfuric acid was pipetted into the tube and mixed slowly. The color of the solution turned from light yellow to purple. Then the capped tube was placed in a boiling water bath for 20 minutes. After cooling, the absorption of the purple solution was read using a spectrophotometer at 580 nm.

¹³C-nuclear magnetic resonance spectroscopy

Solution ¹³C-NMR spectra were obtained with a Bruker WM-250 spectrometer (62.89 MHz) using DMSO-d₆ as solvent. Chemical shifts were determined using internal DMSO-d₆ at 39.5 ppm. Quantitative analyses were based on the signal intensities of the total carbonyl group of urea residue (29).

High resolution solid-state ¹³C-CP/MAS NMR spectra were obtained at 300 MHz on a Chemagnetics CMX300 spectrometer. Most spectra were obtained with a 3-μs CP contact time, 10-second 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 out-

side the center-band of the carbonyl at 159 ppm. Chemical shifts were determined using a standard reference of 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 initial reaction pH during resin synthesis on resin structure were investigated by solution ¹³C-NMR spectroscopy. Table 1 shows the integral ratios of various carbons to total carbonyl carbon of urea residue. The main structure is the methylol group in all resins. The total methylol group was contained most abundantly in the resin prepared at pH 8. The contents of the methylol group increased with an increase of reaction pH at synthesis. There are very low amounts of methylene linkage in the two resins prepared at pH 4.5 and 8. This means the addition reaction of formaldehyde to urea (methylolation) is the main reaction in these two resins. The resin prepared at pH 1 contained methylene linkages because of the condensation reaction under strong acid and higher reaction temperature than the other two resins. The

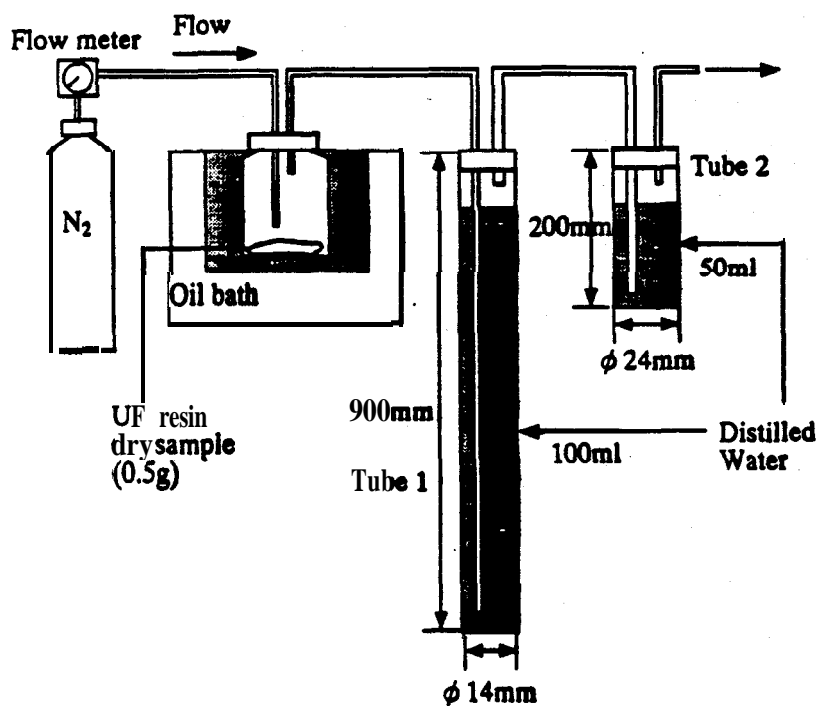
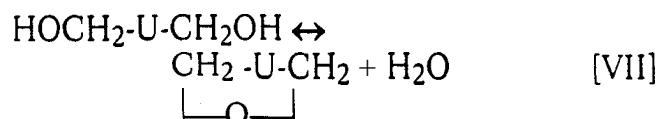
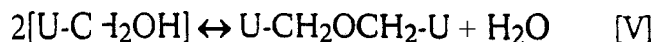
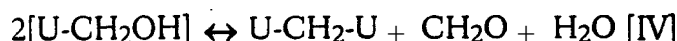
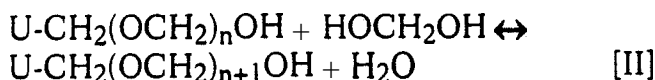
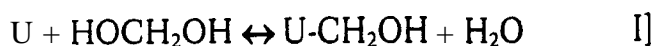


Figure I.--Diagram of the system used to cure and collect emitted formaldehyde.

free formaldehyde content in the resin prepared at pH 1 was slightly lower than the other two resins. The peak at 15.5 ppm assigned the carbonyl carbon in the uron ring which is the circular ether of urea and a characteristic structure in the resin prepared at pH 1 (10, 29). Total ether linkage content was slightly higher in the resin prepared at pH 1 because of included uronic ethers. From these results, the molecular weight of all resins was small and methylol urea monomer would be a main compound.

Figure 2 shows the amount of formaldehyde released during the cure of resins at 120°C and 160°C for 30 minutes. As the curing temperature and reaction pH at resin synthesis increased, the amount of emitted formaldehyde increased. The curing reaction of UF resin is believed to occur through some combination of the following reactions:



All resin samples used in this study were freeze-dried before heating to remove free formaldehyde and moisture. Therefore, formaldehyde collected during cure must be formed due to the reaction of two methylol groups (reaction [IV]) and/or breakage of dimethylene ether linkages to form the methylene linkages (reaction [VI]). Both reactions were kinetically expressed as the second order in terms of the concentration of methylol groups. Then the relationship between the square of methylol group contents in the resins and the amount of formaldehyde released during the cure was plotted in Figure 3; it provided a linear relationship. Therefore, the amount of formaldehyde released during cure is related to the amount of the methylol group in the uncured UF resin.

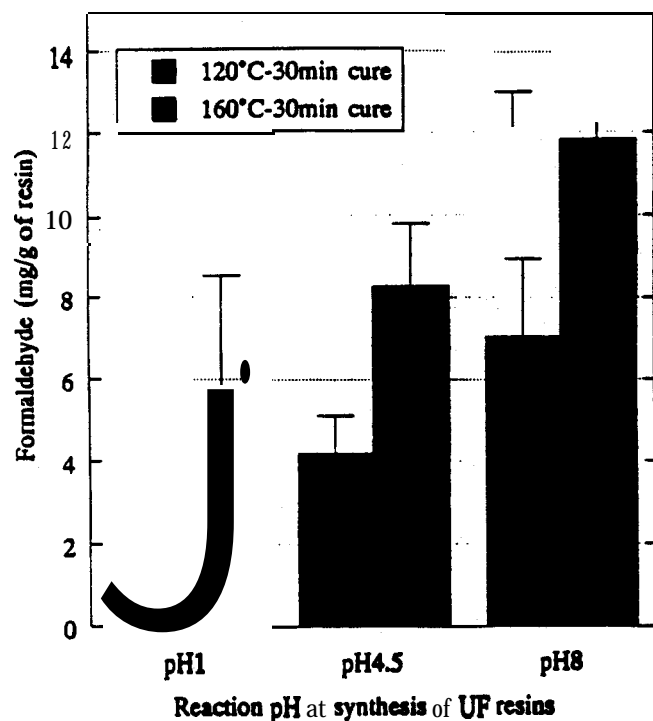


Figure 2.—Effect of reaction pH in synthesizing UF resins on released formaldehyde during curing.

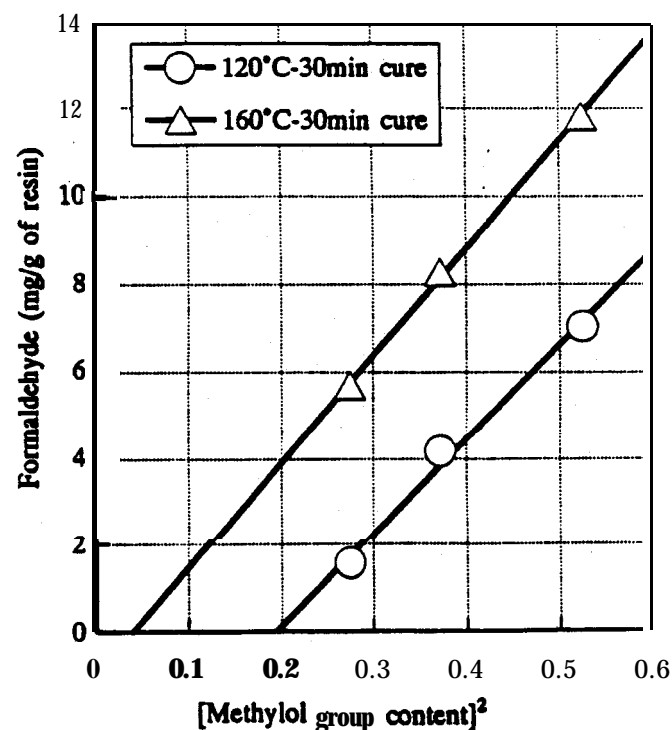


Figure 3.—Relationship between the square of the content of the methylol group in the LUF resins and formaldehyde released during the cure.

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

After cooling the 12 cured resin samples (cured at 120°C for 30 minutes), each set of four cured resin samples were again heated to one of three high temperatures: 120°, 150°, and 180°C for 30 minutes. Figure 4 shows the effect of reaction pH at resin synthesis and of post-heating temperature on formaldehyde emission in the resins cured at 120°C for 30 minutes. Generally, as the temperature and reaction pH increased, the amount of emitted formaldehyde increased. The resin prepared at pH 1 cured at 120°C for 30 minutes showed the most stability toward high temperature heating of the three resins.

The cured resin structure was investigated with the solid-state ^{13}C CP/MAS NMR spectroscopy. Figure 5 shows the comparison of ^{13}C CP/MAS NMR spectra of 120°C, 30-minute cured resin with those of resins after the post-heating at 180°C for 30 minutes. Chemical shifts (1,2,18) and remarks in Figure 5 are listed in Table 1. Although a small peak assigned to the spinning sideband of carbonyl carbon seems to be overlapped at 79 ppm

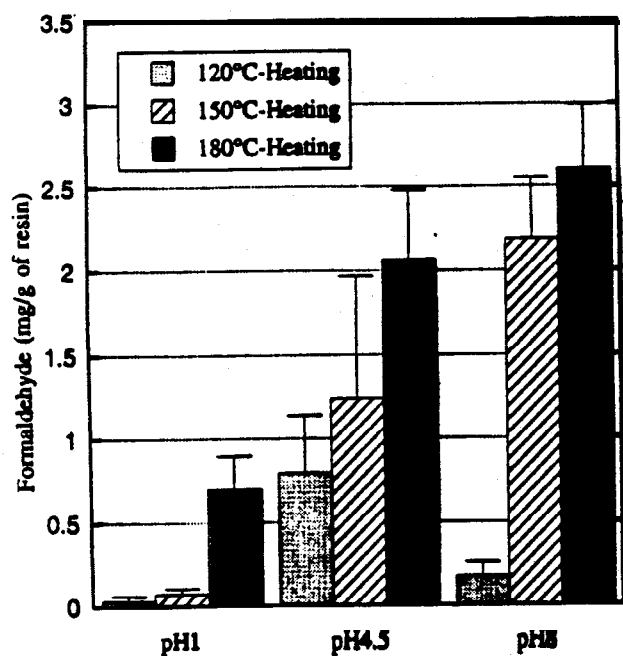


Figure 4.—Effect of the reaction pH and post-heating temperature on formaldehyde emission from the cured UF resins at 120°C for 30 minutes.

on all spectra, the spectra of the resin prepared at pH 1 indicate obviously larger intensity in the peak at 79 ppm than that of the other resins. This large peak intensity at 79 ppm in the spectra proved that the uronic structure existed only in the cured resin prepared at pH 1. In the spectra of the 120°C, 30-minute cured-UF resins, there is a larger amount of linear methylene linkage (a) in the cured resins prepared at pH 4.5 and pH 8 than that of branched methylene linkage (b and c), whereas a reverse relationship in the peaks above was observed in the spectrum of the cured resin prepared at pH 1.

In general, it was found that the methylol group (peaks d and f in Fig. 5) and dimethylene ether group (peaks e and h) decreased after post-heating

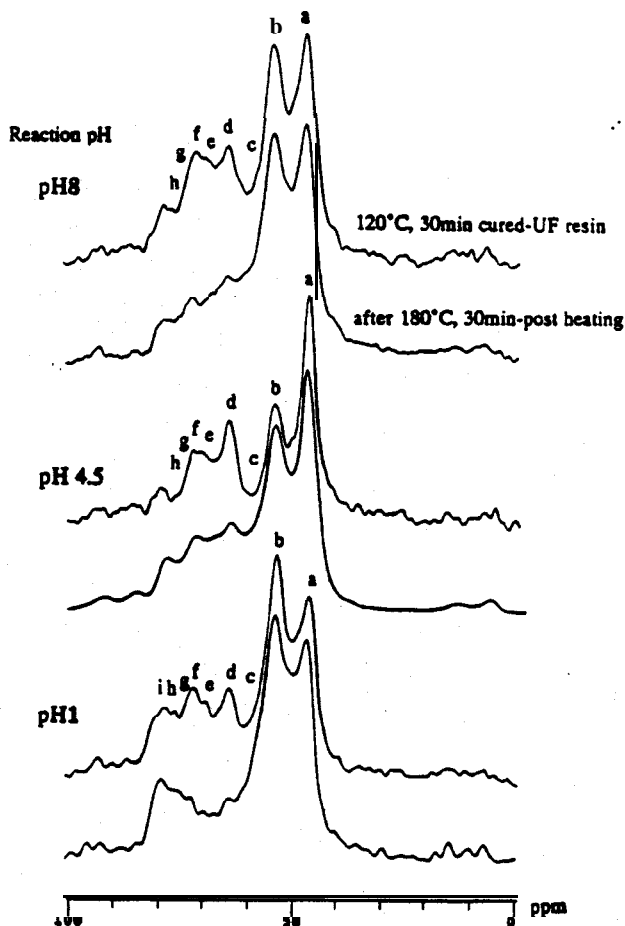


Figure 5.—Comparison of ^{13}C CP/MAS NMR spectra of 120°C, 30-minute cured UF resins with those of resins after 180°C, 30 minutes post heating.

at 180°C for 30 minutes, whereas the branched methylene bonds (peaks of b and c) increased in all resins. These structural results supported the conclusion that the condensation reaction between methylol groups (reaction II and III) and degradation of dimethylene ether group (reaction VI) caused the release of formaldehyde. The order of ratios of the peak intensities of the methylol group to the dimethylene ether group in the spectra between before and after post-heating can be ranked as pH 8 resin > pH 4.5 resin > pH 1 resin, corresponding to the result of formaldehyde emission in Figure. 4. Therefore, the curing reaction would be progressed by post-heating in the resins cured at 120°C for 30 minutes rather than the heat causing

degradation of the cured resin. In other words, the curing condition at 120°C for 30 minutes is not enough for complete cure, and the cured resins retain a potential for further crosslinking. Incidentally, the uron structure which existed characteristically in the resin prepared at pH 1 was revealed to be stable toward the 180°C post-heating.

Although the formaldehyde emission was measured during cure and post-heating in the cured resin without water in this work, further study on the carrier gas controlled moisture content is planned.

Conclusion

A novel method for the measurement of formaldehyde released during cure and heating at high

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

Structure	NMR signal (Fig. 5)	Chemical shift (ppm)	Reaction pH 1	Percent of total formaldehyde (%)	Reaction pH 4.5	Percent of total formaldehyde (%)	Reaction pH 8	Percent of total formaldehyde (%)
Total methylene			0.34	23.1	0.01	0.7		
-NH-CH ₂ -NH-	a		0.20		0.01		..	
-N(CH ₂ -)-CH ₂ -NH-	b	47.54	0.14		
-N(CH ₂ -)-CH ₂ -N(CH ₂ -)-	c	60	--		--		..	
Total methylol			0.62	42.2	0.91	61.0	1.05	72.4
-NH-CH ₂ OH	d	65	0.46		0.78		0.86	
-N(CH ₂ -)CH ₂ OH	f	72	0.16		0.13		0.19	
Total methyl ether			0.23	15.6	0.01	0.7	--	--
-NHCH ₂ OCH ₃	8	74	0.23		0.01		..	
Total dimethylene ether			0.16	10.9	0.1	6.7	0.11	7.6
-NHCH ₂ OCH ₂ -NH-	e		0.13		0.1		0.11	
-N(CH ₂ -)CH ₂ OCH ₂ NH-	h	69.76	0.01		--		--	
Uron -N-CO-N- CH ₂ -O-CL ₂	i	79	0.02		--		--	
Total free formaldehyde			0.12	8.2	0.46	30.9	0.29	20.0
HOCH ₂ OH		83	0.02		0.09		0.04	
HOCH ₂ OCH ₃		91	0.02		0.02		..	
H(OCH ₂) _n OCH ₂ OCH ₃		95	0.08		0.35		0.25	
Total carbonyl carbon			1.00		1.00		1.00	
Uron -N-CO-N- CH ₂ -O-CL ₂		155	0.03		--		--	
=NCONH-, -NHCONH-		160	0.52		0.32		0.32	
-NHCONH ₂		161	0.36		0.56		0.56	
NH ₂ CONH ₂		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

^a Amount of formaldehyde is based on the molar ratio to urea residue (F/U).

temperature was developed. The following can be concluded from this research:

- The amount of formaldehyde released during cure was related to the content of the methylol group in the UF resin.
- The cured resin sample synthesized under strong acid was more stable toward high temperature heating when the resins were prepared with weak acid and alkaline catalysts.
- Methylol group and dimethylene ether linkage in the cured UF resin decreased at high temperature instead of producing an increase in branched methylene linkage.
- The uron structure in the resin formulated with a strong acid catalyst indicated high heat stability.

Literature cited

1. Chuang, I.-S. and G.E. Maciei. 1992. ^{13}C CP/MAS NMR study of the structural dependence of urea-formaldehyde resins on formaldehyde-to-urea molar ratios at different urea concentrations and pH values. *Macromolecules* 25:3204-3226.
2. _____ and _____. 1994. NMR study of the stabiilitites of urea-formaldehyde resin components toward hydrolytic treatments. *J. Appi. Poym. Sci.* 52: 1637-1651.
3. Crowe, G.A. and C.C. Lynch. 1949. Polarographic urea-formaldehyde kinetic studies. *J. Am. Chem. Soc.* 71:3731-3733.
4. de Jong, J. I. and J. de Jonge. 1952. The reaction of urea with formaldehyde. *Rec. Trav. Chim.* 71:643-660.
5. _____ and _____. 1952. The formation and decomposition of dimerhyioiurea. *Rec. Trav. Chim.* 71: 661-667.
6. _____ and _____. 1953. The hydrolysis of methylenediurea. *Rec. Trav. Chim.* 72:202-205.
7. Dunky, M. and K. Lederer. 1982. Studies of molecular weight distributions of urea-formaldehyde resinous glues. *Angew. Makromoi. Chem.* 102:199-213.
8. Dunn, A.S. 1957. The urea-formaldehyde polycondensation 1: Kinetics of the hydrolysis of methoxymethyl-urea. *J. Chem. Soc.* 75:1446-1451.
9. Ebdon, J.R., P.E. Heaton, T.N. Hucherby, and W.T.S. O'Rourke. 1984. Characterization of urea-formaldehyde and melamine-formaldehyde adducts and resins by ^{15}N n.m.r. spectroscopy. *Polymer* 25:821-825.
10. Gu, J., M. Higuchi, M. Morita, and C. HK. 1995. Synthetic conditions and chemical structures of urea-formaldehyde resins 1. Properties of the resins synthesized by three different procedures. *Mokuzai Gakkaishi* 41(12):1115-1121.
11. 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.
12. Ko, K. 1976. How to control pollution of formaldehyde for formaldehyde series thermosetting resin adhesives (in Japanese). *Settyaku Kyokaishi* 12(5): 160-166.
13. Kopf, P.W. and E.R. Wagner. 1973. Formation and cure of novolacs: NMR study of transient molecules. *J. Polym. Sci., Polym. Chem. Ed.* 11:939-960.
14. Kumlin, K. and R. Simonson. 1978. Urea-formaldehyde resins I. Separation of low molecular weight components in urea-formaldehyde resins by means of liquid chromatography. *Angew. Makromol. Chem.* 68: 175-184.
15. Landqvist, N. 1955. On the reaction between urea and formaldehyde in neutral and alkaline solutions. *Acta Chem. Scand.* 9:1471-1476.
16. _____. 1955. On the reaction between urea and formaldehyde in neutral and alkaline solutions. *Acta Chem. Scand.* 9: 1466-1470.
17. Ludlam, R.R. and J.G. King. 1984. Size exclusion chromatography of urea formaldehyde resins in dimethylformamide containing lithium chloride. *J. Appl. Polym. Sci.* 29:3863-3872.
18. Maciei, G.E., N.M. Szeverinyi, T.A. Early, G.E. Myers. 1983. ^{13}C NMR studies of solid urea-formaldehyde resins using cross polarization and magnetic-angle spinning. *Macromolecules* 16: 598-604.
19. McVey, D. 1982. Great strides forward-Formaldehyde emission from the production standpoint, Wash. State Univ., Pullman, Wash. pp. 21-34.
20. Myers, G.E. 1984. How mole ratio of UF resin affects formaldehyde emission and other properties: A literature critique. *Forest Prod. J.* 34(5):35-41.
21. _____. 1985. Effect of separate additions to furnish or veneer on formaldehyde emission and other properties: a literature review (1960-1984). *Forest Prod. J.* 35(6):57-62.
22. _____. 1985. Resin hydrolysis and mechanisms of formaldehyde release from bonded wood products. In: *Proc. Adhesives in 1985: Status and Needs*. Forest Prod. Res. Soc., Madison, Wis. pp. 119-156.
23. _____. 1986. Effects of post-manufacture board treatments on formaldehyde emission: a literature review (1960-1984). *Forest Prod. J.* 36(6):4 1-5 1.
24. Nair, B.R. and D.J. Francis. 1983. Kinetics and mechanism of urea-formaldehyde reaction. *Polymer* 24:626-630.
25. Sionim, I.Y., S.G. Alekseeva, Y.G. Urman, B.M. Arshava, and B.Y. Akseirod. 1978. Study of equilibriums in the urea-formaldehyde system by carbon- 13 NMR. *Vysokomol. Soed.* 20(7):1477-1485.
26. Sundin, B. 1982. Present status of formaldehyde problems and regulations. Wash. State Univ., Pullman, Wash. pp. 3-20.
27. Smythe, L.E. 1953. Urea-formaldehyde kinetics studies. IV. Reactions of methylene-bis-ureas. *J. Am. Chem. Soc.* 75:1508-1510.
28. Tomita, B. and Y. Hirose. 1976. Urea-formaldehyde resins: NMR study on base-catalyzed reaction of formaldehyde with urea in deuterium oxide. *J. Polym. Sci., Polym. Chem. Ed.* 14:387-401.

29. _____ and Y. Hatano. 1978. Urea-formaldehyde resins. III. Constitutional characterization by ^{13}C Fourier transform NMR spectroscopy, J. Polym. Sci. **16**:2509– 2525.
30. _____ 1980. How chemical structure of UF resin affects formaldehyde emission. Mokuzai Kogyo **35**(5): 193-199.
31. Troughton, G.E. 1969. Effect of degree of cure on the acid-hydrolysis rates of formaldehyde glue-wood samples. J. Inst. Wood Sci. **4**(5):51–56.