

Chemistry of Novolac/Furfuryl Alcohol Resins Cured with Hexamethylenetetramine: A Solid-State NMR Study

Xiaoqing Zhang[†] and David H. Solomon*

Polymer Science Group, Department of Chemical Engineering, The University of Melbourne, Parkville, VIC 3052, Australia

Received January 12, 1998. Revised Manuscript Received April 27, 1998

The chemical processes involved in the reactions between novolac resins, furfuryl alcohol (FA), and hexamethylenetetramine (HMTA) have been studied by solid-state NMR spectroscopy. A highly cross-linked homogeneous network which incorporates both novolac and furan entities is formed. The initial reaction below 90 °C is between the novolac and HMTA and produces mainly benzoxazine and benzylamine intermediates. When the temperature is increased to 90–120 °C, FA reacts with these initially formed intermediates to generate methylene-linked novolac/furan structures as the major products. Minor amounts of nitrogen-containing structures are also formed. In the absence of HMTA, only a minor amount of cross-reactions occur between novolac and FA, and cross-linked structures are not formed. The curing reactivity and chemical structures of the finally cured materials can be controlled through variation of the HMTA ratio, FA content, and curing conditions.

Introduction

Both phenol–formaldehyde and furfuryl alcohol (FA) resins have been commercially applied in many applications because of their low manufacturing cost, dimensional stability, chemical resistance, and high tensile strength after curing.^{1–4} When using FA as a solvent for novolac resins, the processing performance can be greatly improved, especially when the resins are used as binding materials.⁵ The viscosity of the system and the binding strength can be controlled by changing the amount of FA. In addition, both resins have been used as starting materials to produce glassy carbons with high carbon yields.^{6–10} Pyrolysis of the novolac/FA mixed system may provide carbons with modified structures and properties. The understanding of the curing chemistry and the phase structure of the novolac/furfuryl alcohol system is therefore of fundamental importance to the application and modification of the materials.

A great deal of effort has been expended toward the understanding of the curing chemistry of each of these two resins,^{11–20} and we have studied the curing reactions of both resins in our group.^{21–28} For the curing of novolac resins with hexamethylenetetramine (HMTA), the reaction produces various benzoxazines and benzylamines as the initial intermediates,^{21,22} and thermal decomposition and further reactions of these first-formed intermediates generate methylene linkages for chain-extension and cross-linking together with some side products.^{22–26} Furfuryl alcohol is shown to undergo thermal polymerization and cross-linking and to be susceptible to acid-catalyzed condensation.^{17–20} However, few studies have addressed the possible chemical interactions when a novolac/FA mixture is polymerized or cross-linked, and there are virtually no reports on the more widely used and practical composition of novolac/HMTA/FA. In this paper we report on the chemical structures formed when novolac resins are

* To whom correspondence should be addressed

[†] Present address: CSIRO Manufacturing Science and Technology, Private Bag 33, Clayton South MDC, VIC 3169, Australia

- (1) Martin, R. W. *Chemistry of Phenolic Resins*; Wiley: New York, 1956.
- (2) Knop, A.; Scheib, W. *Chemistry and Application of Phenolic Resins*; Springer-Verlag: New York, 1979.
- (3) Knop, A.; Pilato, L. A. *Phenolic Resins*; Springer-Verlag: New York, 1985.
- (4) Dunlop, A. P.; Teters, F. N. *The Furans*; Reinhold: New York, 1953.
- (5) Brown, L. H., U.S. Patent 2,965,601, 1960.
- (6) Yamashita, Y.; Ouchi, K. *Carbon* **1979**, *17*, 365.
- (7) Yamashita, Y.; Ouchi, K. *Carbon* **1981**, *19*, 89.
- (8) Riesz, C. H.; Susman, S. *Proceeding of the Fourth Conference on Carbon*; Pergamon: New York, 1960; p 609.
- (9) Fitzer, E.; Schafer, W. *Carbon* **1970**, *8*, 353.
- (10) Sonobe, N.; Kyotani, T.; Tomita, A. *Carbon* **1990**, *28*, 483.
- (11) Fyfe, C. A.; Rudin, A.; Tchir, W. J. *Macromolecules* **1980**, *13*, 1320.
- (12) Fyfe, C. A.; McKinnon, M. S.; Rudin, A.; Tchir, W. J. *Macromolecules* **1983**, *16*, 1216.
- (13) Bryson, R. L.; Hatfield, G. R.; Early, T. A.; Palmer, A. R.; Maciel, G. E. *Macromolecules* **1983**, *16*, 1669.

- (14) Maciel, G. E.; Chuang, I.-S.; Gollob, L. *Macromolecules* **1984**, *17*, 1081.
- (15) Hatfield, G. R.; Maciel, G. E. *Macromolecules* **1987**, *20*, 608.
- (16) Chuang, I.-S.; Maciel, G. E. *Macromolecules* **1991**, *24*, 1025.
- (17) Fawcett, A. H.; Dadamba, W. *Makromol. Chem.* **1982**, *183*, 2799.
- (18) Chuang, I.-S.; Maciel, G. E.; Myers, G. E. *Macromolecules* **1984**, *17*, 1087.
- (19) Eckert, H.; Levedis, Y. A.; Flagan, R. C. *J. Phys. Chem.* **1988**, *92*, 5011.
- (20) Spange, S.; Schutz, H.; Martinez, R. *Makromol. Chem.* **1993**, *194*, 1537.
- (21) Dargaville, T.; de Bruyn, P. J.; Lim, A. S. C.; Looney, M. G.; Potter, A. C.; Solomon, D. H.; Zhang, X. *J. Polym. Sci. Polym. Chem.* **1997**, *35*, 1389.
- (22) Zhang, X.; Looney, M. G.; Solomon, D. H.; Whittaker, A. K. *Polymer* **1997**, *38*, 5835.
- (23) Zhang, X.; Potter, A. C.; Solomon, D. H. *Polymer* **1998**, *39*, 399.
- (24) Zhang, X.; Solomon, D. H. *Polymer* **1998**, *39*, 405.
- (25) Zhang, X.; Potter, A. C.; Solomon, D. H. *Polymer* **1998**, *39*, 1957.
- (26) Zhang, X.; Potter, A. C.; Solomon, D. H. *Polymer* **1998**, *39*, 1967.
- (27) Zhang, X.; Solomon, D. H. *J. Polym. Sci. Polym. Phys.* **1997**, *35*, 2233.
- (28) Zhang, X.; Solomon, D. H., to be published.

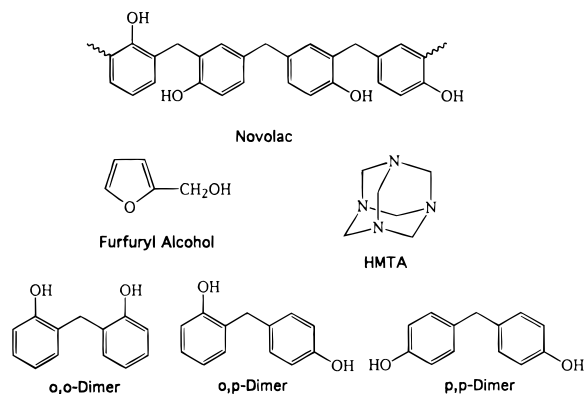


Figure 1. Chemical structures of novolac, furfuryl alcohol, HMTA, ortho,ortho-dimer, ortho,para-dimer, and para,para-dimer.

heated with FA, but in particular we report on the more complex system of novolac/HMTA/FA using ^{13}C - and ^{15}N -enriched HMTA and high-resolution solid-state NMR techniques.

Experimental Section

Samples. The novolac resins used in this study have been described in a previous report.²² The number-averaged chain length is about 8 phenolic units, and the ratio of ortho- and para-phenolic positions of the resins is 88:12. FA and 2,2', 2,4', and 4,4'-methylenediphenol (called ortho,ortho, ortho, para and para,para dimer, respectively) were obtained from Hopkin & Williams Ltd., Aldrich Chemical Co. Ltd. and TCI Co. Ltd., respectively. The ^{13}C - and ^{15}N -labeled HMTA was synthesized using 99% ^{13}C -enriched formaldehyde and 99% ^{15}N -enriched ammonia. The chemical structures of these compounds are shown in Figure 1.

Novolac and HMTA were dissolved in FA in ratios of novolac/HMTA/FA (wt/wt/wt) = 40/8/52, 42/6/52, and 31/4.3/64.7 with vigorous stirring. The mixtures were cured in a Eurotherm 902 oven for 35 h up to 205 °C with a cycle as described previously.²² In the study of model systems, the dimers were used instead of novolac resins. Samples were taken at different temperatures to trace the change of chemical structures and phase structures during the curing process.

NMR Experiments. Solution ^{13}C and ^{15}N NMR spectra were recorded on a JEOL JNM-GX400 instrument (^{13}C spectra, 100 MHz) by using CDCl_3 (99.8%) as a solvent. High-resolution solid-state NMR experiments were carried out using a Varian Unity Inova-300 spectrometer at resonance frequencies of 75 MHz for carbon-13 and 30 MHz for nitrogen-15 under conditions of cross polarization (CP), magic angle sample spinning (MAS), and high-power dipolar decoupling (DD). The 90° pulse-width was of 3.7 μs , while the rate of MAS was at a value around 9–10 kHz, so no spinning sideband appeared in a range of 0–200 ppm for ^{13}C spectra. No spinning sideband was observed for ^{15}N spectra. The contact time for ^{13}C CP/MAS spectra was 1.2 ms, and that for ^{15}N spectra was 2 ms. The repetition time was 2 s. ^1H $T_{1\rho}$ relaxation times were measured through ^{13}C resonance via cross polarization.^{29–32} Broad line ^1H solid-state NMR spectra were measured on a Bruker MSL 300 NMR spectrometer by a solid-echo pulse sequence with a 90° pulse of 3.2 μs and a repetition time of 5 s. The chemical shifts of ^{13}C spectra were determined by taking the carbonyl carbon of solid glycine (176.03 ppm) as an external reference standard. For ^{15}N spectra, the ^{15}N resonance of 99% enriched HMTA (44 ppm) was taken as an

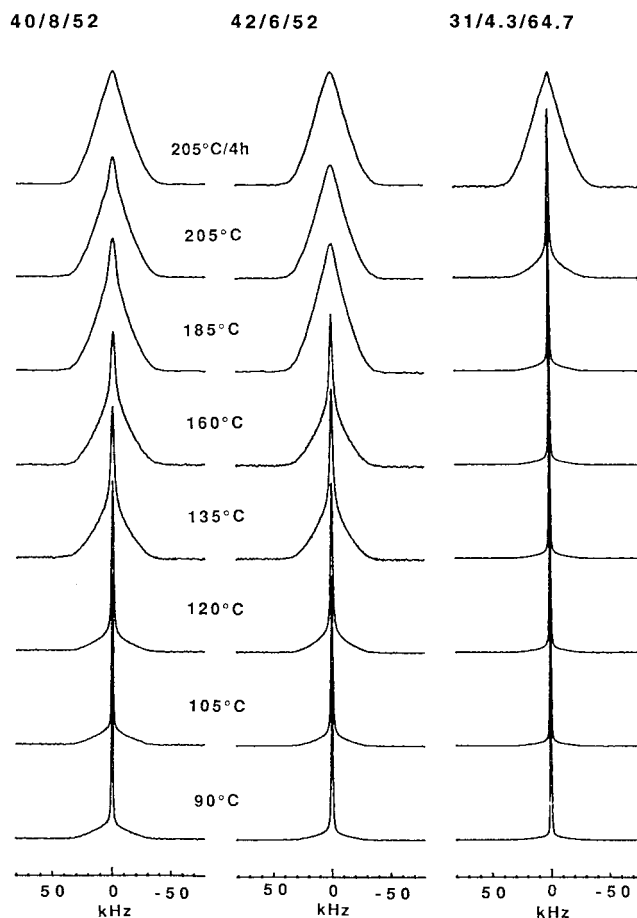


Figure 2. ^1H broad line NMR spectra of Novolac/HMTA/FA = 40/8/52, 42/6/52, and 31/4.3/64.7 systems after curing up to 205 °C/4 h.

external reference.^{15,22} Qualitative comparison was taken among CP/MAS spectra of a resonance in similar systems after curing to the same temperatures assuming a similar cross-polarization capability of the resonance.

Results and Discussion

I. Curing of Novolac/FA Resins. The curing processes of Novolac/HMTA/FA = 40/8/52, 42/6/52, and 31/4.3/64.7 systems were examined by ^1H broad line solid-state NMR. Most of the spectra (shown in Figure 2) consist of a broad line and a narrow line, which are due to the rigid and mobile regions, respectively. The intensity of the broad line increased with the curing temperature while that of the narrow line decreased, indicating the formation of rigid materials. For the 40/8/52 system, the rigid region was detected at 90 °C, and the intensity became predominant above 160 °C. After curing to 205 °C, the line width increased to 30 kHz, indicating the formation of a very rigid cross-linked material. As compared to the 40/8/52 system, the 42/6/52 sample (a lower amount of HMTA was used) formed rigid materials at relatively higher temperatures (see the spectra at 90 °C; a broad part was obtained for the 40/8/52 system, but not for the 42/6/52 sample). The mobile phase disappeared somewhat faster in the 42/6/52 system, as a relatively narrow component was still present for the 40/8/52 system at 185 °C. The spectrum of the 42/6/52 system cured to 185 °C is quite similar to that of 40/8/52 system cured to 205 °C. An increase of FA ratio in the system also delayed the formation of the

(29) Axelson, D. E.; Russell, K. *Prog. Polym. Sci.* **1985**, *26*, 228.

(30) Zhang, X.; Takegoshi, K.; Hikichi, K. *Macromolecules* **1991**, *24*, 5756.

(31) Zhang, X.; Takegoshi, K.; Hikichi, K. *Macromolecules* **1992**, *25*, 2336.

(32) Zhang, X.; Solomon, D. H. *Macromolecules* **1994**, *27*, 4919.

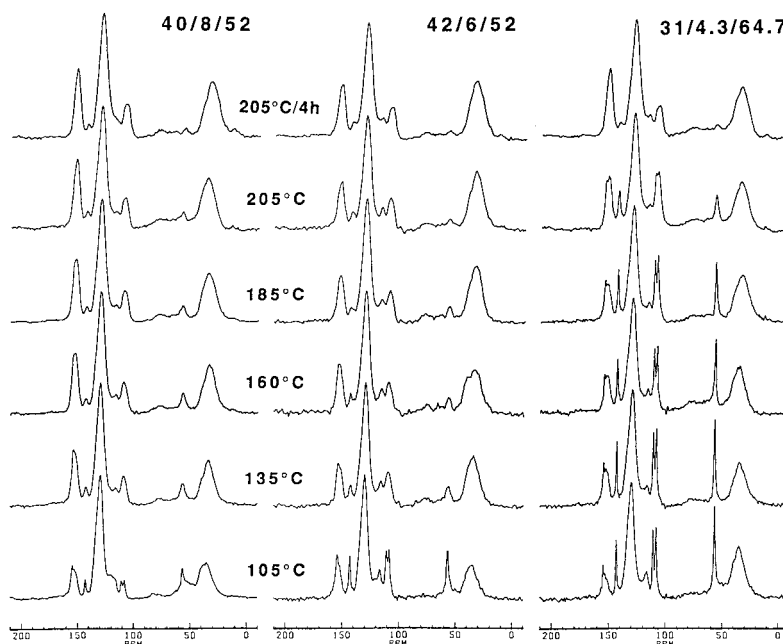


Figure 3. ^{13}C CP/MAS NMR spectra of Novolac/HMTA/FA = 40/8/52, 42/6/52, and 31/4.3/64.7 systems after curing up to 205 °C/4 h.

rigid regions (the broad line could be seen until 185 °C for 31/4.3/64.7). After curing to 205 °C/4 h, the line width of the three systems all became 30 kHz and no mobile regions were detected.

^{13}C CP/MAS NMR spectra of novolac/HMTA/FA systems after curing to 205 °C/4 h are shown in Figure 3 (unlabeled HMTA was used here). The resonances at 151–152 ppm are due to the hydroxy-substituted carbons of novolac and the methylene-substituted carbons of furan rings, while the peak at 30–35 ppm peak is due to the methylenes in the systems. The resonances at 128 and 115 ppm are attributed to the aromatic carbon of novolac. For the FA component, the CH_2OH and 2-, 3-, and 4-carbons of the furan ring appear at 56, 108, 110, and 142 ppm, respectively. The methylene carbons of HMTA locate at 74 ppm. After curing to 105 °C, HMTA disappeared in all cases, but FA still remained, especially in the 31/4.3/64.7 system, as seen from the narrow peaks at 56, 108, 110, and 142 ppm. Increased curing temperature caused the intensity of free FA to decrease, and the line width at 108–110 and 56 ppm also became broad due to the formation of, or association with, rigid materials. For the 31/4.3/64.7 system, FA remained until 185–205 °C, which is consistent with the observations in the ^1H NMR spectra (Figure 2). The results also confirm that the FA component is more mobile. Meanwhile, the relative intensity of the methylenes at 33 ppm increased with the curing temperature, suggesting an increase of the cross-link density of the systems. After curing to 205 °C/4 h, the ^{13}C spectra of the three systems are quite similar, as was observed in the ^1H NMR spectra. The FA component could still be seen at 108 ppm and did not overlap with the novolac peak. The homogeneity of the cured systems was studied by ^1H $T_{1\rho}$ relaxation times.

High-resolution solid-state NMR techniques make it possible to detect relaxation times of each component in a multicomponent system. In this study, the ^1H $T_{1\rho}$ relaxation times of novolac/HMTA/FA samples were

Table 1. ^1H $T_{1\rho}$ Relaxation Times (ms) of Novolac/HMTA/FA Systems Detected via ^{13}C Resonances

temp. °C	novolac		FA				
	128 ppm	115 ppm	142 ppm	108 ppm	56 ppm	33 ppm	151 ppm
Novolac/HMTA/FA = 40/8/52							
105	3.7		3.7	3.3		3.5	3.7
135	4.2			3.9		4.2	4.1
160	6.4			6.1		6.7	6.4
185	7.9			7.3		7.6	7.9
205	11.6			11.8		12.2	11.6
205 (4 h)	12.5			12.2		12.4	12.9
Novolac/HMTA/FA = 42/6/52							
105	3.0	3.4	3.9	3.4	2.0	3.2	3.5
135	3.7	3.1	3.3	3.3	3.0	3.7	3.9
160	4.7	5.0	4.9	4.7		4.8	4.8
185	9.6		9.3	9.6		9.3	9.7
205	9.7	9.9		9.7		9.5	10.9
205 (4 h)	12.9			12.9		12.8	13.8
Novolac/HMTA/FA = 31/4.3/64.7							
105	4.0		5.6	5.2	4.3	4.0	4.2
135	3.7		5.5	5.1	3.8	4.8	4.3
160	4.0		5.6	4.9	4.0	4.0	4.1
185	4.1		4.8	4.2	3.8	4.3	4.2
205	4.9		4.7	4.2		5.0	4.9
205 (4 h)	14.2			14.8		14.7	14.3

measured through high-resolution ^{13}C resonances via the cross polarization technique^{29–32} as listed in Table 1. By this method, mobile regions with a weak CP capability were difficult to detect but rigid regions were discernible. Increased curing temperature resulted in an increase of the $T_{1\rho}$ values. In most cases, the values observed for the FA component were quite close to those of the novolac component, indicating that spin diffusion within the $T_{1\rho}$ time can efficiently average out the relaxation process between novolac and FA components in the rigid phase. After curing to 205 °C for 4 h, the whole system became rigid and relatively long $T_{1\rho}$ values were observed for the 40/8/52, 42/6/52, and 31/4.3/64.7 systems. Note that the values observed for the FA component are also identical to those of the novolac component. This result indicates that the domain size

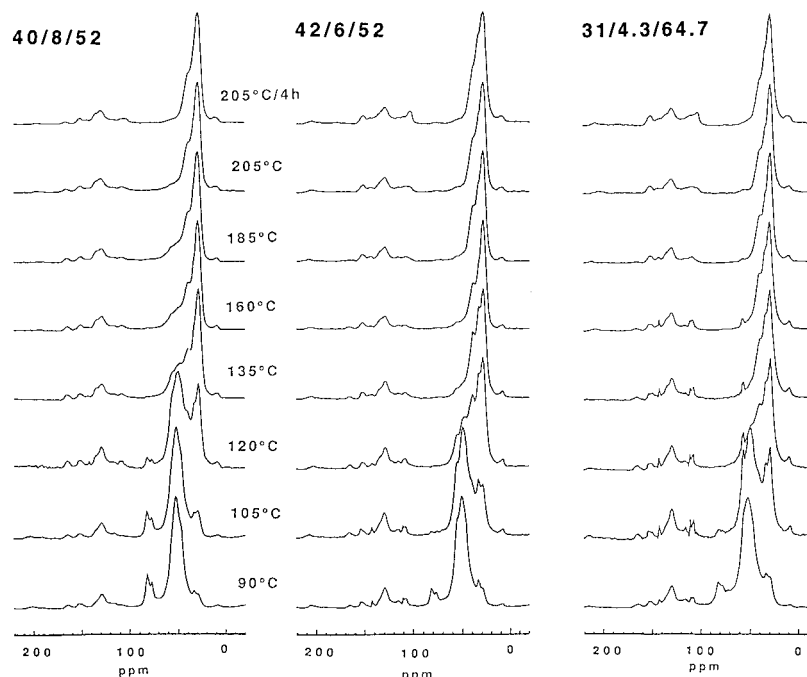


Figure 4. ^{13}C CP/MAS NMR spectra of Novolac/HMTA/FA = 40/8/52, 42/6/52, and 31/4.3/64.7 systems after curing up to 205 °C/4 h (labeled HMTA was used).

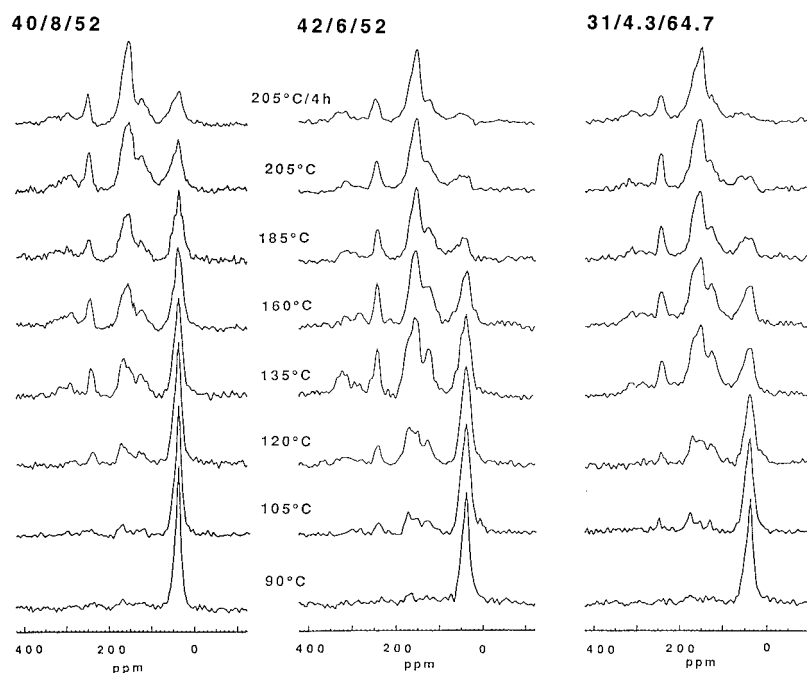


Figure 5. ^{15}N CP/MAS NMR spectra of Novolac/HMTA/FA = 40/8/52, 42/6/52, and 31/4.3/64.7 systems after curing up to 205 °C/4 h (labeled HMTA was used).

of the three finally cured resins is smaller than 2–3 nm; novolac and FA components are homogeneously cross-linked and no phase-separation occurred in the finally cured materials.

II. Chemical Structure Changes during Curing.

To obtain details of the chemical reactions during the curing process, a ^{13}C - and ^{15}N -labeled HMTA was used and both ^{13}C and ^{15}N CP/MAS NMR spectra were measured, as shown in Figures 4 and 5. Comparison of the ^{13}C spectra in Figure 4 with those in Figure 3 shows

that some signals were enhanced greatly, and these must be derived from HMTA. ^{15}N spectra provide detailed information of the changes of nitrogen-containing structures during the curing.³³

In the 40/8/52 system after curing to 90 °C, HMTA resonances disappeared and the major resonances derived from HMTA were located at 82.3, 77.2, and 50–55 ppm in ^{13}C NMR spectra (Figure 4), corresponding to the formation of benzoxazine and tri- and dibenzylamine intermediates.^{21,22} Compared to these strongly enhanced signals, the aromatic resonances of novolac are minor. The broad peak at 48 ppm in ^{15}N spectra

(33) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; John Wiley & Sons: New York, 1979.

(Figure 5) is consistent with this result.^{22,23,25} A peak at 162 ppm (¹³C spectra) appeared above 90 °C and is due to amide/imide structures, which could also be seen in the ¹⁵N spectra at 90–150 ppm.^{22,33} Increased curing temperature decreased the intensities of resonances at 82.3, 77.2, and 50–55 ppm in the ¹³C spectra and the 48 ppm peak in the ¹⁵N spectra while an increase of the peaks at 29.5 and 35 (methylene ¹³C resonances) occurred simultaneously. Coincidentally, the ¹⁵N resonances at 48 ppm decreased its intensity and shifted to 38 ppm due to the decomposition of benzoxazine and benzylamine intermediates and the formation of benzylammonium ions.^{15,22,33} The methylene intensity at 29.5 ppm in ¹³C spectra increased faster than that at 35 ppm, and it became predominant after curing to 135 °C. Above 135 °C, a nitrile group was detected in the system (as seen at 255 ppm in the ¹⁵N spectra,^{27,33} while the CN carbon overlapped with the aromatic carbons at 126 ppm). After curing to 205 °C/4 h, the methylene ¹³C resonances were dominant at 29.5 ppm. The results indicate that the methylenes derived from HMTA are the major linkages in the finally cured resin systems. The amide (125 ppm in the ¹⁵N spectra), imide (150 ppm in the ¹⁵N spectra), and imine (280–320 ppm in the ¹⁵N spectra) structures^{22,27,33} also remained until 205 °C/4 h, with the existence of the ¹³C resonances at 163 ppm as additional evidence. The broad ¹⁵N peak at 38 ppm is due to the residual amines and benzylammonium ions.^{15,22} Methyl (15 ppm in the ¹³C spectra) and nitrile (255 ppm in the ¹⁵N spectra) groups also existed in the finally cured resins.

Changing the formulation from 40/8/52 to 42/6/52 (i.e., keeping the same FA content and decreasing the initial HMTA level) resulted in curing reactions occurring at relatively lower temperatures. For 42/6/52 system, the benzoxazine intermediates (77–82 ppm in the ¹³C spectra, Figure 5) disappeared and the methylene intensities (29–41 ppm) became more intense than those of benzylamines (50–55 ppm) after curing to 120 °C. Similar reactions occurred in the 40/8/52 system at 135 °C. Varying the formulation from 42/6/52 to 31/4.3/64.7 (keeping the same HMTA ratio but increasing the FA ratio) also shifted the curing reaction to relatively lower temperatures, as seen in the ¹³C spectra. The mobile FA component could be detected in the 31/4.3/64.7 system at 142, 108–110, and 56 ppm until 185 °C, which is consistent with the ¹H NMR results (Figure 2). Decreasing the initial HMTA ratio also decreased the nitrogen-content in the finally cured resins, as shown by elemental analysis. The distribution of nitrogen-containing structures was also different. For the 42/6/52 and 31/4.3/64.7 systems, the ratio of imine (280–320 ppm in the ¹⁵N spectra) was lower than that in 40/8/52 system after curing to 205 °C. In addition, the intensity of residual benzylamines and benzylammonium ions (38 ppm in the ¹⁵N spectra) in the 42/6/51 and 31/4.3/64.7 systems was also much weaker for the finally cured resins (Figure 5).

These results indicate that curing the novolac/FA systems with HMTA starts with the formation of benzoxazine and benzylamine intermediates. Further increase of the temperature decomposed these initially formed intermediates and methylene linkages were formed. The strong intensity of the methylene reso-

nances observed for labeled HMTA samples indicates that most of the methylenes are derived from HMTA and they remain in the finally cured resins. During the curing process, amide/imide, nitrile, and imine structures were also formed, and some of these could even remain in the system up to 205 °C. These reaction pathways are quite similar to those for curing individual novolac or FA resins with HMTA. However, the curing reactions occur at relatively lower temperatures in the novolac/FA mixed system as compared to those in the individual systems. We attribute this to the FA acting as a solvent and facilitating the reaction. Decreasing the initial HMTA level or increasing the FA ratio also results in the reactions occurring at relatively lower temperatures.

III. Reactions between Novolac and FA during Curing. Evidence is still required relating to any cross-reaction between novolac and FA when curing the novolac/furfuryl alcohol mixed system. First of all, if no HMTA or other curing reagent is used, is it necessary to establish whether the CH₂OH of furfuryl alcohol can provide methylene linkages for chain extension and cross-linking, similar the curing of resoles? Second, when HMTA is used, do novolac and FA react with HMTA separately, or do cross reactions occur within novolac, furfuryl alcohol, and HMTA to produce a homogeneously cross-linked novolac/FA network?

The reaction between novolac and FA was studied by using novolac dimers instead of resins because they represent a simplified system. After heating the three mixed systems of FA with ortho,ortho-dimer, ortho,para-dimer, or para,para-dimer (in 1:1 molar ratio) to 135 °C, the products still could be dissolved in a solvent (CDCl₃), and the ¹³C solution NMR spectra are shown in Figure 6. Attention was focused on the range of 20–70 ppm, which should provide information on various methylene linkages. The methylenes of the three dimers locate at 30.5, 35.4, and 40.6 ppm, respectively,²² while the CH₂OH of FA appears at 56.6 ppm.²⁷ After heating to 135 °C, the FA intensity at 56.6 ppm decreased slightly in conjunction with the formation of a minor amount of methylene and dimethylene ether linkages between furan rings at 27.5 and 63.5 ppm, respectively. No methylene linkage between a phenol ring and a furan ring was detected in ortho,para-dimer/FA and para,para-dimer/FA systems. Note that there was a weak resonance at 34.1 ppm in the ortho,ortho-dimer/FA system which may be assigned to the methylene linkages between a furan ring and a para-phenolic position of the dimer. Further heating of the three systems to 170 °C (the boiling point of FA) did not vary the situation as seen in Figure 6; only minor methylene linkages (34.1 ppm) were formed between a para-site of the ortho,ortho-dimer and furan rings. This result indicates that the direct reaction between novolac and FA resins is very minor and does not lead to highly cross-linked materials.

The effect of HMTA on the curing was studied by mixing the three dimers with ¹³C-labeled (10%) HMTA and FA in a ratio of 31/4.3/64.7, respectively. After heating to 135 °C using the same heating cycle, the three systems could still be dissolved in CD₃OD, and the ¹³C NMR spectra (25–45 ppm, the methylene range) are shown in Figure 7. The natural abundance meth-

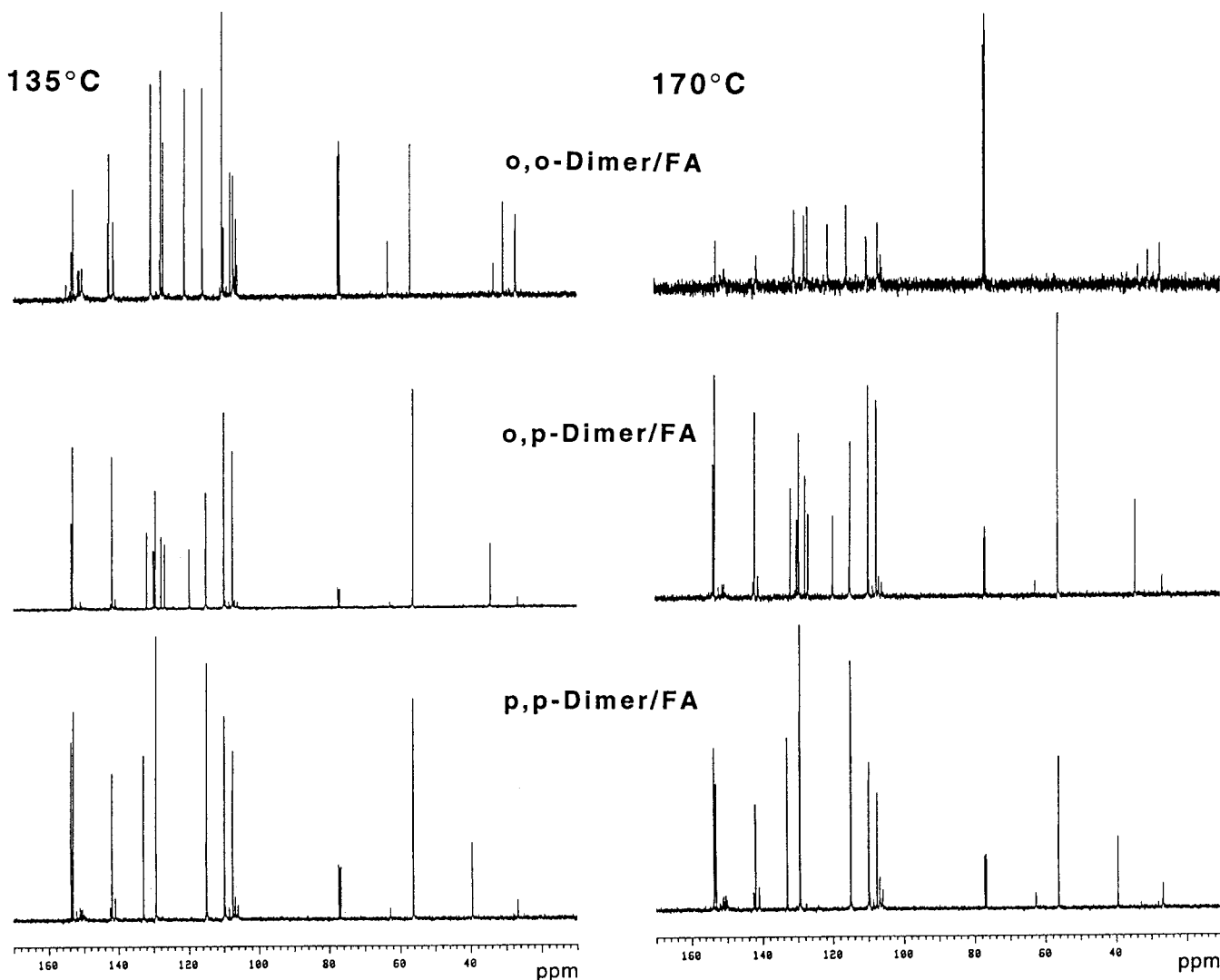


Figure 6. ^{13}C solution NMR spectra of ortho,ortho-dimer/FA, ortho,para-dimer/FA, and para,para-dimer/FA = 1/1 after heating to 135 and 170 °C. CDCl_3 was used as a solvent.

ylens of the three dimers (labeled as black peaks) are very weak and the strong resonances are due to the formation of new methylenes derived from HMTA. For the ortho,ortho-dimer/HMTA/FA system, a strong methylene resonance at 29.5 ppm was detected and could be assigned to the linkage between an ortho-site of the dimer and a furan ring (Figure 8, 1), while the peak at 34.5 ppm could be the linkage between a para-site of the dimer and a furan ring (Figure 8, 2). The resonances at 36.1, 40.1, and 41.1 are attributed to the ortho,para and para,para methylenes between the dimers formed during the curing, but their intensities are relatively weak. All of these resonances were derived from HMTA (stronger intensities) as compared to the naturally occurring methylene carbons at 30–31 ppm. This result indicates that the curing of novolac/FA systems with HMTA does result in linkages between novolac and furan rings. Strong methylene peaks at 29.3 and 29.7 ppm were also observed in the ortho,para-dimer/FA system corresponding to the formation of linkages between furan rings and two types of ortho-sites in the ortho,para-dimer (Figure 8, 3 and 4). The peak at 34.4 ppm is assigned to the methylene between a para-site of the ortho,para-dimer and a FA ring (Figure 8, 5). Minor resonances due to the formation

of para,para-linkages between dimers were also noticed at 40–41 ppm. The para,para-dimer/FA system was relatively simple since only one type of ortho-reactive site is available in the para,para-dimer. The strong methylene resonance at 29.4 ppm could be assigned to the linkages between an ortho-site and a furan ring (Figure 8, 6), and the minor peak at 29.8 is consistent with structure 7, shown in Figure 8. In all cases, the intensities of the methylene linkages between a dimer and a furan ring were much higher than that between dimers, and no methylene linkage between two furan rings was detected at 27–28 ppm.

These results indicate that the cross-reaction between novolac and FA is dominant in a system containing a high FA fraction (>50% in the cases discussed above), and the methylene linkages were mainly derived from HMTA. This is consistent with the results shown in the solid-state NMR spectra. Note that the methylene carbons of the three systems after curing to 205 °C/4 h appeared as a broad peak around 33 ppm when unlabeled HMTA was used, but when labeled HMTA was used, a sharp peak at 29.5 ppm could be observed. The novolac resins used in the study contain a high ratio of ortho-reactive site (88%); thus, the methylene linkage between an ortho-site and a furan ring (at 29.5 ppm)

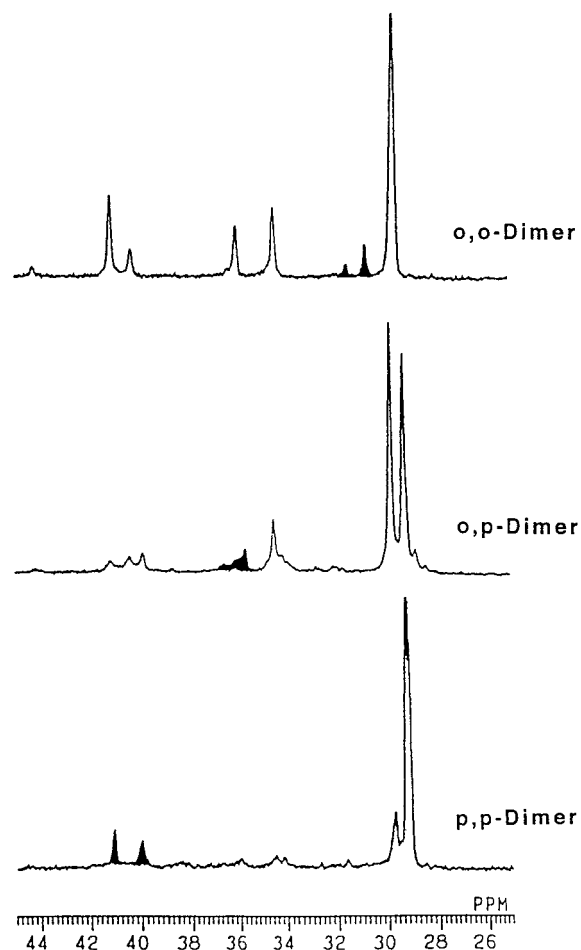


Figure 7. ^{13}C solution NMR spectra (25–45 ppm) of ortho, ortho-dimer/HMTA/FA, ortho,para-dimer/HMTA/FA, and para, para-dimer/HMTA/FA = 31/4.3/64.7 systems after heating to 135 °C. ^{13}C -labeled (10%) HMTA was used in the curing systems, and CDCl_3 was used as a solvent.

was dominant in the three finally cured systems and was enhanced when labeled HMTA was applied. These methylenes linked novolac and furan rings to form a highly cross-linked homogeneous novolac/FA network.

Since the reaction between FA and HMTA starts above 135 °C,²⁷ while the reaction between novolac and HMTA can begin as low as 90 °C,²² we conclude that novolac resins react with HMTA first to form benzoxazine and benzylamine intermediates. With the existence of FA as a solvent, these initial reactions occur at low temperatures (<90 °C) as compared to novolac/HMTA systems which are solid mixtures. Further reaction between FA and these initially formed intermediates produces methylene linkages between novolac and FA for chain extension and cross-linking, in conjunction with other nitrogen-containing structures. We have carried out the reactions between FA and model benzoxazines and benzylamines. The results confirmed that the reactions started at 90–120 °C to form methylenes between a phenol ring and a furan ring together with amines, amides/imides, imines, and nitriles as side products at higher temperatures. The detailed results of the study on model systems will be reported in a subsequent paper.²⁸

The weight loss during the curing of each of the three systems is shown in Figure 9. The major weight loss occurs in two temperature ranges, 105–135 and above

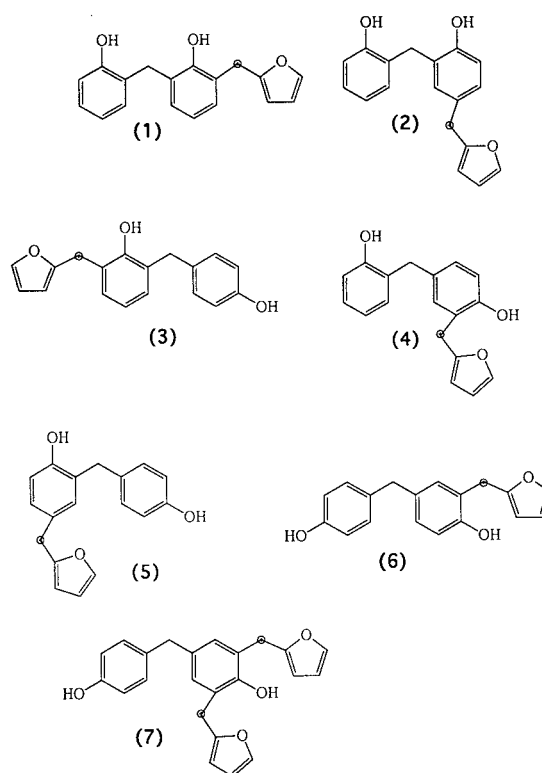


Figure 8. Chemical structures of the possible products formed in dimer/HMTA/FA reactions.

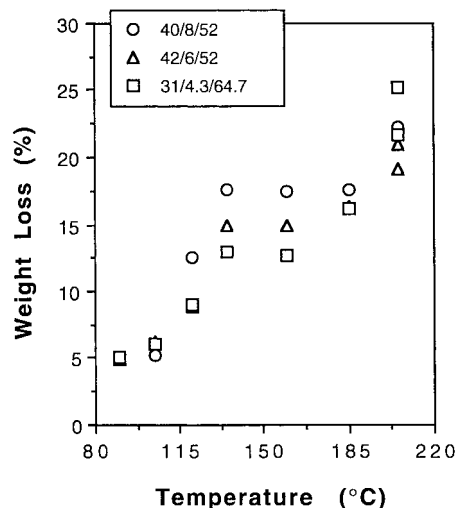


Figure 9. The weight loss of Novolac/HMTA/FA = 40/8/52, 42/6/52, and 31/4.3/64.7 systems after curing up to 205 °C/4 h.

185 °C. Note that the higher the HMTA amount, the higher the weight loss in the first stage. On the other hand, the higher the amount of FA in the system, the higher the weight loss in the second stage. The curing weight loss in the first stage was possibly due to the reactions relative to HMTA, such as formation of benzoxazine and benzylamine intermediates with the novolac, and then decomposition and reactions of these intermediates with FA to form methylene linkages and more stable side products. The process should release small molecular species, such as water, NH_3 , and formaldehyde, together with some FA monomer. With a higher initial amount of HMTA, more reactions occurred which resulted in a higher weight loss. The

weight loss in the second stage should be due to the loss of excess FA monomer above 185 °C. The boiling point of FA is 170 °C, but it requires a higher temperature to break the interactions (mainly hydrogen bonding) between the cross-linked network and associated FA. Therefore, the 31/4.3/64.7 system produced the highest weight loss during the second stage. The total weight loss after curing to 205 °C was 22%, 21%, and 25% for 40/8/52, 42/6/52, and 31/4.3/64.7 systems, respectively. Thus, the novolac/furan rings ratios in the three finally cured systems were estimated to be 54/46, 55/45, and 43/57, respectively.

Conclusion

Both novolac and FA resins can form highly cross-linked networks when they react individually with HMTA. When curing a novolac and FA mixed system with HMTA, the initial reaction is between the novolac and HMTA and starts below 90 °C to produce benzoxazine and benzylamine intermediates. These reactions occur at even lower temperatures when FA is used since the FA acted as a solvent for the solid HMTA and novolac resins. Increasing the temperature to 90–120 °C causes reactions between FA and these initially formed intermediates to produce predominantly methylene linkages between novolac and FA, together with a minor amount of linkages between two phenol rings and between two furan rings. These methylenes act as bridges for chain extension and cross-linking of the systems. A highly cross-linked, rigid network is produced after curing in which novolac and FA segments are both incorporated into the network. Nitrogen-

containing structures such as amines, amides/imides, imines, and nitriles are also formed during the curing process as minor products. Some of these minor products can remain up to 205 °C. The higher the initial HMTA ratio, the higher the amount of these nitrogen-containing structures in the finally cured resins. Decrease of the initial HMTA ratio and/or increase of the initial FA content causes the curing reaction to occur at a relatively low temperature. If the initial FA content is too high, some FA can remain in the system up to high temperatures, e.g. 185–205 °C, which is above the boiling point of FA. Without HMTA, only a minor amount of cross-reactions occurs between novolac and FA, and cross-linked materials are not formed. By using the novolac/HMTA/FA system with FA as a solvent to control the viscosity of the system, the processing performance can be greatly improved, especially when the resins are applied as binding materials. After curing, most furan rings will remain in the cured system and no phase-separation occurs for the whole system; thus, the material should have uniform mechanical properties. The curing reactivity, the chemical structures, and properties of the finally cured can be controlled or modified by variation of the HMTA ratio, FA content, and curing conditions.

Acknowledgment. The work was supported by the Australian Industry Research and Development Board (Grant No. 15068), the Australian Research Council, and Comalco Aluminium Ltd. We thank Mr. M. J. Caulfield for preparing the ¹³C- and ¹⁵N-labeled HMTA. CM9800175