Resorcinol-Formaldehyde Reactions in Dilute Solution Observed by Carbon-13 NMR Spectroscopy

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ABSTRACT: A recently discovered coupling agent, hydroxymethylated resorcinol (HMR), based on resorcinol-formaldehyde, can greatly enhance wood-to-epoxy resin bond durability in exterior applications. However, for HMR to be most effective, it needs to be prepared a few hours before it is applied to the wood surface. In this study, carbon-13 nuclear magnetic resonance (NMR) spectroscopy was used to monitor composition of HMR as a function of time to characterize which chemical groups are present in solution when HMR is applied. A quantitative assessment of formaldehyde-derived groups required the use of 99% ^{13}C-enriched formaldehyde. Hydroxymethyl groups, primarily attached to the 4-position of resorcinol, and hemiformal groups formed very quickly. Signals from methylene linkages between resorcinol rings began to appear 20 min into the reaction. Formaldehyde was consumed quickly; 95% was bound to resorcinol rings within 1.7 h. By 3 h, 16% had been converted to methylene linkages, and by 8.3 h, 40% was converted. Another set of NMR experiments was used *to* monitor the dependency of peak positions of resorcinol solution as a function of pH. These experiments showed significant effects, especially between pH 7.7 and 9.1, which explains chemical shift changes observed during the HMR reaction. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1760-1768, 2000

Key words: hydroxymethylated resorcinol; carbon-13 nuclear magnetic resonance; resorcinol-formaldehyde, chemical groups; reaction time

INTRODUCTION

A recently discovered coupling agent produces unprecedented durability for structural bonds between wood and epoxy resins for exterior conditions.[1–4] This coupling agent also enhances bonds between other thermosetting adhesives and wood.[5] The coupling agent, hydroxymethylated resorcinol (HMR), is composed of a dilute, weakly alkaline solution of reacting resorcinol-formaldehyde (R-F). The inventors[2] hypothesized that hydroxymethylated species were an important part of the system.

For maximal effectiveness, HMR has to be reacted for several hours at room temperature before being applied to wood surfaces. Recent work[5] has shown that, for Douglas-fir and a particular epoxy adhesive, there is a period between about 3 and 8 h after HMR is mixed when it can be used effectively to promote good exterior-quality bonds. However, the time lag between HMR preparation and application may be a problem for industrial processes. Ultimately, the goal is to modify HMR so that it can be applied almost immediately, without altering its effectiveness.

Unfortunately, simple changes in the proportions of chemicals, including dilutions, have not produced a more flexible procedure for preparing HMR. To modify the procedure, more information is needed on the progress of reactant composition. Vick et a1.[5] showed that the reactions reached a balance of early monomeric and oligomeric species, which occurred when 20% to 50% of the

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Journal of Applied Polymer Science, Vol. 75, 1760-1768 (2000)

initial heat of reaction had been consumed. Vick et a1.[5] demonstrated that the HMR indeed contained significant amounts of hydroxymethylated species throughout the effective period. There is a widespread distribution of molecular sizes, ranging from monomers to large methylene-linked oligomers. This study reports in detail on the chemical composition of the mixture during the progress of the reaction.

An R-F system such as HMR is so reactive that it is extremely difficult to isolate individual components.[6] Such reacting systems either result in a thermoplastic novolak (lacking hydroxymethyl groups), if the formaldehyde-to-resorcinol mole ratio is less than about 0.8 or in a cured intractable mass. However, analysis of the resol HMR solutions by carbon-13 NMR permits insight into the composition as it evolves.

Although ^{13}C-NMR has been used to determine the structure of R-F resins, most of those resins have been novolaks,[7–10] which had lost the ability to react further. Werstler[11] analyzed slowly reacting resols and assigned dozens of resonance peaks to carbons of many of the reacting species. Werstler also set up equations to enable calculations of others and tested those calculations with observations. Although he displayed spectra from two reaction times, he did not provide a scenario of how quickly various species might form and disappear. The intent of this study is to provide information on the sequence and rate of formation of types of chemical groups in the R-F reactions of the HMR coupling agent.

EXPERIMENTAL MATERIALS

HMR Coupling Agent

The HMR coupling agent was prepared as a 5% aqueous solution by reacting formaldehyde with resorcinol in a formaldehyde-to-resorcinol (F/R) 1.54 molar ratio at mildly alkaline conditions. The standard ingredients (in weight percentages) were 3.36% crystalline resorcinol, 1.41% formaldehyde solids (as aqueous solution), and 0.26% sodium hydroxide solids (as 3 *M* solution). The remainder was water (and some methanol when 37% formaldehyde solution was used). To provide a lock signal for the NMR experiments, 20% of the solvent weight was deuterated water.

Reagents

Resorcinol (99 + %, ACS reagent) and deuterium oxide (99.9 atom % D) were from the Aldrich Chemical Co. (Milwaukee, WI). Formaldehyde solution (USP grade, 37.1% by assay, 10% methyl alcohol) and analytical reagent grade sodium hydroxide pellets were from Mallinckrodt Specialty Chemical Co. (Paris, KY). Formaldehyde enriched to 99% ^{13}C (20% aqueous solution) was obtained from Isotec Inc. (Miamisburg, OH). The standard for chemical shift measurements was 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt, 99.8%, hereafter referred to as DSS.

EXPERIMENTAL METHODS

General

All NMR spectra were acquired on a Bruker (Billerica, MA) DPX250 spectrometer at 30°C observing ^{1}H and ^{13}C at 250 and 62.9 MHz, respectively, with a 10-mm broadband probe using 30° pulses. Proton decoupled ^{13}C spectra were collected using Bruker's power-gate pulse sequence with a l-s relaxation delay and a 30° pulse angle. All free-induction decays (FIDs) were accumulated across a spectral width of 15,700 Hz with 16K data points; they were zero-filled to 32K, and a line broadening of 2 Hz was applied before Fourier transform. The number of scans varied depending on the stage of the reaction because, as the HMR reaction proceeds, molecular weight increases, resulting in a spread of resonant frequencies and in decreased spin-spin relaxation time (T_2), due to longer rotational correlation time (τ_c). Both phenomena produce broader signals and overall lower signal-to-noise (S/N) ratios. Therefore, the later acquisitions were acquired with more scans to obtain S/N ratio comparable to the early acquisitions.

Quantitative

A series of spectra was obtained using an inverse-gated ^{1}H decoupling sequence, to eliminate nuclear Overhauser enhancement, and a 60-s relaxation delay. Ninety-nine percent ^{13}C-enriched formaldehyde provided about a 100-fold increase in S/N ratio for groups derived from formaldehyde. Thus, even with the long relaxation delay (60 s) for quantitative work, formaldehyde-derived species could be monitored in a relatively short time frame; however, the signals from the unenriched resorcinol remained small. The reaction was monitored as a function of time. At the end of each time period, the NMR acquisition was

halted, and a new experiment was begun. Therefore, each experiment contained data only from the time period specified. Because of the signal enhancement due to the ^{13}C enrichment, the first several spectra were acquired with only four to eight scans (in 4 to 8 min). Molecular relaxation times decrease as molecular weight increases or as molecular symmetry decreases. As the reaction proceeded, the number of scans was gradually increased to maintain approximately the same S/N ratio. Signals were integrated and tabulated as a function of reaction time.

Formaldehyde-to-Resorcinol Ratio

Another series of spectra was acquired to aid in the identification of the earliest derivatives. To control the extent and rate of reaction, formaldehyde was added in increments of F/R = 0.4, beginning with no formaldehyde in the mixture. Quantitative spectra were acquired for 15 min after each addition of formaldehyde.

pH

The effect of pH on peak positions became a concern because the chemical shifts for some peaks changed noticeably as reactions continued for hours. With the method of Nakashima and Maciel,[12] two solutions of 0.30 *M* resorcinol, one without sodium hydroxide and the other with 1 *M* sodium hydroxide, were mixed in various proportions to obtain a series of solutions of different pH values at constant resorcinol concentration. The pH of the solutions was measured with a Corning Model 125 pH meter (Corning, NY) and a Ross Model 81-02 combination electrode (Orion Research, Cambridge, MA) calibrated with buffers at pH 4.01, 6.86, and 9.18. Proton-decoupled ^{13}C spectra were obtained as specified above.

Chemical Shift Predictions

Many predictions for ^{13}C-NMR resonance peaks of possible carbon types within R-F structures were made by use of the ^{13}C module of Chem Window3, a computer software package from Soft-Shell International, Ltd. (Grand Junction, CO).

RESULTS AND DISCUSSION

Reaction Monitoring with Normal Carbon-13 NMR Spectra

Early Stages

A ^{13}C-NMR spectrum of unreacted resorcinol in alkaline solution (Fig. 1) shows four signals from the aromatic carbons: Cl and C3 at 160.8 ppm, C2 at 106.1 ppm, C4 and C6 at 110.2 ppm, and C5 at 133.4 ppm. DSS with signals at 57.1, 21.8, 17.6, and 0.0 ppm was used as an internal standard for peak height. Formaldehyde was subsequently mixed into this solution to start the HMR reaction.

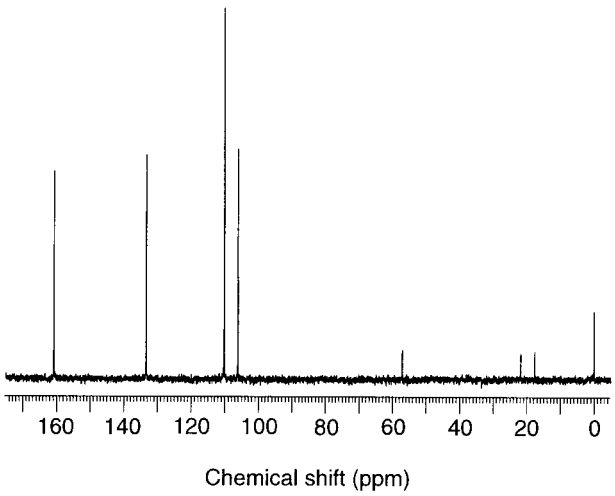


Figure 1 Carbon-13 NMR spectrogram of 0.30 *M* resorcinol in alkaline water (with DSS added for reference) preparatory to forming HMR.

The first spectrum from a freshly mixed HMR solution [Fig. 2(a)] was collected from 4 to 19 min after mixing. During this time, more than half of the resorcinol reacted, as indicated by an approximately 60% decrease in intensity of 160, 133, and 106 ppm signals. A number of new peaks appeared, some very strong, in the aromatic region between 105 and 161 ppm. Five peaks in the C5 carbon region between 132 and 135 ppm indicated that there were at least five different molecular species. Most of the initial reaction of resorcinol was substitution at the C4 or C6 carbons, as indicated by the set of new signals for substituted C4 and C6 carbons from 120 to 122 ppm.[11] Several very small, new signals around 117 ppm indicated some substitution at C2 positions.[11] Signals between 55 and 65 ppm arose from hydroxymethyl groups on resorcinol rings[11] and were observed in the first 19 min. Specifically, the signals at 60 to 65 ppm represented hydroxymethyl groups attached to C4 and C6 carbons, respectively. The signals around 55 to 60 ppm were those associated with hydroxymethyl substitution on the C2 carbon. Quantitative comparisons of substitution at the 4- and 6-positions compared with the 2-position will be discussed in the ^{13}C-enriched formaldehyde experiment.

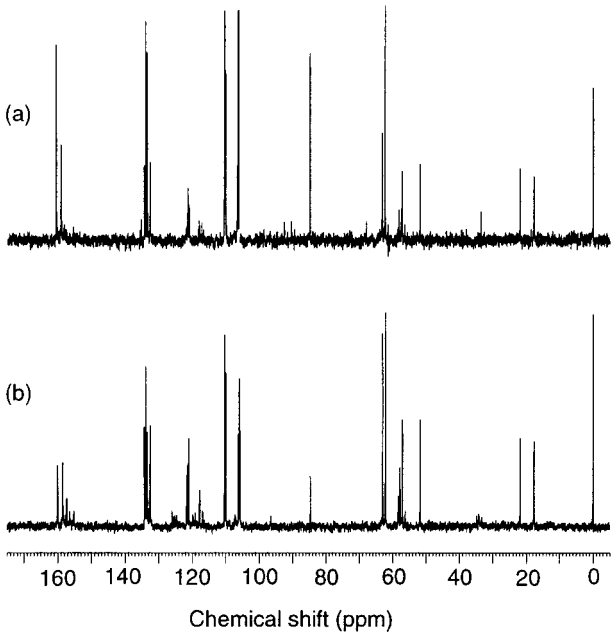


Figure 2 Carbon-13 NMR spectrograms of HMR obtained from reaction times between (a) 4 and 19 min and (b) 60 and 75 min.

Formaldehyde in aqueous solution is hydrated to form methylene glycol or oligomeric chains of formaldehyde. Both were observed during the first 45 min with the methylene glycol at 84.6 ppm and the oligomer of $n = 2$ at 88.5 ppm.[11] Signals at 67.7 and 90.3 ppm are attributed to the benzyl methylene and hemiformal carbons, respectively, from the reaction of formaldehyde with a hydroxymethyl group attached to C4[11] (see Structure A). The methylene glycol, its oligomers, and the hemiformal groups are labile sources of formaldehyde for further HMR reaction.

pH-Dependent Shifts

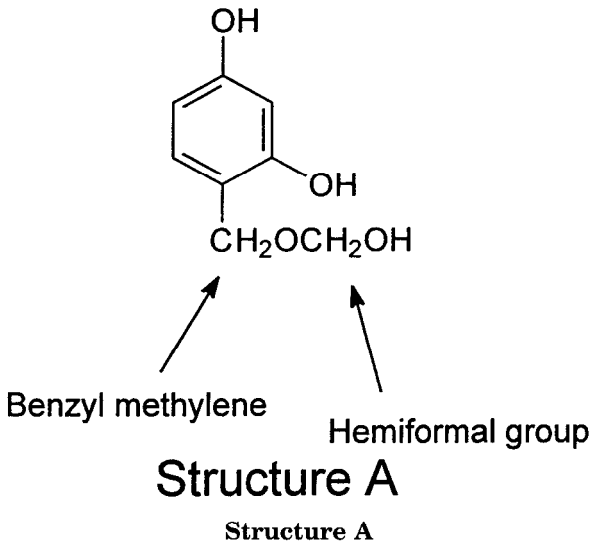
In this study, the positions for some resorcinol signals shifted with time. The signal assigned to C1 and C3 carbons of resorcinol moved upfield from 160.8 to 160.1 ppm in a little more than an hour and then decreased no further. The signals for the other carbons of resorcinol moved less than 0.1 ppm. Hydroxyl groups and their attached carbons are particularly sensitive to changes in pH. The changes are attributed to decreasing alkalinity of the system during the course of the experiment, from an initial 9.2 to 8.7 in 2.2 h. Decreasing alkalinity is presumed to be caused primarily by the Cannizzaro reaction,[13] which results in sodium formate.

Changes of chemical shifts for carbons in phenol have been measured between pH values of 0.2 and 13.4.[12] The strongest effect with increasing alkalinity is an increase of chemical shift for the Cl carbon of phenol in the pH region between 8 and 11. The magnitude of changes for the *ortho* and *para* carbon chemical shifts were less than for Cl, but in the region between pH 9 and 10, they switched relative positions in the spectrum. Peak positions for *meta* carbons were unchanged. Changes of chemical shift for a number of phenol-formaldehyde derivatives in aqueous DMSO were measured, while 64 mol % alkali was added in three increments.[14] As alkalinity increased, the chemical shifts for Cl and most *ortho* carbons increased, shifts for the *para* carbons decreased, and shifts for *meta* carbons changed little.

An experiment on the effect of sodium hydroxide levels on chemical shifts of 0.30 *M* resorcinol (no formaldehyde) gave the data shown in Figures 3 (pH dependence) and 4 (concentration dependence). Signals for C1, C2, and C3 moved upfield with alkali concentration, whereas signals for C4, C5, and C6 peaks moved downfield. The former three peaks had a stronger dependence on concentration or pH than the latter three. The changes of chemical shifts were more linear with concentration than with pH. Between pH values of 7.74 and 9.67, the chemical shift of C1 and C3 carbons increased by 2.0 ppm.

Late Stages

With the chemical shift reference, DSS, used as a constant reference for monitoring changes in



Structure A

Structure A

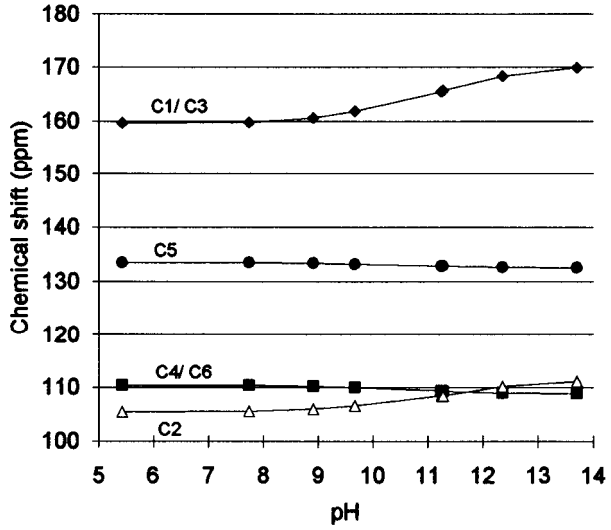


Figure 3 Effect of alkalinity on NMR chemical shifts for resorcinol: dependence on sodium hydroxide concentration.

peak intensity over time, the intensity of the resorcinol signal declined about 90% by 60 to 75 min [Fig. 2(b)]. A shallow, broad peak appeared in the region of 36 to 33 ppm, which represented various methylene linkages formed between resorcinol rings (diarylmethanes) by the condensation of hydroxymethyl groups at the 4- or 6-positions.[11]

By 90 to 120 min [Fig. 5(a)], there were definite signs of broad aggregates of signals underlying sharp peaks in the aromatic region. By 3.5 to 4.5 h [Fig. 5(b)], the multiple peaks were broadened and the sharp peaks had much reduced intensity, indicating little remaining unreacted resorcinol.

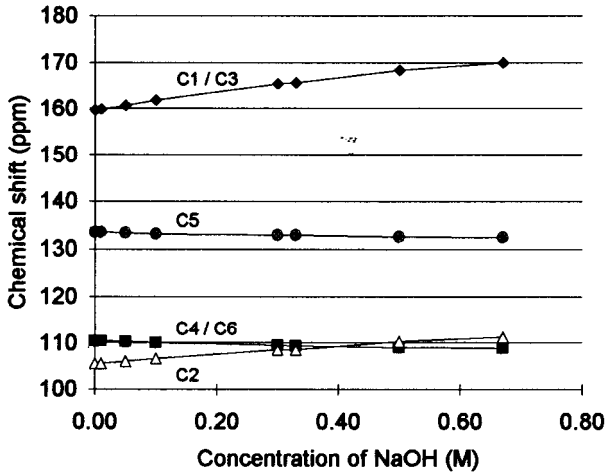


Figure 4 Effect of alkalinity on NMR chemical shifts for resorcinol: pH dependence.

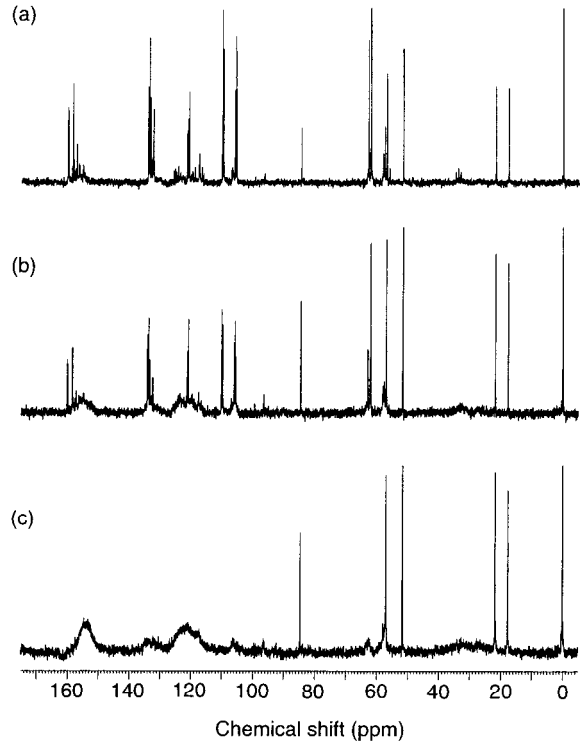


Figure 5 Carbon-13 NMR spectrograms of HMR obtained from reaction times between (a) 1.5 and 2 h, (b) 3.5 and 4.5 h, and (c) 7 and 11 h.

After 7 to 11 h [Fig. 5(c)], all of the aromatic signals were broad, with no sharp resorcinol signals. The few sharp signals that remained were for DSS and methylene glycol. A gel permeation chromatography analysis[5] showed that only 0.1% unreacted resorcinol persisted after 24 h at room temperature. The NMR peak widths indicate multiplicity of species and polymerization.

First Derivative Formed

In addition to tracking the types of groups formed over time, I hoped to determine the first few derivatives. However, only the first derivative, 4-hydroxymethyl resorcinol, was identified because subsequent spectra unfortunately were too complex for other derivatives to be identified. The assignments made here [Fig. 2(a)] and previously for 4-hydroxymethyl resorcinol are displayed in Table I.

According to both Werstler[11] and ChemWindow3, the 4-hydroxymethyl substitution should move the C5 signal upfield. However, a 0.5-ppm downfield shift for the C5 carbon was observed. The values for C5 in subsequent derivatives fell on either side of those for resorcinol. A possible

Table I Chemical Shift for 4-Hydroxymethylresorcinol

	Chemical Shift (ppm)		
Carbon Position	Study Result[a]	Werstler's Result[b]	Lamartine's Result[c]
C1	—[d]	158.07	158.40
C3	159.0	156.92	157.17
C5	133.8	(131.84)[e]	129.48
C4	121.2	120.00	119.12
C6	109.9	(109.2)	107.00
C2	106.2	(104.3)	103.42
CH_2	62.0	61.49	61.70

[a] In dilute sodium hydroxide solution, approximate pH 9; acquisition from 4 to 19 min.
[b] In water, pH unspecified.
[c] In unspecified solvent.
[d] The peak for Cl may be hidden behind the Cl and C3 peaks for resorcinol.
[e] Values in parentheses were calculated by this author according to Werstler's scheme.

explanation for the observed downfield shift would be for the 4-substituted species to be a hemiformal group.[11] However, two pieces of evidence argue against the derivative being a hemiformal. First, hemiformal methylene peaks present in the early spectra were very small and subsided into the noise signals within the first hour, whereas the C5 signal at 133.8 ppm was fairly strong for 7 h. Second, in the experiment using small, incremental additions of formaldehyde, the first increment of F/R = 0.4 produced peaks for the same first derivative but was not sufficient to produce significant hemiformal groups, confirmed by the absence of peaks in the regions of 67.7 and 92.3 ppm. The minor discrepancy with Werstler's prediction is very reasonably attributed to a pH effect and does not preclude the confident assignment of the first derivative to 4-hydroxymethyl resorcinol.

Spectra from ^{13}C-Enriched Formaldehyde

Spectra of reaction mixtures that used ^{13}C-enriched formaldehyde better illustrate how formaldehyde reacted to create various chemical species, because enrichment provides approximately a 100-fold increase in those carbon signals derived from the formaldehyde. Formaldehyde-derived species exhibit signals in the region from about 15 to 100 ppm. (An inconsequential exception to this range was a signal from sodium formate at 173.8 ppm generated by the Cannizzaro reaction.) Table II gives peak areas of seven specific shift regions over several time periods.

Early Species

The spectrum in Figure 6(a), taken between 4 and 12 min of reaction, shows significant hydroxymethyl substitution at the 4- and 6-positions (60-65 ppm) and at the 2-position (55-60 ppm) as well as labile sources of formaldehyde [methylene glycol monomer (84.7 ppm) and dimer (88.5 ppm) and hemiformal groups (67.8 and 90.3 ppm)]. In the first few minutes, the hydroxymethyl peaks account for about 36% of the carbons initially present as formaldehyde, with 2-hydroxymethyl species accounting for less than 20% of the total hydroxymethyl peak area.

Methylene Bridges

As the HMR reaction progresses, the hydroxymethyl groups are converted to diaryl methanes (methylene bridges between rings). The groups of resonance peaks for various methylene bridges are shown in Figure 6(b) (acquired from 7.3 to 9.3 h). The 4,4′-methylene bridge (30-38 ppm) was first observed as early as 21 to 25 min into the HMR reaction, but at 45 min, this still constituted less than 4% of the carbons initially present as formaldehyde.

Much later, at about 2.5 h, the first indication of 2,4′-methylene bridges (22-30 ppm) was observed. At this point, 4,4′-methylene bridges were about 6.5 times more common than 2,4′-methylene bridges.

A broad signal, previously unreported for resorcinolic resins, appeared between 38 and 45 ppm after 5 h [Fig. 6(b)]. Assignment of this signal

Table II Proportions of Formaldehyde-Derived Chemical Groups by Integrated Peak Areas for the Chemical Shift Range

Reaction Time	Formald. (95-80 ppm)[a]	HF (70-66 ppm)[b]	Hydroxymethyl 65-60 ppm	Hydroxymethyl 60-55 ppm	Methylene Linkages 45-38 ppm	Methylene Linkages 38-30 ppm	Methylene Linkages 30-22 ppm
4-12 min	0.59	0.05	0.31	0.05	0.00	0.00	0.00
12-17 min	0.39	0.06	0.46	0.09	0.00	0.00	0.00
17-21 min	0.31	0.03	0.54	0.10	0.00	0.02	0.00
21-25 min	0.26	0.02	0.56	0.12	0.00	0.05	0.00
25-29 min	0.23	0.02	0.59	0.12	0.00	0.04	0.00
29-33 min	0.20	0.02	0.61	0.14	0.00	0.02	0.00
33-37 min	0.20	0.03	0.61	0.13	0.00	0.03	0.00
38-42 min	0.17	0.02	0.63	0.15	0.00	0.03	0.00
42-46 min	0.12	0.02	0.66	0.17	0.00	0.03	0.00
50-58 min	0.09	0.02	0.67	0.18	0.00	0.04	0.00
58-74 min	0.07	0.01	0.69	0.19	0.00	0.05	0.00
1.55-1.80 h	0.05	0.01	0.65	0.20	0.00	0.10	0.00
2.53-3.07 h	0.03	0.00	0.62	0.19	0.01	0.13	0.02
3.07-3.60 h	0.05	0.00	0.59	0.18	0.01	0.14	0.02
3.80-4.33 h	0.04	0.00	0.55	0.18	0.02	0.17	0.04
4.40-4.93 h	0.03	0.00	0.54	0.17	0.02	0.19	0.05
5.30-6.30 h	0.04	0.00	0.48	0.17	0.04	0.21	0.06
6.30-7.30 h	0.04	0.00	0.44	0.16	0.04	0.24	0.09
7.30-9.30 h	0.04	0.00	0.42	0.14	0.06	0.25	0.09
9.30-11.30 h	0.03	0.00	0.33	0.13	0.05	0.30	0.15
11.30-15.30 h	0.02	0.00	0.26	0.12	0.06	0.36	0.18
15.30-19.30 h	0.02	0.00	0.17	0.10	0.07	0.39	0.25

[a] Formald. refers to methylene glycol, its oligomers, and labile hemiformal methylenes.
[b] HF refers to hemiformal benzyl methylene carbons.

seemed useful because it coincides with the useful period of the HMR coupling agent. This group of resonances cannot be attributed to 2,2′-methylene bridges, which appear at about 18 to 20 ppm[8] and are observed as a high-field shoulder on the broad 2,4′-methylene bridge signal centered at 27 ppm. The unexpected signal cannot be attributed to a methine group attached to two resorcinolic rings and to a hydroxymethyl group, because that would not be consistent with the rest of the spectrum. Such a hydroxymethyl group would have a peak at about 70 ppm of approximately equal area to that of the 38-ppm peak. No such 70-ppm signal is observed at that reaction time.

One plausible explanation, however, is a benzylic methylene joined to a methine link between two other resorcinolic rings. Solid-state NMR spectroscopic support for this type of linking structure was shown by Maciel for cured furfuryl alcohol resins[15] and less certainly for cured phenol-formaldehyde resins.[16] The chemical shift prediction software predicts the methylene group

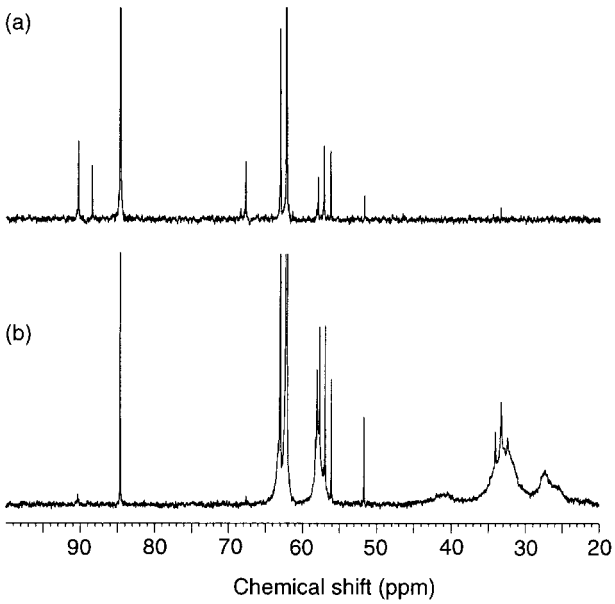


Figure 6 Carbon-13 NMR spectrograms of HMR, using ^{13}C-enriched formaldehyde, obtained from reaction times between: (a) 4 and 12 min and (b) 7.3 and 9.3 h.

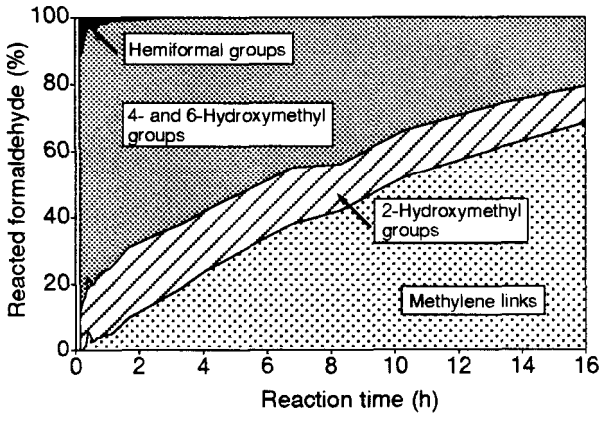


Figure 7 Summary plot of changes in the distribution of formaldehyde-derived species in HMR with time (acquisition of data started several minutes after the reaction began).

signal at 39 ppm and the methine signal at 32 ppm, both of which could be accommodated by these spectra.

Formaldehyde Consumption

Formaldehyde was rapidly consumed, with 95% bound in various forms to resorcinol within 1.7 h and 98% bound after 17 h. The progress of changes in various formaldehyde-derived groups bound to resorcinol is shown in Figure 7. Initially, about 76% of the formaldehyde that was consumed took the form of 4- or 6-hydroxymethyl groups, 12% took the form of 2-hydroxymethyl groups, and the remainder took the form of methylene in hemiformal methylenes (essentially no methylene bridges). As the HMR reaction progressed, hydroxymethyl groups condensed to form methylene bridges, but labile formaldehyde species continued to form more hydroxymethyl groups. By 3 h, 16% of the initial formaldehyde had been converted to methylene bridges, and after 8.3 h, 40% had been converted. These two times cover the effective application period of the primer for producing durable epoxy bonds to Douglas-fir.[5]

The benzyl methylenes bound to resorcinol rings as part of hemiformal groups were most abundant in the earliest period, at about 12% of formaldehyde consumed. The hemiformal content decreased rapidly at first and disappeared after about 2 h. The early disappearance of most formaldehyde species suppressed the Cannizzaro reaction that initially changed the pH of the reaction.

CONCLUSION

To characterize the chemical composition of the HMR coupling agent during the critical period of its application time, ^{13}C-NMR spectra were acquired as the reactions were occurring. Formaldehyde enriched to 99 atom % ^{13}C was used to acquire quantitative spectra in a short time.

Among the methylene species formed in the first minutes of the HMR reaction, hydroxymethyl groups were dominant. The ratio of 4-hydroxymethyl to 2-hydroxymethyl groups was more than 6 : 1. Hemiformal benzyl methylene carbons accounted for about 12%, but they rapidly dissipated. The first 4,4′-methylene linkages were detected after 20 min and 2,4′-methylene linkages after 2.5 h.

Formaldehyde, in its various labile forms, decreased quickly as reactions occurred. After 1.7 h, 95% of formaldehyde species had reacted with resorcinol. Within the critical HMR application period, the percentage of methylene linkages between resorcinol rings increased from about 16% to 40%.

The chemical shift values of resorcinol, especially for the C1 or C3 carbons, changed with HMR reaction time. This was due to pH changes of the HMR. Values ceased to change as formaldehyde was consumed by reaction with the resorcinolic rings.

This information should facilitate development of a more easily used form of HMR. Eventually, this could lead to a more flexible, efficient process for making durable bonds to wood with epoxy and a number of other thermosetting resins.

The author thanks Kolby C. Hirth for collecting spectra, suggesting enhancements to experiments, and comments on the manuscript.

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