

REACTIVITY OF HYDROXYMETHYLATED RESORCINOL COUPLING AGENT AS IT AFFECTS DURABILITY OF EPOXY BONDS TO DOUGLAS-FIR

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ABSTRACT

Epoxy adhesives develop strong bonds to wood, but they lack the structural durability to withstand the severe stresses from repeated water soaking and drying. Research at the Forest Products Laboratory led to a discovery that hydroxymethylated resorcinol (HMR) physicochemically couples to both epoxy adhesive and lignocellulosics of wood to produce bonds that are extraordinarily resistant to delamination. The HMR coupling agent is quite reactive at room temperatures; therefore, the length of its reaction time, or the time between preparing the solution and applying it to the wood surface, strongly influences the durability of adhesion. The experiments in this study defined the optimum range of reaction time when adhesion is maximum for epoxy bonds to HMR-primed Douglas-fir. Heats of reaction (by differential scanning calorimetry), molecular-size distribution (by gel permeation chromatography), and chemical structures of HMR (by carbon-13 nuclear magnetic resonance spectroscopy) are described for this range of optimum reaction times.

Keywords: Hydroxymethylated resorcinol coupling agent, epoxy adhesive, Douglas-fir, heat of reaction, molecular-size distribution, resistance to delamination.

INTRODUCTION

The lack of structural durability of epoxy bonds to wood has always been a problem for fabricators of adhesively bonded wood products that are intended for service in exterior environments. Epoxy adhesives develop dry shear strength values that exceed the strength

of the wood itself; but when exposed to the severe stresses of water soaking and drying, epoxy bonds eventually delaminate. For this reason, epoxies fail to qualify as structural adhesives in laminated wood products intended for wet-use exposure, according to industry standard ANSI/AITC A190.1-1992 (AITC 1992). Recent research at the USDA Forest Service, Forest Products Laboratory (FPL), demonstrated that hydroxymethylated resorcinol (HMR) physicochemically couples to both epoxy adhesive and lignocellulosics of wood to produce bonds of extraordinary struc-

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tural durability (Vick et al. 1995; Vick and Okkonen 1996). HMR is also effective at enhancing adhesion of other thermosetting wood adhesives, including phenol-resorcinol-formaldehyde, emulsion polymer/isocyanate, polymeric methylene diphenyl diisocyanate, melamine-formaldehyde, melamine-urea-formaldehyde, and urea-formaldehyde resin adhesives (Vick 1996). A U.S. patent covering this invention has been assigned to the U.S. Department of Agriculture (Vick et al. 1996).

The HMR coupling agent is prepared as a dilute aqueous solution by reacting formaldehyde with resorcinol under mildly alkaline conditions at room temperature. HMR is quite reactive at these conditions; therefore, the length of the reaction time (the time between preparing the solution and applying it to the wood surface) will strongly affect the molecular-size distribution and reactivity of HMR. Previous studies (Vick et al. 1995; Vick 1996; Vick and Okkonen 1996) have demonstrated that delamination resistance of several thermosetting adhesives was effectively enhanced by applying H M R to wood surfaces after HMR had reacted 4 h at room temperature. Previous unpublished experiments have also indicated that the length of the reaction time has an influence on the durability of adhesion. Thus, reaction times either shorter or longer than the optimum range might result in bonds to HMR-primed wood being much less resistant to delamination.

Reaction products of resorcinol and formaldehyde in aqueous sodium hydroxide are well known, although specific molecular species and reactivity of HMR are not known for specific reaction times. It is evident that effectiveness of H M R at improving adhesion is highly dependent on reaction time; therefore, knowledge of molecular-size distribution and reactivity of HMR, as related to the durability of adhesion and measured after specific reaction times, is essential to maximizing adhesion and optimizing control of the bonding process.

To achieve these objectives, chemical reactivity of HMR was determined from heats of cure measured by differential scanning calo-

TABLE 1. *Ingredients for HMR coupling agent.*

Ingredient	Percentage by weight
Water, deionized	90.43
Resorcinol, crystalline	3.34
Formaldehyde, 37% formalin	3.79
Sodium hydroxide, 3 molar	2.44
Total	100.00

rimetry (DSC). Molecular-size distribution was determined by gel permeation chromatography (GPC) and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR). Adhesion durability of epoxy to Douglas-fir was determined from tests of resistance to delamination according to specification ASTM D 2559 (ASTM 1994).

EXPERIMENTAL MATERIALS

HMR coupling agent

The HMR coupling agent was prepared as a 5% aqueous solution by reacting formaldehyde with resorcinol in a 1.5 mole ratio at mildly alkaline conditions, using the concentrations of ingredients shown in Table 1. Dodecyl sulfate sodium salt (0.5% by weight) was added to this mixture at the end of the reaction time to aid wetting of the wood surfaces.

Reaction times for this experiment were generally at 2-h intervals up to a total reaction time of 24 h, although sampling was more frequent in DSC, GPC, and NMR analyses during the first 8 h. The temperature of reaction for HMR was controlled by storing batches in a temperature-controlled room at 23°C.

Water interferes with epoxy adhesion to wood, so water was evaporated from the HMR-primed wood surfaces before the adhesive was spread. The primed wood surfaces were conditioned at 23°C and 50% relative humidity (RH) for 24 h before bonding. Supplemental heat was not used to accelerate evaporation of water because heat rapidly accelerates the reaction of HMR. Previously unpublished work has indicated that completely

TABLE 2. *Ingredients of FPL 1A epoxy adhesive.*

Ingredient	Parts by weight
D.E.R. 331 epoxy resin ^a	100.00
Benzyl alcohol	12.50
Hydrophobic fumed silica (N70-TS grade) ^b	2.50
D.E.H. 24 hardener (triethylenetetramine) ^a	11.10

^aProduct of the DOW Chemical Company.^bProduct of the Cabot Corporation.

reacted HMR renders the coupling agent useless.

Epoxy adhesive

An epoxy adhesive based on diglycidylether of bisphenol-A resin, formulated at FPL and identified as FPL 1A, was used for these experiments. It developed strong and highly durable bonds to a range of moderate to high density softwood and hardwood species when the wood surfaces were primed with HMR (Vick and Okkonen 1996). The formulation of FPL 1A epoxy adhesive is shown in Table 2.

Douglas-fir

Laminates for test joints were prepared from the heartwood of Douglas-fir. All pieces of wood were straight-grained, free of defects, and flat- to quarter-sawn. The average and range of growth rates were 19 and 8–42 annual rings/25.4 mm, respectively, as determined from sampling 30 pieces of wood.

The wood was conditioned at 23°C and 50% R H to approximately 9-1/2% equilibrium moisture content (EMC). Twenty-four hours before bonding, laminates were knife-planed to a thickness of 1.9 cm.

Reagents for NMR and GPC

Resorcinol for the NMR experiments was 99+%, A.C.S. reagent. Deuterium oxide contained 99.9 atom % deuterium substitution for hydrogen. Formaldehyde solution was 37.1% formaldehyde and 10% methyl alcohol by assay. Sodium hydroxide was in pellet form, 98.9% by assay. Acetic acid was 100% analyzed reagent. Dimethylformamide (DMF)

was 99.9+%, HPLC grade. Formaldehyde enriched to 99% ¹³C (20% aqueous solution) was obtained from Isotec Inc.² The standard for chemical shift measurements was 3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt, 99.8%, often referred to as DSS.

EXPERIMENTAL METHODS

DSC analysis

The residual reactivities of molecular species of HMR after periods of continuous reaction were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter. Perkin-Elmer large-volume capsules (LVCs) made of stainless steel and fitted with Viton o-rings were used to completely contain samples during the heating process (weight losses were less than 1%). To obtain reaction exotherms, LVCs with samples were heated from 30°C to 200°C at a rate of 10°C per min. To establish a baseline for the cured HMR, LVCs were cooled to 30°C then reheated to 200°C. The area between the scan line of the exothermic reaction and the baseline of the cured resin was the measure of heat of reaction of HMR. The samples weighed 38.3 (±2.8 s.d.) mg, which gave sufficient signal for a good measurement, even after 24 h reaction time. Thermograms were prepared for HMR reaction products after reaction times of 0, 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, and 24 h.

GPC analysis

Apparent molecular sizes of HMR species were measured by a GPC system that contained a Scientific Systems 222C high pressure liquid chromatograph (HPLC) pump, an Alcott Chromatography 738 autosampler, and a Perkin-Elmer 235C diode array detector with a Kel-F flow-cell insert. The separations system consisted of a 0.2-μm filter, a Polymer Laboratories PLgel guard column, and two

²The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

PLgel analysis columns. The analysis columns were 300 by 7.5 mm and contained 5 μm beads, with 50 and 5 nm pore sizes in sequential columns. The system was eluted with a solution of DMF, water, and acetic acid, proportioned in a 93:5:2 volumetric ratio at a flow rate of 0.7 ml/min at 22°C. Total pressure was 11.7 MPa under these conditions.

At 1, 3, 5, 10, and 20 min after mixing HMR, and at 20-min intervals thereafter, a sample of HMR was withdrawn and mixed with an equal part of phenol and 75 parts of pre-filtered elution solvent. Phenol was added as an unreactive reference compound that could be compared directly with the elution times and concentration changes of HMR and its derivatives. The sample was mixed by vortexing before it was put into an autosampler for injection into the HPLC. Each GPC analysis required 34 min; therefore, samples accumulated so that times between sampling and analysis varied between 3 and 17 h. Reactivity was suppressed both by high dilution and neutralization of the sodium hydroxide reaction catalyst with acetic acid in the eluant.

An experiment determined how well the solvent mixture retained HMR reactants in solution and suppressed further reaction. An HMR sample representing 5 min of normal reaction was diluted with eluant and stored. Samples from this dilution were injected into the system after storage times of 0.06, 0.68, 19.08, 22.51, and 23.22 h. Chromatograms were recorded, peak areas and retention times for the peaks were measured, and variability was calculated.

A calibration kit of polyethylene glycol standards was used for molecular-size references. In calibration runs, retention times were measured and fitted to a third-order equation. Standard error of the mean was calculated to be only 0.0009.

¹³C NMR analysis

The chemical linkages created by polymerization of resorcinol with formaldehyde were determined by ¹³C NMR spectroscopy. Aque-

ous HMR reaction mixtures were analyzed in a Bruker DPX250 spectrometer at 62.9 MHz, with frequency lock provided by deuterium oxide. The spectra were detected at 27°C with a 10-mm tunable probe. Proton-decoupled ¹³C spectra were obtained with a 30° pulse angle. A power-gated sequence pulse with a relaxation delay of 1.0 sec was used for an initial resorcinol spectrum. An inverse-gated pulse sequence, which suppresses the nuclear Overhauser effect, was used for subsequent spectra of formaldehyde-related species. The 90° ¹³C pulse angles were 11.9 msec. Free-induction decays (FIDs) of 16,000 data points were accumulated over a spectral width of 15,700 Hz. The FIDs were zero-filled to 32,000 data points, and a line broadening of 2 Hz was applied prior to Fourier transformation.

To accurately detect the first appearance of methylene linkages and their number relative to hydroxymethyl groups, ¹³C-enriched formaldehyde (99% ¹³C, 20% aqueous solution) was substituted for reagent-grade formaldehyde. This substitution increased approximately 100 times the signals of formaldehyde-derived chemical species that could be detected by NMR. The improved signal-to-noise ratio allowed a large delay time of 60 sec for the relatively speedy quantitative spectra of formaldehyde-derived groups. However, resorcinol-derived resonances were of very low intensity in these spectra.

The HMR reaction mixture was first prepared as a solution of resorcinol, water with 20% deuterium oxide, and sodium hydroxide. Then, a weighed amount of the formaldehyde solution was mixed with the first solution to start the reaction. We accumulated and averaged 32 scans (32 min) for the analysis after 3 h, and 128 scans for the analysis between 7 and 9 h, while maintaining favorable signal-to-noise ratios.

Integration of the various peaks and groups of peaks was performed on time-averaged data over consistent chemical-shift regions. To select areas of the spectrum for peak integration, we first looked over all spectra to find the maximum width for each peak, or set of peaks,

assigned to each particular chemical group. Then, allowing a small baseline region on each side, wherever possible, a defined region was chosen for that chemical group. Integration for each region was then made on each spectrum. We chose to set the area for the region from 95 to 80 ppm (parts per million) to equal 1.00 and to gauge the other regions relative to it. The regions defined were 95-80 ppm for formaldehyde species (methylene glycol and its oligomers, and the labile part of hemiformal groups); 70-66 ppm for the carbons of the hemiformal groups attached directly to resorcinol rings; 65-60 ppm for the 4- and 6-hydroxymethyl groups; 60-55 ppm for the 2-hydroxymethyl groups; 45-38 ppm for an unassigned carbon type; 38-30 ppm for 4,4'-methylene links; and 30-22 ppm for 2,4'-methylene links. The values for all these groups derived from the original formaldehyde were added together to get a total. The percentage of formaldehyde consumed was calculated as the area for the 95-80 ppm region divided by the total area, multiplied by 100. To calculate percentages of derived groups based on the amount of consumed formaldehyde, the area for the region of interest was divided by the area for consumed formaldehyde, multiplied by 100.

Delamination resistance and statistical analysis

The effectiveness of HMR in improving the durability of FPL 1A epoxy bonds to Douglas-fir was evaluated by measuring delamination after laminated joints were subjected to the severe cyclic delamination test in ASTM D 2559 (ASTM 1994). Industry standard ANSI/AITC A 190.1-1992 (AITC 1992) specifies that all wet-use adhesives intended for exterior service in structural lumber laminates must be qualified according to this ASTM specification.

The statistical analysis was based on a completely randomized model that compared seven treatments (Snedcor and Cochran 1967). A treatment was one of seven reaction times of

HMR and the resultant delamination at that reaction time. Each treatment was replicated four times. A replicate was a six-ply laminate, from which three sections were cut. Delamination was measured from five bondlines on each end of the three sections in each laminate. From 12 sections, approximately 838 lineal cm of bondline length were measured for delamination for each treatment.

Specimen preparation

A delamination specimen was a 7.6-cm-long cross section cut from a six-ply laminate (replicate). A laminate was prepared by bonding six pieces of wood, each piece measuring 1.9 cm thick, 7.6 cm wide, and 30.5 cm long.

Except for laminates without HMR treatment, wood surfaces were primed before bonding with 5% HMR solution. Both surfaces were spread by brush with 0.15 kg/m² on each surface. The primed surfaces were dried 24 h at 23°C and 50% RH before bonding. Adhesive was spread with a roller on both surfaces to total 0.34 kg/m². Closed assembly time ranged from 60 min after spreading the first bondlines to 50 min after spreading the last bondline. The initial pressure was about 69 kPa, or enough to ensure a small amount of adhesive squeeze-out along the full length of every bondline. The laminates were kept under pressure about 15 h at room temperature. To ensure that all bondlines were cured to the same degree, the laminates were heated at 71°C for 5 h. The relative humidity of the heating air was increased to maintain the EMC of the wood so that bondlines would not be stressed by shrinkage of the wood while curing.

Test procedure

Delamination specimens were subjected to the following three cycles of the delamination test in ASTM D 2559 (ASTM 1994):

1st cycle:

- (1) Vacuum-soak in water 18-21°C at 84.4 kPa for 5 min.

- (2) Pressure-soak in water 18–21°C at 517 kPa for 1 h.
- (3) Repeat events (1) and (2).
- (4) Dry at 65.5°C for 21 to 22 h.

2nd cycle:

- (1) Steam at 100°C for 1–1.5 h.
- (2) Pressure-soak in water 18–21°C at 517 kPa for 40 min.
- (3) Repeat event 4 in the 1st cycle.

3rd cycle:

Repeat events in the 1st cycle.

Immediately after the final cycle, delamination was measured along all end-grain surfaces to the nearest 1.0 mm with a ruler under a stereo-microscope. This technique is more accurate than using the unaided eye and a 0.127-mm-thick feeler gauge, as recommended in the ASTM specification. Delamination was expressed as a percentage of total bond-line length for each specimen. Statistical analysis was based on delamination measured after all three cycles were completed.

RESULTS AND DISCUSSIONS

Delamination resistance and reaction time

After only a few hours of reaction, HMR produced a sharp increase in delamination resistance of epoxy bonds in HMR-primed Douglas-fir laminates, as shown in Fig. 1a. Delamination averaged 3.5% after 4-h reaction time—well below the 5% maximum specified by ASTM D 2559-92 (ASTM 1994). Without the coupling agent, delamination was 30.5%. After 6- and 8-h reaction time, delamination averaged 2.9 and 5.1%, respectively. Only at 4- and 6-h reaction times did the upper limits of the standard errors of both averages fall below the 5% delamination requirement. Reaction times beyond the 4- to 6-h range progressively reduced resistance to delamination as reactivity of HMR decreased and molecular size increased. The approximate effective range of reaction time for this particular wood species and epoxy adhesive extends from 3 to 8 h.

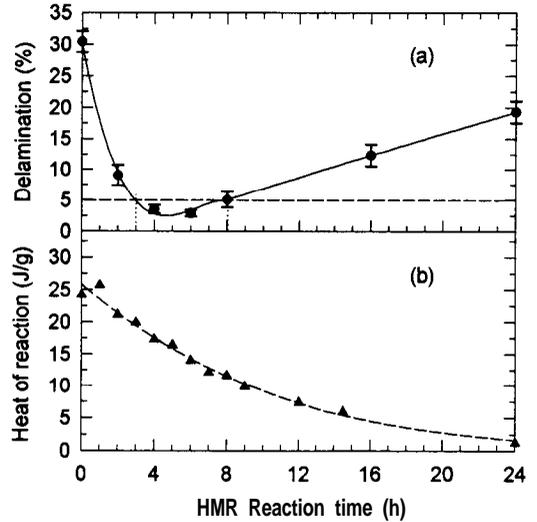


FIG. 1. Effect of HMR reaction time between initial mixing and either application or analysis: (a) epoxy-to-Douglas-fir bond durability by delamination test, and (b) residual primer reactivity as measured by DSC. The error bars in plot (a) indicate the standard error of the mean.

Statistical analysis indicated that average delaminations at and below 5% (e.g., 3.5, 2.9, and 5.1%) were not significantly different. Their respective reaction times ranged between 4 and 8 h. All three of these delamination percentages were significantly less than delamination percentages at any of the other reaction times (Fig. 1a).

Reactivity and reaction time

The heats of reaction of the 5% solids aqueous solution of HMR are plotted over time of reaction in Fig. 1b. Thirteen measurements of heats of reaction, ranging from the initial 24 J/g to 2.5 J/g after 24 h (solution basis), showed an exponentially declining rate of reactivity. A plot of the logarithm of heat of reaction against reaction time produced a straight line, indicating apparent first-order reaction kinetics. Essentially, all reactivity was completed 24 h after mixing the HMR solution.

Within the most effective time range of reaction before application to wood, the heats of reaction were 19.8 J/g at 3 h and 11.4 J/g at

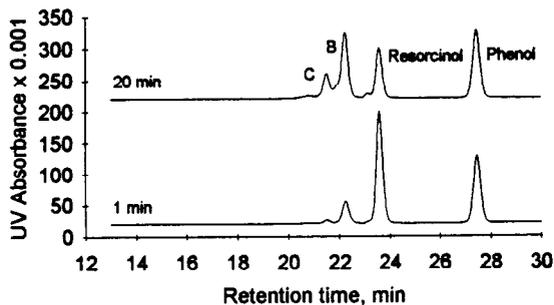


FIG. 2. Gel permeation chromatograms of HMR after reaction times of one min and 20 min. The peak at 27.4 min is caused by reference phenol in the diluent, and the peak at 23.35 min is caused by resorcinol.

8 h (Fig. 1b). Thus, some reaction (about 20%) had to occur before the HMR coupling agent could become effective enough to produce low delamination percentages for the epoxy bonds. Moreover, if too much reaction in solution (>50%) occurred before HMR was applied to wood, the HMR proved ineffective in producing acceptable delamination results. Thus, certain types of molecules (or a mixture of types) needed to exist, before application to wood, for the HMR coupling agent to be effective.

Molecular-size distribution and reaction time

HMR could be reacted for some time, diluted in eluant, then stored, with essentially no additional reaction. An HMR solution was reacted for 5 min, then diluted in eluant. Each of five injections of the diluted sample, during a 23-h storage at 22°C produced four visible peaks that had relative standard deviations (RSD) of 1.1, 1.5, 5.6, and 5.6% for chromatogram areas. The latter two values were from much smaller peaks than the former two. Also, the retention times of the four peaks were constant with RSDs of 0.30%.

The reaction of HMR proceeded quickly at 22°C and 8.6 pH. After the first 1 min of reaction, the chromatogram in Fig. 2 showed that some resorcinol (elution time 23.35 min) had already reacted with formaldehyde to produce two derivatives (elution times 22.2 and 21.5 min). Note that phenol, the internal ref-

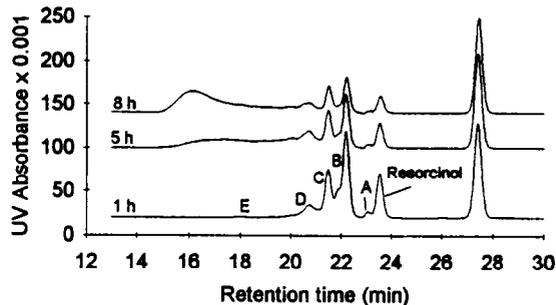


FIG. 3. Gel permeation chromatogram of HMR after reaction times of 1, 5, and 8 h. Peaks are labeled in order of decreasing retention time in the GPC system. Peak E is a summation of all peaks below a retention time of about 20.3 min.

erence standard, elutes at 27.4 min. After 20 min of reaction, the peak areas for resorcinol and the first derivative were about equal.

By the end of the first hour of reaction, at least four derivatives had formed at A, B, C, and D in Fig. 3, with the two newer ones at A and D peaking at 23.08 and 20.7 min, respectively. There was a hint of another one as a shoulder on peak B. The resorcinol peak is no longer as prominent as either of its two major derivatives, peaks B and C.

After 5 h of reaction, Fig. 3 shows peaks for resorcinol and its four derivatives still remain. All were considerably reduced in size compared with their areas at 1 h. Again, note the unreactive phenol peak. New derivatives formed, however, in the higher molecular-size region with elution times from 20.3 to 16 min.

After 8 h of reaction, Fig. 3 shows that the area below 20.3 min was about 60% of the area produced by the resorcinol derivatives. Thus, by 8 h, resorcinol and its first two derivatives were still a significant portion of the reaction mixture. By 12 h, the percentage of higher oligomers and polymers had increased to 80%, and by 24 h to 99% (chromatograms not shown).

The progress of the reaction is shown as summary plots of peak areas as a function of time. Figure 4 shows the course of the reaction for 24 h. Note that two different lots of the reaction mixture were needed to cover the en-

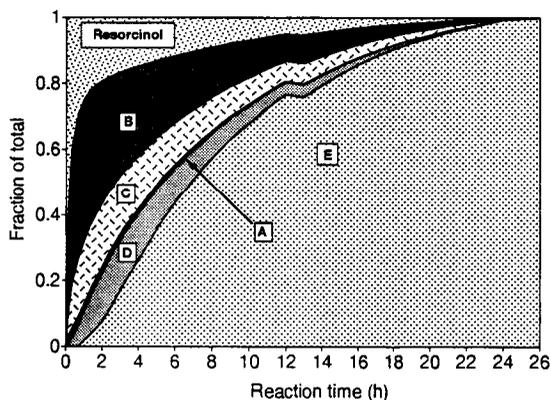


FIG. 4. Progress of peaks in the gel permeation chromatograms of HMR over 26 h reaction time. The letters on the area portions refer to the peaks labeled in Fig. 3. (The apparent discontinuity between 12 and 14 h is due to the use of two runs to establish the full curve.)

ture 24 h. Peaks B and C were the first derivatives to be observed; peaks A and D came later (see lettered peaks in Fig. 3). Peak E is the summation of all later derivatives (e.g., oligomers and polymers), which were not resolvable. Figure 5 shows the first 2 h of the reaction in more detail. The y-axis quantities are for ultraviolet (UV) absorption by chemical species in the eluant. We do not know the exact relationship of UV absorption to amount of substance for these species, but Hope et al. (1973) tabulated extinction factors for resor-

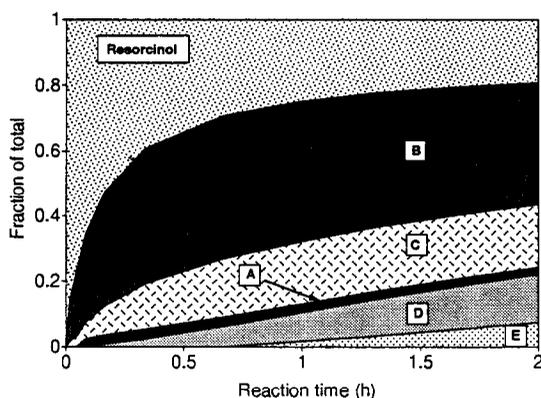


FIG. 5. Progress of peaks in the gel permeation chromatograms of HMR over 2-h reaction time, to emphasize the first appearance times of various peaks. The letters on the area portions refer to the peaks labeled in Fig. 3.

cinolic novolac oligomers. Relative to the value for resorcinol (number of rings, $n = 1$), the extinction factors per ring rose from 1.420 for $n = 2$ to 1.570 for $n > 5$. The effect of hydroxymethylating phenolic rings seems to be to increase UV absorption (Much and Pasch 1982). Thus, the sizes of the chromatographic peaks are considered only rough estimates of the actual concentrations of the eluting species. We suspect the first derivative of resorcinol that appears as peak B (Fig. 3) should be 4-hydroxymethyl resorcinol because of the expected sequence of reactions and the NMR evidence discussed in the next section.

At the lowest molecular weights, a GPC system does not operate only, or even primarily, by size exclusion principles, rather by molecular attraction forces between resorcinolic species and surfaces of the polystyrene gel in the analysis columns. Dargaville et al. (1977) showed that a molecular weight cannot be assigned to isomers of phenolic compounds, based simply on retention times, even for novolac (non-hydroxymethylated) resins. In the present work, it is reasonable to expect that one or more hydroxymethyl groups on some of the species would complicate GPC analyses even further.

Attempts to calibrate for molecular weight using polyethylene glycol standards did not produce sensible values for the first derivatives of HMR or for simple phenolic species. The combination of eluant, the stiff molecular architecture of the oligomeric molecules, and solvation effects associated with hydroxyl groups, probably combined to prevent this. However, the gross relative molecular-size effects are evident and serve the purpose of this study. It was possible to follow changes of the distribution of resorcinol and the earliest derivatives with time and see the formation of a widespread size distribution. Eventually, it might be possible to identify the earliest derivatives, which are quite reactive, with other techniques.

HMR species in the reaction mixture

Spectra of reaction mixtures (Fig. 6) that contained ^{13}C -enriched formaldehyde illustrate

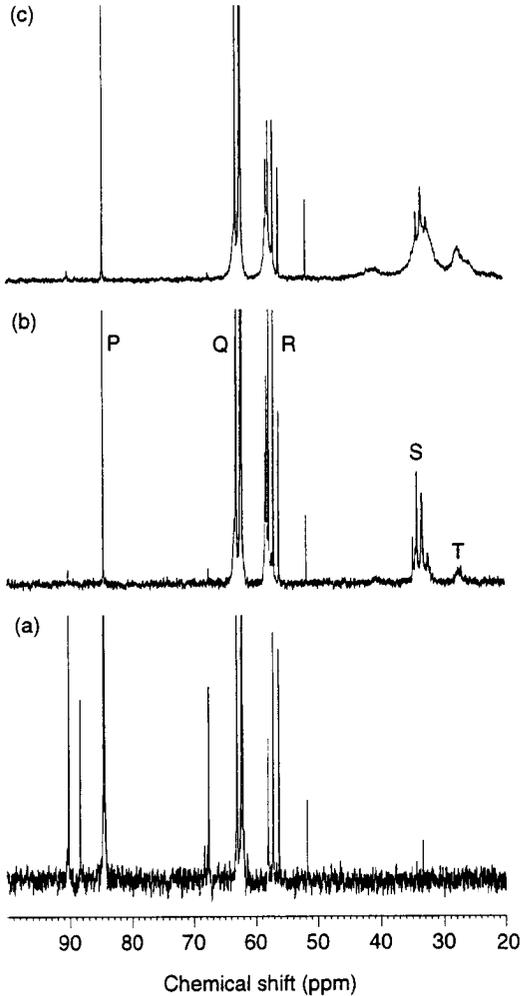


FIG. 6. ^{13}C NMR spectrograms of HMR primer solution acquired during periods after mixing in ^{13}C -enriched formaldehyde: (a) between 14 and 19 min, (b) at 3 h (\pm 15 min), and (c) between 7 and 9 h.

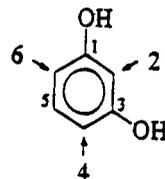
steps in the sequence of how formaldehyde reacted to create various chemical species—primarily hydroxymethyl groups and methylene linkages between resorcinol rings. Spectra show little of the resorcinol species because signals from the carbons of the ^{13}C -enriched formaldehyde were two orders of magnitude greater than those from resorcinol. Assignments of resonance peaks are based on the work of Werstler (1986).

Signals from formaldehyde-based groups

show up in the region from about 100 to 15 ppm. Residual formaldehyde in aqueous solution is hydrated into methylene glycol form, which shows up as a peak at 84.6 ppm and as two small peaks between 92 and 90 ppm.

Within 4 to 12 min after reaction begins, Fig. 6a shows that the methylene glycol peak is large (84.6 ppm), but 44% of the formaldehyde already has been consumed by reaction with resorcinol. The group of peaks between 65 and 55 ppm indicates various hydroxymethyl functional groups on resorcinol rings. The chemical species represented by this group of peaks constitute 88% of the consumed formaldehyde. The other 12% (peak at 67 ppm) appear to be hemiformal groups associated with hydroxymethylated resorcinol molecules. The spectrum does not yet show resonance peaks from 40 to 20 ppm, which would indicate the existence of methylene linkages.

The spectrum in Fig. 6b shows how the reaction has progressed after 3 h, which is near the time when HMR first imparts high resistance to delamination (see Fig. 1a). Peak P for methylene glycol (unconsumed formaldehyde) is small in comparison to peaks for formaldehyde-derived groups. Peaks Q at 65 to 60 ppm represent hydroxymethyl groups attached to the C4 and C6 carbons, which are expected to be the most reactive in forming the initial chain structure. Peaks R around 60 to 55 ppm are associated with hydroxymethyl substitution on the C2 carbon that lies between the two hydroxyl groups on the resorcinol ring (see chemical structure of resorcinol). The C2 carbons are expected to be heavily involved during cure, especially in the cross-linking between polymeric chains of resorcinol-formaldehyde.



Resorcinol (sites of formaldehyde reaction are indicated)

Very small peaks attributed to methylene links between resorcinolic rings are first barely visible in the 35 ppm region, (peaks S in Fig. 6b), between 21 and 25 min. These peaks are assigned to 4,4'-methylene links (Dankelman and De Wit 1977; Lippmaa 1981; Werstler 1986). Since these methylene links only began to appear after a 21- to 25-min time delay, the GPC peaks for the earliest derivatives (Fig. 2), which were substantially abundant before 20 min, must be attributed to monomeric derivatives of resorcinol. These early derivatives (peaks B and C) must be variations of hydroxymethylated resorcinol. A diffuse resonance area around 27 ppm, (peaks T in Fig. 6b) appeared after 2.5 h. Peaks in this area are caused by 2,4'-methylene links, which have been assigned to lower chemical shifts than the 4,4'-links (Dankelman and DeWit 1977; Lippmaa 1981; Werstler 1986).

Of the 95% of formaldehyde that had been consumed by 3-h reaction time, 81% was in the form of hydroxymethyl groups. The other 19% had already been converted to methylene linkages between rings.

Near the end of the useful life of the primer (i.e., for 128 scans between 7 and 9 h) Fig. 6c shows that the hydroxymethyl groups have decreased to 58% of the consumed formaldehyde. Methylene linkages have increased to 42% of consumed formaldehyde. The higher proportion of methylene linkages indicates that more of the resorcinol had been converted to larger size molecules, as indicated by the GPC measurements. As polymerization continued, some hydroxymethyl groups were on the oligomeric chains, but as the GPC analysis indicated, a significant number of both resorcinol monomer and hydroxymethylated resorcinol species remained for further reaction.

A more extensive NMR investigation of the reactions of HMR will be given in a related report. That report will not only give more detail on the reactions of resorcinol and formaldehyde, but it will evaluate the influence of factors that might affect NMR results on this and related systems.

CONCLUSIONS

- Hydroxymethylated resorcinol (HMR) coupling agent has an optimum reaction time for producing the highest and acceptable levels of resistance to delamination of epoxy bonds to wood. In laminates of Douglas-fir bonded with FPL 1A epoxy adhesive, 3- to 8-h reaction times were required before priming the wood surfaces with HMR.
- From the beginning of this optimum reaction time to its end, 20 to 50% of the total heat of reaction of HMR was consumed.
- During this optimum reaction time, a diverse distribution of molecular sizes formed in HMR, ranging from resorcinol itself, through its simple formaldehyde derivatives, to its methylene-linked oligomers and polymers. Outside of this optimum range of molecular sizes, the average molecular sizes were either too small or too large to produce epoxy bonds with acceptable levels of delamination resistance on wood.
- By the end of this optimum reaction time, about 58% of the consumed formaldehyde in HMR had reacted with resorcinol to form hydroxymethyl groups on resorcinolic rings, and about 42% had formed methylene linkages between rings to form resorcinolic oligomers and polymers.

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