

Accelerated Cure of Phenol–Formaldehyde Resins: Studies With Model Compounds

Anthony H. Conner, Linda F. Lorenz, Kolby C. Hirth

USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53705–2398

Received 17 October 2001; accepted 13 February 2002

ABSTRACT: 2-Hydroxymethylphenol(2-HMP) and 4-hydroxymethylphenol (4-HMP) were used as model compounds to study the reactions that occur during cure of phenol–formaldehyde(PF) resin to which cure accelerators (ethyl formate, propylene carbonate, g-butyrolactone, and triacetin) have been added. The addition of cure accelerators significantly increased the rate of condensation reactions. The cure accelerators were consumed during the reaction, indicating that they do not act as true catalysts. Major dimeric and trimeric reaction products were isolated and their structures determined. The results are consistent with a mechanism in which the hydroxymethyl group of 2-HMP (or 4-HMP) is first transesterified by the cure accelerator. The ester group is then displaced by reaction with the negatively charged *ortho* or *para* position of a second molecule

(S_N2 mechanism) or is converted to a reactive quinone methide intermediate, which subsequently reacts with the negatively charged *ortho* or *para* position of a second molecule (quinone methide mechanism). When accelerators were added to the reaction mixture, the self-condensation of 2-HMP was faster than that of 4-HMP. As is well documented in the literature, the exact opposite is true without added accelerators. This result would seem to indicate that the phenolic oxygen helps activate the esterified *ortho*-hydroxymethyl group. The number and nature of crosslinks in a PF resin cured with added cure accelerator might be different than those in a PF resin cured without an added cure accelerator. ©2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3256–3263, 2002

INTRODUCTION

Alkaline cured phenol–formaldehyde (PF) resins are very important adhesives in the forest products industry for the production of composite wood products. In general, high pressing temperatures and long pressing times are required to cure PF resins used for bonding wood. Faster curing PF resins would allow wood to be bonded at lower press temperatures or for shorter press times. Potential savings in energy costs could be realized due to the lower temperatures required for adhesive cure, and increased productivity would be possible with reduction in pressing times. A lower press temperature should also result in lower emissions of volatile organic compounds into the environment during the manufacture of bonded wood products.

Recent literature has shown that adding compounds such as esters, lactones, or organic carbonates to PF resins increases their cure rates.^{1–11} We conducted experiments with the model compounds 2-hydroxymethylphenol (2-HMP) and 4-hydroxymethylphenol (4-HMP) to investigate the types of reactions and reaction mechanisms that might occur during acceler-

ated cure of PF resins. Preliminary results of these experiments were reported previously.¹²

EXPERIMENTAL

Reaction of 2-HMP (1) or 4-HMP (2) with cure accelerators

Hydroxymethylphenol (2-HMP or 4-HMP, 0.8 mmol) was dissolved in water:dimethylformamide (5:1 v/v) to give a 10% solution. Sodium hydroxide (NaOH, as a 10% solution, 0.4 mmol), and 0.3 mmol ethyl formate, propylene carbonate, or g-butyrolactone or 0.1 mmol of triacetin were added. The pH of the reaction mixtures was 10, from 0 through 180 min. All the reactions were run at 20 °C, except the reactions without cure accelerator, which were run at 60 °C.

High-performance liquid chromatography (HPLC) analysis of reaction mixtures

Samples (10 µL) were removed from the reaction mixtures after 0, 1, 5, 10, 30, 60, 120, 130, and 180 min and diluted to 5.0 mL in methanol. Thirty microliters of each diluted sample was analyzed with a Hewlett–Packard (Palo Alto, CA) 1050 Series HPLC on an Inertsil (GL Sciences, Tokyo, Japan) ODs-3 column (25 cm long, 5-µm particle size), with a gradient from 10 to 25% acetonitrile in water for 15 min, and then to 60% acetonitrile in water after 32.5 min at 1.0 mL/min.

Correspondence to: A.H. Conner (ahconner@fs.fed.us).

The eluted compounds were detected by ultraviolet (UV) absorbance at 273 nm. Each sample was analyzed by HPLC in duplicate, and the areas of the peaks were averaged. The percentage of the total area for each peak was plotted as a function of time.

Isolation of reaction products of hydroxymethyl phenols with cure accelerators

After the last sample was removed for analysis by HPLC, the reaction mixture was neutralized with 10% acetic acid and extracted with chloroform. The chloroform layer was separated from the water layer and spotted on the preadsorbent area of a preparative thin-layer chromatography (TLC) plate (PLK5F, silica gel, 80 Å, 1000 µm thick, 20 × 20 cm, Whatman, Clifton, NJ). The plate was developed in chloroform:methanol, 90:10, or chloroform:ethyl acetate:acetic acid, 75:25:1. The components were visualized with short-wave UV light (254 nm). The silica gel containing each component was scraped off the plate and eluted with chloroform:methanol, 80:20. The solvent was decanted, filtered through glass wool, and evaporated to dryness. The residue was dissolved in methanol- d_4 for ^{13}C NMR analysis.

^{13}C -NMR analysis

The components isolated by TLC were dissolved in methanol- d_4 for analysis on a Bruker (Billerica, MA) DPX250 spectrometer. The ^{13}C NMR spectra, DEPT-135, and short-range (g-HSQC) and long-range (g-HMBC) ^1H - ^{13}C correlations were obtained with standard Bruker pulse sequences with a relaxation delay of 1 s.

Gas chromatography/mass spectral (GCMS) analysis

Data were collected on a Thermoquest model GCQ GCMS instrument. The samples were analyzed on a 30-m DB5 column (J&W Scientific, San Jose, CA). The injection port temperature for the samples was 250 °C. The temperature was held at 50 °C for 1 min and programmed to 250 °C at a 20 °C ramp. The temperature was held at 250 °C for 10 min. A splitless injection was performed for 0.5 min. A total ion chromatogram was taken for compounds 6 and 7 that ranged from 50 to 550 m/z units. Compound 7 was analyzed as the tetramethylsilane (TMS) derivative. All GCMS samples were run in a methylene chloride solvent.

2-Hydroxymethyl-4-(2-hydroxyphenylmethyl)phenol (3)

^{13}C -NMR, chemical shift in ppm (assignment): 35.8 (methylene); 61.3 (hydroxymethyl); 115.8 (A6/B3),

116.0 (A6/B3); 120.5 (B5); 128.0 (B4); 128.2 (A2); 129.8 (B1); 129.9 (A5/B6); 130.0 (A3); 131.5 (A5/B6); 133.6 (A4); 154.3 (A1); and 156.2 (B2). DEPT: secondary carbons — 35.8, 61.4; tertiary carbon — 115.8, 116.0, 120.5, 128.0, 129.9, 130.0, 131.5; quaternary carbons — 128.2, 129.8, 133.6, 154.3, 156.2 ppm. The long-range ^1H - ^{13}C correlation showed that the protons (3.82 ppm) on the methylene carbon had prominent cross peaks with carbons at 129.8, 129.9, 130.0, 131.5, 133.6, and 154.3 ppm. The protons (4.59 ppm) on the hydroxymethyl carbon had prominent cross peaks with carbons at 128.2, 130.0, and 156.2 ppm.

2-(3-Hydroxymethyl-4-hydroxyphenylmethyl)-4-(2-hydroxyphenylmethyl)phenol (5)

^{13}C -NMR, chemical shift in ppm (assignment): 35.8 (β -methylene and 35.9 (α -methylene); 61.5 (hydroxymethyl); 115.9 (A5, B6, and C3); 120.6 (C5); 128.1 (C4); 128.0 (A3); 128.5 (B5); 129.3 (B2); 129.8 (C1); 129.9 (A6); 130.0 (A2); 131.4 (C6); 132.2 (B3); 133.5 (B4); 133.7 (A1); 154.1 (B1); 154.2 (A4); and 156.1 (C2). DEPT: secondary carbons — 35.8, 35.9, 61.5; tertiary carbon — 115.9 (3), 120.6, 128.1, 128.5, 129.9, 130.0, 131.4, 132.2; quaternary carbons — 128.0, 129.3, 129.8, 133.5, 133.7, 154.1, 154.2, 156.1 ppm. The long-range ^1H - ^{13}C correlation showed that the protons (4.58 ppm) on the hydroxymethyl carbon had prominent cross peaks with carbons at 128.0, 130.0, and 154.2 ppm. The protons (3.75 ppm) on the β -methylene carbon had prominent cross peaks with carbons at 128.5, 129.8, 131.4, 132.2, 133.5, and 156.1 ppm. The protons (3.78 ppm) on the α -methylene carbon had prominent cross peaks with carbons at 129.3, 129.9, 130.0, 132.2, 133.7, and 154.1 ppm.

4-(4-Hydroxyphenylmethyl)phenol (6)

^{13}C -NMR spectrum, chemical shift in ppm (assignment): 41.2 (methylene); 116.1 (A2, A6, B3, and B5); 130.7 (A3, A5, B2, and B6); 134.3 (A4 and B1); and 156.5 (A1 and B4). GCMS: M^+ = 200 m/z ; $\text{C}_{13}\text{H}_{12}\text{O}_2$ required 200 m/z .

2-(4-Hydroxyphenylmethyl)-4-hydroxymethylphenol (7)

^{13}C -NMR, chemical shift in ppm (assignment): 35.8 (methylene); 65.3 (hydroxymethyl); 115.9 (A6); 116.0 (B3 and B5); 127.5 (A5); 129.7 (A2); 130.9 (B2, B6, and A3); 133.5 (A4); 133.6 (B1); 155.6 (A1); and 156.3 (B4). The long-range ^1H - ^{13}C correlation showed that the protons (3.82 ppm) on the methylene carbon had prominent cross peaks with carbons at 129.7, 130.9, 133.6, and 155.6 ppm. The protons (4.45 ppm) on the hydroxymethyl carbon had prominent cross peaks with carbons at 127.5, 130.9, and 133.5 ppm. GCMS M^+ = 446 m/z ; $\text{C}_{23}\text{H}_{38}\text{Si}_3\text{O}_3$ required 446 m/z .

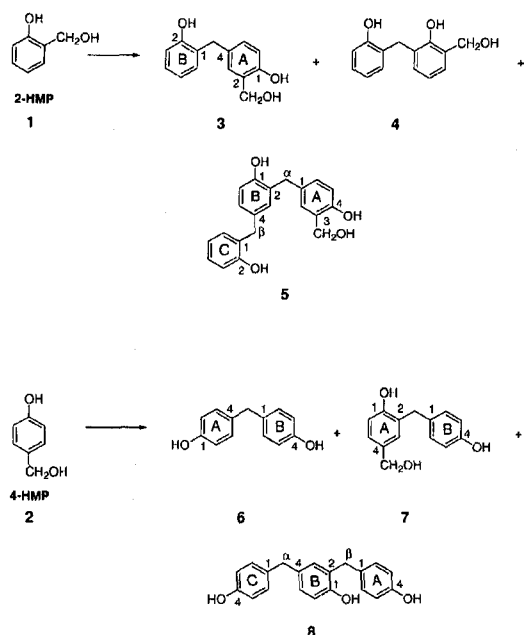


Figure 1 Self-condensation reaction of 2-hydroxymethylphenol (1) and 4-hydroxymethylphenol (2), yielding dimeric and trimeric compounds. Compounds 3, 4, 6, and 7 were reported previously as products of these self-condensation reactions.^{14,16} We isolated the trimeric compounds with the structures shown, but we did not observe that major amounts of compound 4 were formed from self-condensation of 1.

2-(4-Hydroxyphenylmethyl)-4-(4-hydroxyphenylmethyl)phenol (8)

¹³C-NMR, chemical shift in ppm (assignment): 35.8 (β -methylene), 41.2 (α -methylene), 116.0 and 116.1 (A3, A5, B6, C3, and C5), 128.3 (B5), 129.5 (B2), 130.7 (C2 and C6), 130.8 (A2 and A6), 131.9 (B3), 133.7 (A1), 134.2 (B4/C1), 134.4 (B4/C1); 154.2 (B1); 156.3 (A4/C4); and 156.4 (A4/C4). The long-range ¹H-¹³C correlation showed that the protons (3.68 ppm) on the β -methylene carbon had prominent cross peaks with the carbons at 41.2, 128.3, 130.7, 131.9, 134.2, and 134.4 ppm. The protons (3.77 ppm) on the α -methylene carbon had prominent cross peaks with the carbons at 35.8, 129.5, 130.8, 131.9, 133.7, and 154.2 ppm. In the short-range ¹H-¹³C correlation, cross peaks were not observed for the carbons at 129.5, 133.7, 134.2, and 134.4 ppm, indicating that these are quaternary carbons.

RESULTS AND DISCUSSION

Base-catalyzed PF resins (resols) are formed by reacting phenol and formaldehyde at relatively low temperatures to form a complex mixture of oligomers containing free hydroxymethyl end groups. On further heating, the hydroxymethyl groups within the

resin undergo condensation to form a crosslinked polymeric network. 2-Hydroxymethylphenol (2-HMP, 1) and 4-hydroxymethylphenol (4-HMP, 2), which form as transient compounds during resin synthesis, are excellent model compounds for studying the condensation reactions that occur during prepolymer formation and cure.

The condensation of hydroxymethylphenols has been studied extensively.¹³ A number of studies have been conducted on the self-condensation of 2-HMP and 4-HMP or their reactions with phenol.¹⁴⁻¹⁷ These studies have shown that (1) the self-condensation of 4-HMP is ~6-7 times faster than that of 2-HMP and (2) the major condensation products formed from self-condensation at low reaction temperatures are dimers (Figure 1). A number of mechanisms have been proposed for the condensation of hydroxymethyl groups.¹³ Two mechanisms in particular have frequently been used to explain the condensation reactions between methylolphenols under basic conditions. The first mechanism involves the formation of a quinonemethide intermediate^{17,18} (Figure 2), and the second is an S_N2 type mechanism (Figure 3).^{13,19} The formation of dimers 3 and 4 during the self-condensation of 2-HMP is consistent with either of these mechanisms. Higuchi et al.¹⁷ published data consistent with the fact that the mechanism involving the quinone methide is the operative mechanism for the self-condensation of 2-HMP. The formation of dimers 6 and 7 obtained from self-condensation of 4-HMP is consistent with either mechanism. However, the formation of dimer 6 by these mechanisms requires attack by an anion on the sterically crowded C-4 position. Therefore, theoretically one might expect that the formation of dimer 7, being less sterically hindered, would be favored. Yet, 6 is the major dimeric product observed experimentally.

Several reaction mechanisms have been proposed to explain the accelerated cure of PF resins on the addition of esters, lactones, or organic carbonates. Higuchi and Tohmura propose a mechanism in which the bi-carbonate anion derived from propylene carbonate

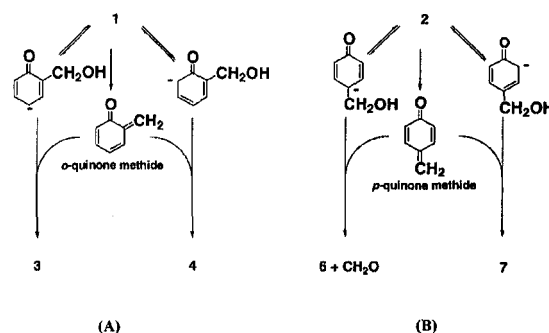


Figure 2 Quinone methide mechanism for the formation of dimeric products from (a) 2-HMP and (b) 4-HMP.

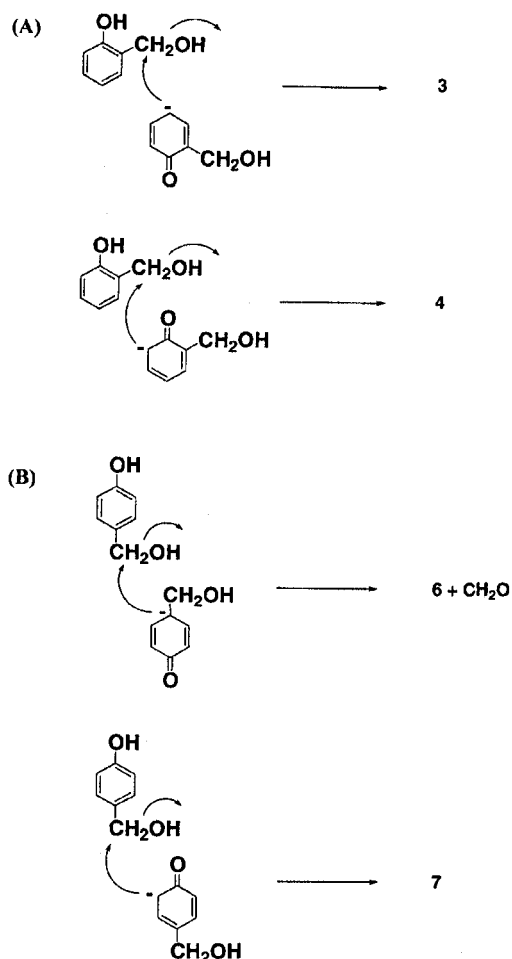


Figure 3 S_N2 mechanism for the formation of dimeric products from (a) 2-HMP and (b) 4-HMP.

coordinates with two hydroxymethylated phenol molecules forming a transition-state structure that facilitates reaction.^{2,8} Pizzi and Stephanou propose a mechanism in which carbon dioxide from propylene carbonate is incorporated into the polymeric structure of the cured resin.^{6,7} In the mechanism proposed by Miller and Detlefsen,³ the hydroxymethylated phenol is transesterified by an organic ester, which facilitates faster conversion to the reactive quinone methide intermediate.

In our study, 2-HMP and 4-HMP were reacted under alkaline conditions at 20 °C, with and without cure accelerators and without the addition of formaldehyde. The cure accelerators were ethyl formate, propylene carbonate, γ -butyrolactone, and triacetin. The disappearance of 2-HMP (or 4-HMP) and the appearance of reaction products with time were determined by HPLC. The rates of disappearance of 2-HMP and 4-HMP (Figure 4) were different depending on the cure accelerator. The rates decreased in the order of

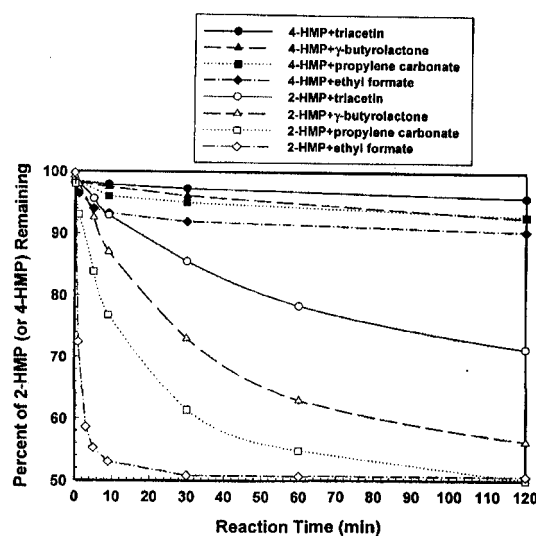


Figure 4 Comparison of effect of cure accelerators on rate of self-condensation of 2-HMP (1) and 4-HMP (2) at 20 °C. See Figures 5 and 10 for the rate of self-condensation of 1 and of 2 without cure accelerators.

ethyl formate > propylene carbonate > γ -butyrolactone > triacetin.

The data presented in Figure 5 show the dramatic effect of ethyl formate on the condensation of 2-HMP. Without ethyl formate, the condensation was very slow and with ethyl formate, very fast. However, even in the presence of ethyl formate, the condensation of 2-HMP slowed appreciably after ~10 min, and the rate of condensation approximated that of the reaction without added ethyl formate. Significant quantities of 2-HMP (~52%) remained in the reaction mixture. Thus, 2-HMP is not rate limiting. This result suggests that the cure accelerator, the only other component added to the reaction mixture (other than NaOH), is consumed in the course of the reaction. Adding more ethyl formate to the

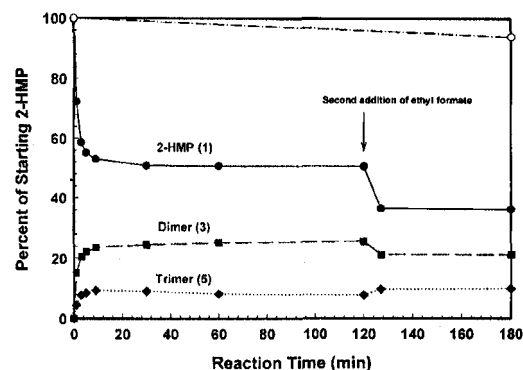


Figure 5 Reaction profile for self-condensation of 2-HMP (1) at 20 °C with added ethyl formate (filled symbols). Disappearance of 2-HMP at 20 °C without added ethyl formate (open symbols) is shown for comparison.

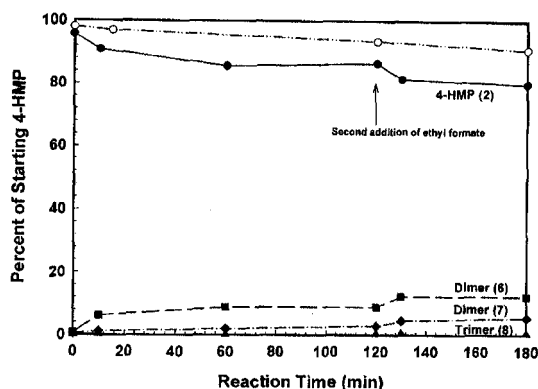


Figure 6 Reaction profile for self-condensation of 2-HMP (1) at 20 °C with added propylene carbonate.

reaction mixture caused the rate of disappearance of 2-HMP to increase temporarily, confirming this hypothesis. Similar results were observed with propylene carbonate (Figure 6). These results suggest that the cure accelerator does not act as a true catalyst, as suggested by the mechanism proposed by Higuchi and To-

hmura.^{2,8} These data are consistent with the observation that propylene carbonate, although lowering the gel time of PF resin, does not seem to act like a standard catalyst because its performance is concentration and temperature dependent.⁴

The mixtures of reaction products formed by reacting 2-HMP at 20 °C with added propylene carbonate as cure accelerator and at 60 °C without added cure accelerator were compared by HPLC (Figure 7). These results indicate that the same mixtures of condensation products were formed in both reactions. However, the relative proportions of the individual products varied, which suggests that the cure accelerator was not incorporated into the reaction products and would appear to rule out the mechanism proposed by Pizzi and Stephanou.^{6,7} However, it should be noted that ¹³C NMR data on PF resins cured in the presence of propylene carbonate contained peaks that might be interpreted as being consistent with their mechanism.¹⁰

The two major reaction products formed by the self-condensation of 2-HMP with added ethyl formate

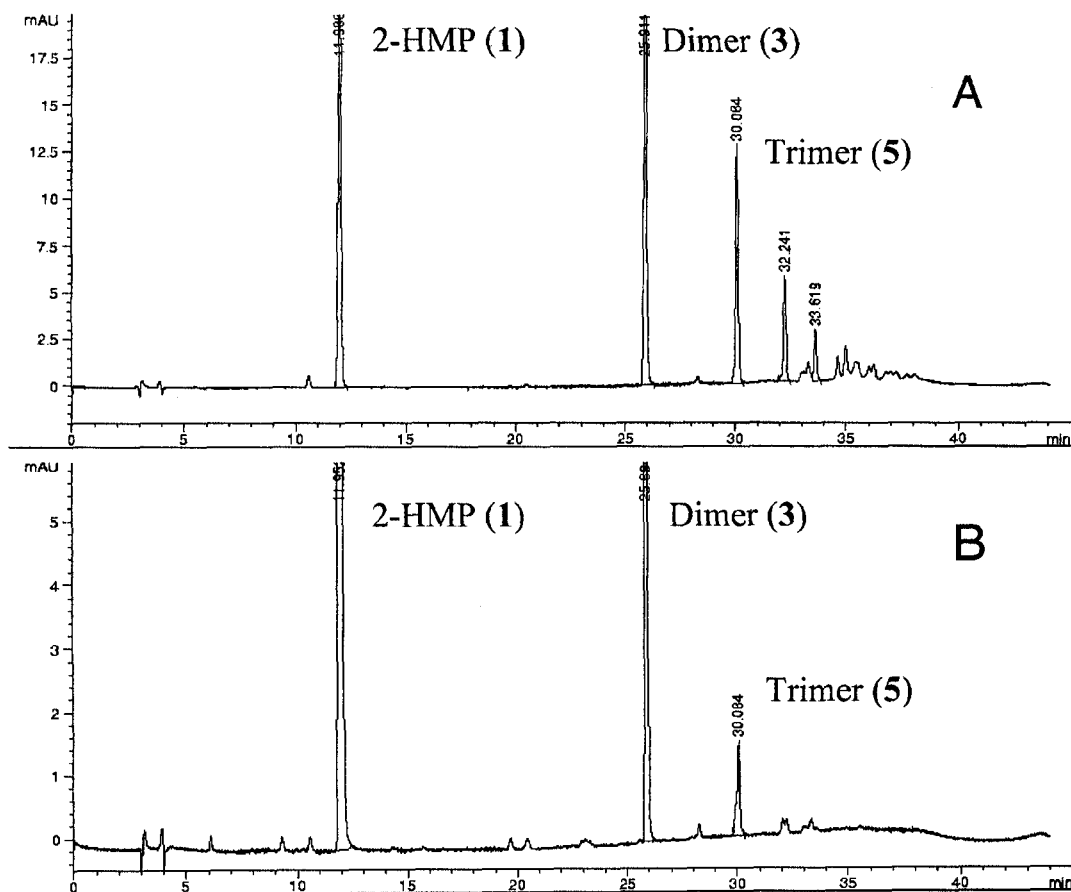


Figure 7 Comparison of (a) 2-HMP reacted at 20 °C with added propylene carbonate as cure accelerator and (b) 2-HMP reacted at 60 °C without added cure accelerator by HPLC.

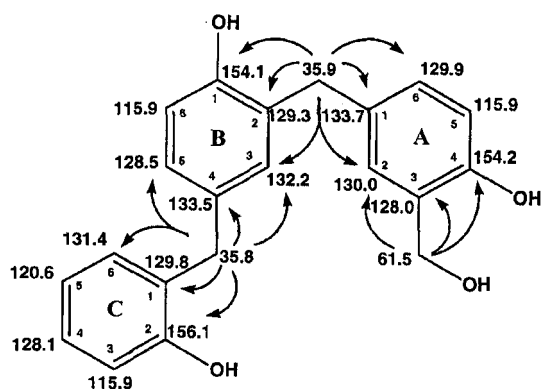


Figure 8 Assignment of experimental ^{13}C NMR data to proposed structure of trimer 5 isolated from self-condensation reaction of 2-HMP (1). Chemical shifts (ppm) for each carbon are indicated. Cross peaks in ^1H - ^{13}C long-range NMR correlation spectra were observed between hydrogen atom(s) on the carbon atom at which the arrows originate (hydrogen atoms not shown) and carbon atoms at the ends of the arrows.

were isolated by preparative TLC and analyzed by ^{13}C NMR. The ^{13}C NMR spectra and long-range ^1H - ^{13}C correlation spectra were consistent with the structures of dimer 3 and trimer 5 (Figure 8). The proposed structures of the isolated dimer and trimer were consistent with either the $\text{S}_{\text{N}}2$ or quinone methide mechanism. The ^{13}C NMR spectrum of dimer 3 closely matched the spectrum of the dimer with the same structure reported in the literature.¹⁴ The structures of the isolated products were consistent with the previous observation that the cure accelerator is not incorporated into the reaction products.

In agreement with reports in the literature^{14,16} we observed that 4-HMP reacted faster than 2-HMP in the absence of cure accelerators. In contrast, in the presence of cure accelerators, we found that 2-HMP reacted much faster than 4-HMP under the same reaction conditions (Figure 4). This result would seem to indicate that the phenolic oxygen somehow helps activate the esterified *ortho*-hydroxymethyl group towards reactivity. This result also indicates that the number and nature of the crosslinks in a PF resin cured with added cure accelerator might be different than those in a PF resin cured without an added cure accelerator. Indeed, recent ^{13}C NMR relaxation time studies suggest that PF resins cured with propylene carbonate as the cure accelerator are more flexible than PF resins cured without propylene carbonate.¹⁷

The reaction of 4-HMP with and without the addition of each of the cure accelerators resulted in the same mixture of condensation products. The reaction products of 4-HMP at 20 °C with added ethyl formate as the cure accelerator and at 60 °C without added cure accelerator are compared in Figure 9. Although the relative proportions of the individual products

varied, the same mixtures of condensation products were found in both reactions.

The results in Figures 4 and 10 show that the effect of ethyl formate on the condensation of 4-HMP was not as dramatic as its effect on 2-HMP. In fact, 4-HMP reacted much more slowly with added ethyl formate than did 2-HMP. Only 15% of 4-HMP reacted after 24 h compared with 48% of 2-HMP after 10 min. In contrast, without added cure accelerators, 4-HMP reacted much more quickly than 2-HMP, with 44% of 4-HMP compared with 9% of 2-HMP reacted after 24 h at 60 °C.

Three major condensation products formed from 4-HMP with added ethyl formate as the accelerator were isolated by preparative TLC and analyzed by ^{13}C NMR. The ^{13}C -NMR spectra were consistent with the structures of dimers 6 and 7 and trimer 8 (Figure 11). The ^{13}C NMR spectra of dimers 6 and 7 closely matched the spectra of the dimeric compounds reported in the literature.¹⁴ These observations are consistent with either the $\text{S}_{\text{N}}2$ or quinone methide mechanism.

CONCLUSIONS

1. Without added cure accelerators, the self-condensation reaction of 4-HMP is faster than the self-condensation reaction of 2-HMP.
2. Addition of cure accelerators to the reaction mixture dramatically increases the self-condensation rate of 2-HMP.
3. Addition of cure accelerators to the reaction mixture increases the self-condensation rate of 4-HMP, but not as dramatically as the self-condensation rate of 2-HMP.
4. With added cure accelerators, the self-condensation reaction of 4-HMP is slower than that of 2-HMP. This result suggests that the types and amounts of cross links in a cured PF resin might differ, depending on whether the resin was cured with or without added accelerator. This result further suggests that the properties of the respective cured resins might differ, as recently suggested by ^{13}C NMR relaxation time studies.¹⁷
5. The cure accelerators are consumed during the course of the reaction, which indicates that they are not acting as true catalysts.
6. The same mixture of condensation products resulted from the self-condensation reaction of 2-HMP (or 4-HMP) at 20 °C with added cure accelerator and at 60 °C without added cure accelerator. This result indicates that the cure accelerators are not incorporated into the condensation products.
7. The structures of the dimers and trimers isolated from the self-condensation reaction products of

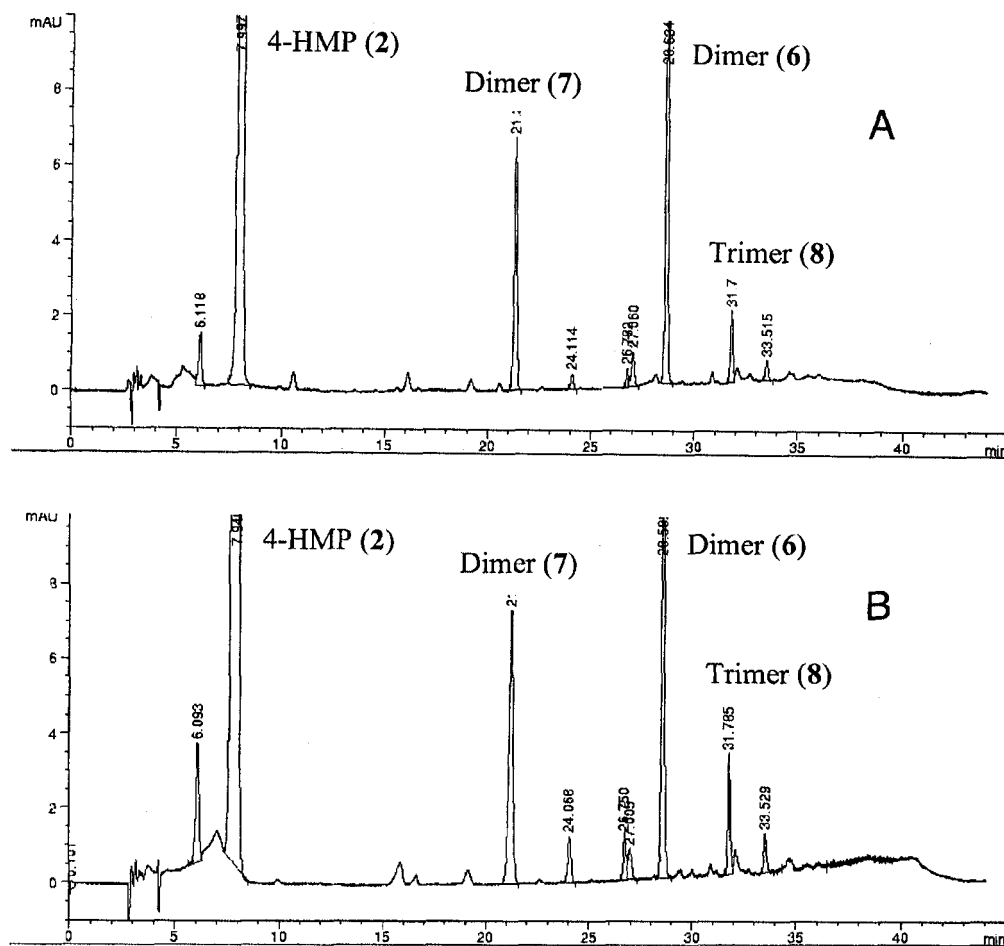


Figure 9 Comparison of (a) 4-HMP reacted at 20 °C with added ethyl formate as cure accelerator and (b) 4-HMP reacted at 60 °C without added cure accelerator by HPLC.

2-HMP (or 4-HMP) with added cure accelerators were the normal types of condensation products expected for the condensation of hydroxymeth-

ylphenols. This result further indicates that the cure accelerators are not incorporated into the condensation products.

8. The reaction products isolated from the self-condensation of 2-HMP (or 4-HMP) are consistent with either the quinone methide or S_N2 reaction mechanism.

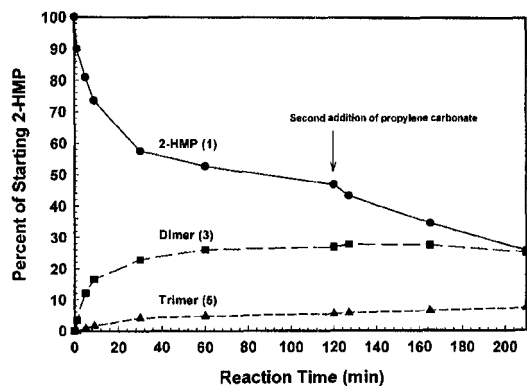


Figure 10 Reaction profile for self-condensation of 4-HMP (2) at 20 °C with added ethyl formate (filled symbols). Disappearance of 4-HMP at 20 °C without added ethyl formate (open symbols) is shown for comparison.

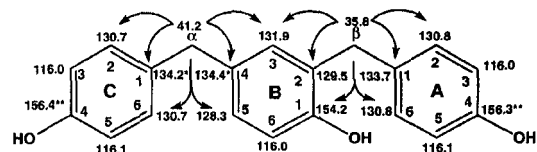


Figure 11 Assignment of experimental ^{13}C NMR data to proposed structure of trimer 8 isolated from self-condensation reaction of 4-HMP (2). Chemical shifts (ppm) for each carbon are indicated. Cross peaks in ^1H - ^{13}C long-range NMR correlation spectra were observed between hydrogen atom(s) on the carbon atom at which the arrows originate (hydrogen atoms not shown) and carbon atoms at the ends of the arrows.

We thank Adrian A. Cargill, Jr., for technical assistance in isolating the 4-HMP reaction products and Daniel O. Foster for obtaining the mass spectral data.

References

1. Detlefsen, W.D.; Phillips, E.K.; Norton, R.V. Composition and process for bonding lignocellulosic material. U.S. Patent 4,961,795, October 9, 1990.
2. Higuchi, M.; Tohmura, S.; Sakata, I. *Mokuzai Gakkaishi* 1994, 40, 604–611.
3. Miller, T.R.; Detlefsen, W.D. In *Wood Adhesives 2000*; Christiansen, A.W.; Conner, A.H., Eds.; Forest Products Society: Madison, Wisconsin, 2001; pp. 455–467.
4. Park, B.-D.; Riedl, B.; Hsu, E.W.; Shields, J. *Polymer* 1999, 40, 1689–1699.
5. Pizzi, A.; Garcia, R.; Wang, S. *J Appl Polym Sci* 1997, 66, 255–266.
6. Pizzi, A.; Stephanou, A. *J Appl Polym Sci* 1993, 49, 2157–2170.
7. Pizzi, A.; Stephanou, A. *Holzforschung* 1994, 48, 150–156.
8. Tohmura, S.; Higuchi, M. *Mokuzai Gakkaishi* 1995, 41, 1109–1114.
9. Zhao, W.; Pizzi, A.; Garnier, S. *J Appl Polym Sci* 1999, 74, 359–378.
10. Park, B.-D.; Riedl, B. *J Appl Polym Sci* 2000, 77, 841–851.
11. Park, B.-D.; Riedl, B.; Hsu, E.W.; Shields, J. *Wood Sci Technol* 2001, 35, 311–323.
12. Lorenz, L.F.; Conner, A.H. In *Wood Adhesives 2000*; Christiansen, A.W.; Conner, A.H., Eds.; Forest Products Society: Madison, Wisconsin, 2001; pp. 391–395.
13. Knop, A.; Scheib, W. *Chemistry and Application of Phenolic Resins*; Springer-Verlag: New York, 1979; pp. 28–59.
14. Grenier-Loustalot, M.-F.; Larroque, S.; Grenier, P.; Bedel, D. *Polymer* 1996, 37, 955–964.
15. Yeddapanalli, L.M.; Francis, D.J. *Makromol Chem* 1962, 55, 75–86.
16. Troughton, G.E. *Holzforschung* 1972, 26, 170–173.
17. Higuchi, M.; Urakawa, T.; Morita, M. *Polymer* 2001, 42, 4563–4567.
18. Jones, R.T. *J Polym Sci, Poly Chem Ed* 1983, 21, 1801–1817.
19. Tohmura, S.-I.; Higuchi, M.; Hattori, Y.; Sakata, I. *Mokuzai Gakkaishi* 1994, 40, 390–398.