Accelerated Cure of Phenol-Formaldehyde by the Addition of Cure Accelerators: Studies with Model Compounds

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Abstract

Fast curing phenol-formaldehyde (PF) resins could potentially allow wood to be bonded at higher moisture contents and at lower press temperatures than those currently used commercially. Recent reports in the literature have shown that the addition of esters, lactones, or organic carbonates increased the curing rate of PF resins. Several mechanisms have been proposed to explain the accelerated cure. The PF model compounds 2- and 4-hydroxymethyl phenol (2-HMP and 4-HMP) were reacted in alkaline conditions at 20°C, with and without cure accelerators, such as ethyl formate, propylene carbonate, g-butyrolactone, and triacetin. The disappearance of 2-HMP (or 4-HMP) and the appearance of reaction products with time were determined by high-pressure liquid chromatography (HPLC). The addition of cure accelerators significantly increased the rate of product formation from reactions that are similar to those that occur during the cure of PF resins. A dimeric and a trimeric reaction product were isolated by preparative thin-layer chromatography, and their structures were determined by ^{13}C-NMR spectroscopy. These results are consistent with a mechanism in which the hydroxymethylated phenol is esterified by the cure accelerator, facilitating its conversion to a reactive quinone methide intermediate.

Introduction

In general, low wood moisture contents and high pressing temperatures are required to use phenol-formaldehyde (PF) resins for bonding wood. Faster curing PF resins could potentially allow wood to be bonded at higher moisture contents and at lower press temperatures. Potential savings in energy use could be realized from the reduced extent of wood drying and the lower temperatures required for adhesive cure. Also, because the wood would be bonded closer to the moisture content expected for its final end use, the bonded assembly would undergo less dimensional change, leading to increased durability. Reduced drying times and lower press temperature would also result in lower emissions of volatile organic compounds during the manufacture of bonded wood composites. Recent reports in the literature have shown that adding compounds such as esters, lactones, or organic carbonates to PF resins increases their cure rates (1,3-10).

Several mechanisms have been proposed to explain the accelerated cure. Higuchi and others (3) and Tohmura and Higuchi (9) propose a mechanism in which the bicarbonate anion derived from polyethylene carbonate coordinates with two hydroxymethylated phenol molecules forming a transition state structure that facilitates reaction. Pizzi and Stephanou (7,8) propose a mechanism in which carbon dioxide from propylene carbonate is incorporated into the polymeric structure of the cured resin. Miller and Detlefsen (4) propose a mechanism in which the hydroxymethylated phenol is transesterified by an organic ester facilitating a faster conversion to a reactive quinone methide intermediate.

Results and Discussion

In this study, 2- and 4- hydroxymethyl phenol (2-HMP and 4-HMP respectively) were used as model compounds for studying the mechanism responsible for the acceleration. 2-HMP and 4-HMP were reacted under alkaline conditions at 20°C, with and without cure accel-

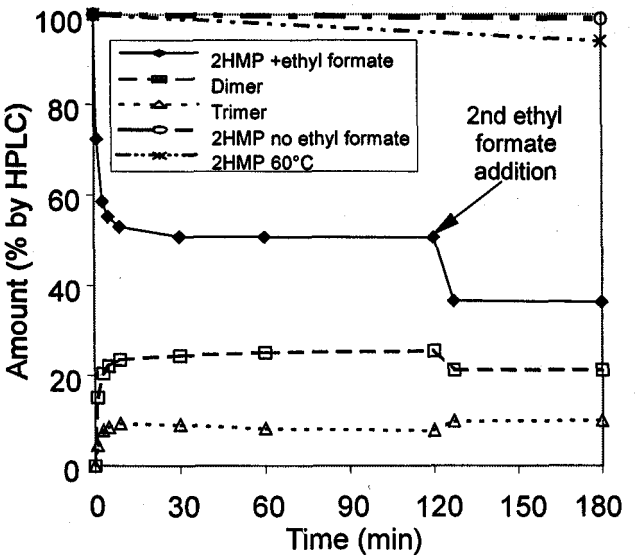


Figure 1. *–The effect of ethyl formate on the condensation of 2-HMR*

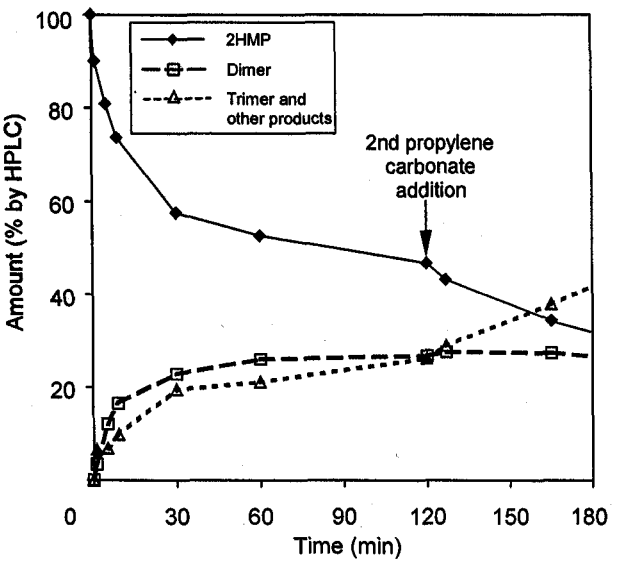


Figure 2. *–The effect of propylene carbonate on the condensation of 2-HMR*

erators and without formaldehyde. The cure accelerators used were ethyl formate, propylene carbonate, g-butyrolactone, and triacetin. The disappearance of 2-HMP (or 4-HMP) and the appearance of reaction products with time were determined by high-pressure liquid chromatography (HPLC). The reaction of 2-HMP with each of the four cure accelerators resulted in the same mixture of condensation products (Figs. 1, 2, and 3). In selected cases, reaction products were isolated by preparative thin-layer chromatography, and their structures were determined by carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectroscopy.

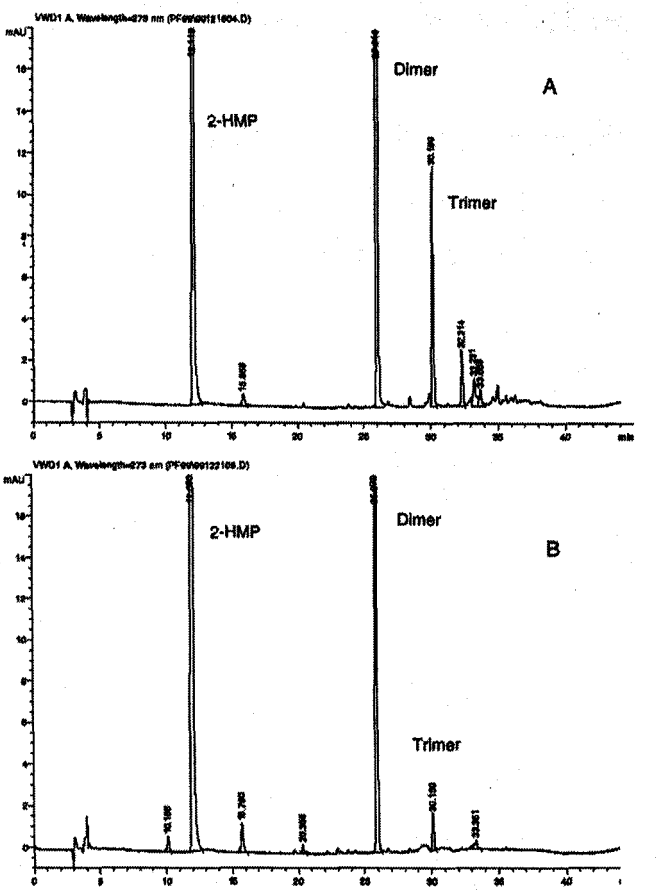


Figure 3. *–HPLC chromatograms of (A) 2-HMP reacted at 20°C with a cure accelerator and (B) 2-HMP reacted at 60°C without a cure accelerator.*

The data presented in Figure 1 show the dramatic effect that ethyl formate has on the condensation of 2-HMP. Without ethyl formate, the condensation of 2-HMP is very slow at 20°C; 90 percent remains unreacted after 24 hours. With ethyl formate, the condensation of 2-HMP is very fast; only 52 percent remains unreacted after 10 minutes. However, the condensation of 2-HMP slows appreciably after 30 minutes. Adding additional ethyl formate to the reaction mixture causes the rate of disappearance of 2-HMP to increase temporarily. Similar results are observed with propylene carbonate (Fig. 2). These results suggest that the cure accelerator does not act as a true catalyst as suggested by the mechanism proposed by Higuchi and others (3) and Tohmura and Higuchi (9). Instead, these data suggest the cure accelerator takes part in the reaction and is consumed as the reaction proceeds.

The mixtures of reaction products formed by reacting 2-HMP at 60°C without a cure accelerator and by reacting 2-HMP at 20°C with a cure accelerator were compared by HPLC (Fig. 3). These results indicate that the same mixtures of condensation products were

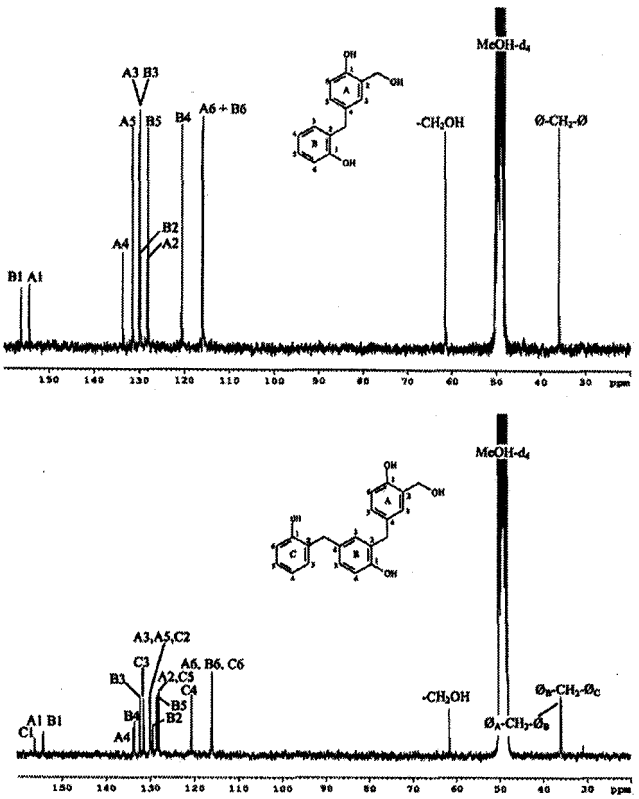


Figure 4. *–The major reaction products formed by the condensation of 2-HMP with ethyl formate. The structures for the isolated dimer and trimer were determined by ^{13}C-NMR.*

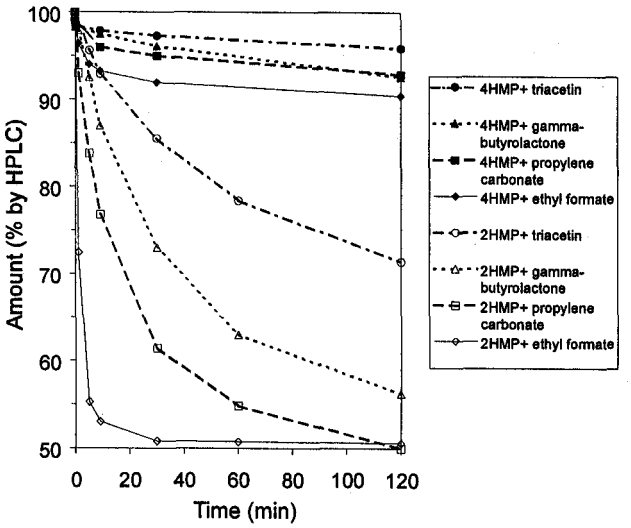
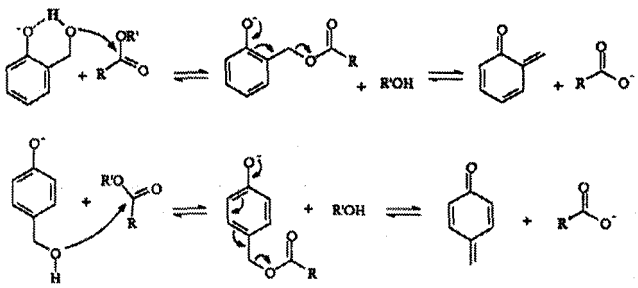


Figure 5. *–Comparison of the rates of disappearance of 2-HMP and 4-HMP reacted with cure accelerators under the same reaction conditions.*



Reaction 1.

formed in both reactions, although the relative proportions of the individual products varied. This suggests that no portion of the cure accelerator is incorporated into the reaction products and would appear to rule out the mechanism proposed by Pizzi and Stephanou (7,8).

The major reaction products formed by the condensation of 2-HMP with ethyl formate were isolated by preparative thin-layer chromatography, and their structures were determined by ^{13}C-NMR (Fig. 4). The structures of the isolated dimer and trimer are consistent with the observations above and with the reaction mechanism proposed by Miller and Detlefsen (4) for the reaction of cure accelerators with the hydroxymethyl groups present in PF resins.

Grenier-Loustalot and others (2) studied the self-condensation of methylolphenols and showed that 2-HMP disappears more slowly than does 4-HMP under the same reaction conditions. In contrast, we found that 2-HMP disappears much faster than 4-HMP in the presence of cure accelerators under the same reaction conditions (Fig. 5). In the presence of cure accelerators, 2-HMP reacts faster than 4-HMP because intramolecular hydrogen bonding with the phenolic oxygen makes the 2-hydroxymethyl group comparatively more nucleophilic than the 4-hydroxymethyl group and, therefore, more reactive for nucleophilic addition in transesterification, as shown in Reaction 1.

Without cure accelerators, intramolecular hydrogen bonding of 2-HMP reduces the effective charge on the phenolic oxygen, thereby reducing the rate of formation of the quinone methide. The effect of intramolecular hydrogen bonding on the rate of formation of the quinone methide explains why the self-condensation of 2-HMP is slower than that of 4-HMP as shown in Reaction 2.

Materials and Methods

Reaction of 2- and 4-hydroxymethylphenol with Cure Accelerators

Hydroxymethyl-phenol (2-HMP or 4-HMP; 0.8 mmol) was dissolved as a 10% solution in water: dimethylformamide (DMF) 5:1 (v/v), to which were added sodium hydroxide (NaOH, as a 10% solution, 0.4 mmol) and 0.3 mmol of ethyl formate, propylene carbonate, or g-butyrolactone, or 0.1 mmol of triacetin.

The pH of the reaction mixtures was 10, from 0 through 180 minutes. All the reactions were run at 20°C except the reactions without cure accelerator, which were run at 60°C.

HPLC Analysis of the Reaction Mixtures

Samples (10 µL) were removed from the reaction mixtures after 0, 1, 5, 10, 30, 60, and 120 minutes and diluted to 5.0 mL in methanol. The pH of the diluted samples was about 5, which is the pH of methanol without the samples. Ten mL 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 percent acetonitrile in water in 15 minutes, and then to 60 percent acetonitrile in water after 32.5 minutes at 1.0 mL/min. The eluted compounds were detected by UV 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 vs. time.

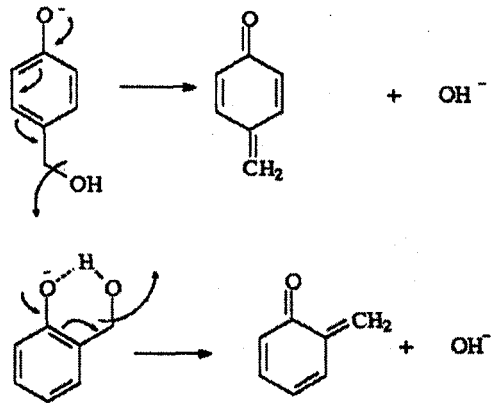
Isolation of Reaction Products of Hydroxymethyl Phenols with Cure Accelerators

After the last sample was removed for analysis by HPLC, the reaction mixture was neutralized with 10 percent acetic acid and extracted with an equal amount of 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, 80Å 1,000 µm thick, 20 by 20 cm, Whatman (Clifton, NJ)]. The plate was developed in chlorofordmethanol, 90: 10. The components were visualized with short-wave UV light. The silica gel containing each component was scraped off the plate, put into a vial, and eluted with chlorofordmethanol, 80:20. The solvent was decanted and evaporated to dryness. The residue was dissolved in methanol-d_4 for ^{13}C-NMR analysis.

^{13}C-NMR Analysis of the Reaction Products

The components isolated by TLC were dissolved in methanol-d_4 for analysis on a Bruker (Billerica, MA) DPX250 spectrometer. The ^{13}C-NMR spectrum, DEPT-135, short range (g-HSQC) and long range (g-HMBC) ^{1}H-^{13}C correlations were obtained using standard Bruker pulse sequences with a relaxation delay of 1 second. The ^{13}C-NMR spectrum (Fig. 4) shows assignments for the dimer:

methylene carbon (35.8 ppm);
hydroxymethyl carbon (61.4 ppm);
A6 and B6 (115.8 and 116.0 ppm);
B4 (120.5 ppm);
B5 (120.8 ppm);
A2 (128.2 ppm);



Reaction 2.

B2 (129.8 ppm);
A5 and B3 (129.9 and 131.5 ppm);
A3 (130.0 ppm);
A4 (133.6 ppm);
A1 (154.3 ppm); and
B1 (156.2 ppm).

Assignments for the trimer are:

methylene carbons (35.8 and 35.9 ppm);
hydroxymethyl carbon (61.5 ppm);
A6, B6, C6 (115.9 ppm);
C4 (120.6 ppm);
C5 (128.0 ppm);
A2 (128.1 ppm);
B5 (128.5 ppm);
B2 (129.3 ppm);
C2 (129.8 ppm);
A5 (129.9 ppm);
A3 (130.0 ppm);
C3 (131.4 ppm);
B3 (132.2 ppm);
B4 (133.5 ppm);
A4 (133.7 ppm);
B1 (154.1 ppm);
A1 (154.2 ppm); and
C1 (156.1 ppm).

Conclusions

Cure accelerators, such as ethyl formate, propylene carbonate, g-butyrolactone, and triacetin significantly increase the condensation rate of the PF model compounds 2-HMP and 4-HMR Without ethyl formate, the condensation of 2-HMP is very slow at 20°C; 90 percent remains unreacted after 24 hours. With ethyl formate, the condensation of 2-HMP is very fast, with only 52 percent unreacted after 10 minutes. Similar results were observed with the other cure accelerators.

The cure accelerators that were studied do not act as true catalysts but are consumed during the course of the reaction.

The same mixtures of condensation products were formed by 2-HMP reacted at 20°C with a cure accelerator and by 2-HMP reacted at 60°C without a cure accelerator.

The structures of the isolated dimer and trimer reaction products of the condensation of 2-HMP with a cure accelerator were determined by ^{13}C-NMR spectroscopy.

The data collected in this study are most consistent with the reaction mechanism proposed by Miller and Detlefsen (4) for the reaction of cure accelerators with hydroxy-methyl groups.

In the presence of cure accelerators 2-HMP reacts significantly faster than 4-HMP because intramolecular hydrogen bonding with the phenolic oxygen makes the 2-hydroxymethyl group comparatively more nucleophilic than the 4-hydroxymethyl group and, therefore, more reactive for nucleophilic addition in transesterification.

Acknowledgments

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Literature Cited

1. Detlefsen, W.D., E.K. Phillips, and R.V. Norton. 1990. Composition and process for bonding lignocellulosic material. U.S. Patent 4,961,795. Oct. 9.
2. Grenier-Loustalot, M.-F., S. Larroque, P. Grenier, and D. Bedel. 1996. Phenolic resins: 4. Self-condensation of methylolphenols in formaldehyde-free systems. Polymer. 37(6):955-964.
3. Higuchi, M., S. Tohmura, and I. Sakata. 1994. Acceleration of the cure of phenolic resin adhesives V. Catalytic actions of carbonates and formamide. Mokuzai Gakkaishi. 40(6):604-611.
4. Miller, T.R. and W.D. Detlefsen. 1999. A primer on phenol-formaldehyde resin for the wood products industry. *In*: Proc. FPS Annual Meeting. June 27. Forest Products Society, Madison, WI.
5. Park, G.D., B. Riedl, E.W. Hsu, and J. Shields. 1999. Differential scanning calorimetry of PF resins cure-accelerated by carbonates. Polymer. 40(7):1689-1699.
6. Pizzi, A., R. Garcia, and S. Wang. 1997. On the networking mechanisms of additives-accelerated PF polycondensates. J. of Appl. Polym. Sci. 66(2):255-266.
7. Pizzi, A. and A. Stephanou. 1993. On the chemistry, behavior, and cure acceleration of phenol-formaldehyde resins under very alkaline conditions. J. of Appl. Polym. Sci. 49(12):2157-2170.
8. Pizzi, A. and A. Stephanou. 1994. Phenol-formaldehyde wood adhesives under very alkaline conditions. Part II: Esters curing acceleration, its mechanism and applied results. Holzforschung. 48(2):150-156.
9. Tohmura, S. and M. Higuchi. 1995. Acceleration of the cure of phenolic resin adhesives VI. Cure-accelerating action of propylene carbonate. Mokuzai Gakkaishi. 41(12):1109-1114.
10. Zhao, W., A. Pizzi, and S. Garnier. 1999. Fast advancement and hardening acceleration of low-condensation alkaline PF resins by esters and copolymerized urea. J. of Appl. Polym. Sci. 74(2):359-378.