J Wood Sci (2004) 50:236–241
DOI 10.1007/s10086-003-0564-4

ORIGINAL ARTICLE

Naruyuki Kamo · Hiroyuki Okamura · Mitsuo Higuchi
Mitsuhiro Morita

Condensation reactions of phenolic resins V: cure-acceleration effects of propylene carbonate

Received: March 3, 2003 / Accepted: June 4, 2003

Abstract Propylene carbonate (PC) is known as one of the cure accelerators for alkaline phenol–formaldehyde resins. To elucidate the cure-acceleration mechanisms, the effects of PC on the condensation reactions of monomeric hydroxymethylphenols (HMPs) were investigated and compared with those of PC hydrolysate, sodium bicarbonate ($NaHCO_3$) and ethyl formate. Immediately after the reaction started, PC, decomposing itself simultaneously, accelerated the formation of the *ortho-para* methylene-bonded dimer of 2,4,6-trihydroxymethylphenol. This effect of PC was very similar to that of ethyl formate. To the contrary, PC hydrolysate accelerated the formation of the *para-para* methylene-bonded dimer throughout the course of the reaction. This effect of PC hydrolysate was identical to that of $NaHCO_3$. These results indicate that PC increases the reactivity of the *ortho*-hydroxymethyl group, presumably through transesterification. On the other hand, $NaHCO_3$ is formed by the hydrolysis of PC or decomposition of the transesterified HMPs and it increases the reactivity of the *para*-hydroxymethyl group.

Key words Phenolic resin · Propylene carbonate · Cure acceleration · Self condensation · Hydroxymethylphenol

Introduction

Alkaline phenol–formaldehyde (PF) resin is one of the most important adhesives for manufacturing composite wood materials. Its usefulness will be widened if the cure conditions (high temperature and long duration) can be mitigated. Many researchers have studied cure acceleration of PF resin, and advanced prepolymerization and use of cure accelerators have achieved considerable improvements. However, PF resin still needs curing temperatures higher (about 10°C) than those for amino resins. To seek further improvement, the mechanisms of curing reactions of PF resins and the actions of the cure accelerators need to be elucidated. Thus, in this article, the actions of propylene carbonate (PC), one of the well-known cure accelerators, are discussed.

As to the cure-accelerating actions of PC, there are some discrepant experimental results and interpretations. Pizzi and Stephanou[1–3] reported that PC reacted with phenols to form cross-linkages between phenolic rings. On the other hand, Tohmura et al.[4] compared the effect of PC with that of sodium carbonate (Na_2CO_3) and found that there was no difference between the effects of the two accelerators. They reported that the accelerating effect of PC was ascribed to the catalytic action of sodium bicarbonate ($NaHCO_3$) formed by the hydrolysis of PC. Furthermore, they reported that infrared absorptions for 1,4-disubstituted phenols and 1,2,4-trisubstituted phenols, which had been reported by Pizzi Stephanou, were not detected. Later, Pizzi et al.[5] investigated the cure behavior of PF resin with added PC and with Na_2CO_3 by thermomechanical analysis (TMA) and argued that PC acted as a reactant. Park et al.[6] and Park and Riedl[7] analyzed the cure behavior of the PF resin by differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) spectroscopy, and reported that the cure behavior of resin with added PC differed from that of the resin with added Na_2CO_3, supporting the mechanism proposed by Pizzi et al. Conner et al.[8] studied the self-condensation reactions of 2-hydroxymethylphenol (2-HMP) and 4-hydroxymethylphenol (4-HMP) with the addition of some esters (PC, ethyl formate, and others). They found that PC as well as the other esters accelerated the self condensation of 2-HMP significantly while it accelerated that of 4-HMP to a lesser extent, and supported the mechanism proposed by Miller and Detlefsen[9] in which the hydroxymethyl group was transesterified by an organic ester, facilitating a fast conversion to a reactive quinone methide intermediate. In this study, some hydroxymethylphenols (HMPs), 2-HMP, 4-HMP, and 2,4,6-

N. Kamo · H. Okamura · M. Higuchi · M. Morita (✉)
Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
Tel. +81-92-642-2996; Fax +81-92-642-2996
e-mail: mimorita@agr.kyushu-u.ac.jp

trihydroxymethylphenol (THMP), were used as model compounds and the effects of PC on the condensation reactions of those HMPs are discussed.

Materials and methods

Chemicals

Phenol (99%), formaldehyde (37%), sodium hydroxide (96%), propylene carbonate (97%), sodium bicarbonate (99.8%), and ethyl formate (97%) were purchased from Wako. 2-HMP (99%) was purchased from Tokyo Kasei Kogyo. 4-HMP (99%) was purchased from Aldrich. THMP was prepared by the procedure described in the previous paper.[10]

Observation of reaction procedures

Each of the HMPs or phenol was dissolved in an aqueous NaOH solution with cooling and then each accelerator (PC, PC hydrolysate, $NaHCO_3$, and ethyl formate) was added in the solution. PC hydrolysate was made by the reaction of PC with an aqueous NaOH solution at 70°C for 1 hour. One-milliliter portions of the solution were sealed in glass ampoules. Each ampoule was immersed in a constant-temperature bath for its allotted time to make the reaction progress. Then the ampoule was cooled in an ice–water bath. For high performance liquid chromatography (HPLC) analyses, the contents were diluted with an acetonitrile–water solution containing acetic acid of a required amount for neutralizing the reaction system. After being made to a known volume with the use of a volumetric flask, the reaction system was subjected to HPLC analyses. Reaction products were identified by NMR analyses and by HPLC analyses with the use of authentic samples. The changes in the concentrations of the monomeric HMPs during the reactions were calculated from the corresponding peak areas of the HPLC chromatograms. The concentrations of the reaction products were determined from the corresponding peak areas of the HPLC chromatograms with the use of calibration curves prepared with the use of authentic samples. The errors involved in the concentrations of the HMPs determined by this method were confirmed to be lower than 1%, and the reproducibility of each reaction was checked by a duplicate experiment.

HPLC analysis

A Waters 600 liquid chromatograph with a Waters 486 UV and a Waters 410 refractive index (RI) detector was used. The following conditions were adopted: column: Inertsil ODS-3 (5μm, 4.6 × 250mm) (GL Science); water–acetonitrile gradient system for phenol and 2-HMP systems: starting with water/acetonitrile volume ratio of 95/5, 90/10 at 10min, 80/20 at 15min, 70/30 at 20min, 30/70 at 25min, 0/100 after 40min; for 4-HMP and THMP systems: starting with water/acetonitrile volume ratio of 85/15, 30/70 at 10min, 0/100 after 30min; flow rate: 1.0ml/min; column temperature: 25°C; UV detection: 280nm.

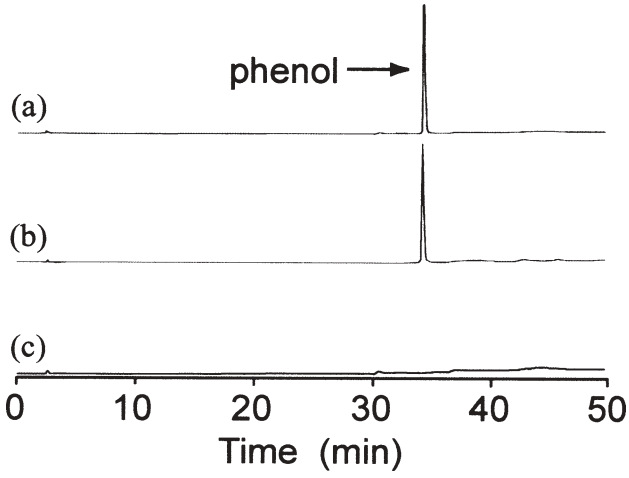


Fig. 1. HPLC chromatograms of the reaction systems of phenol–NaOH–PC (**a**), phenol–NaOH (**b**), and NaOH–PC (**c**). PC, propylene carbonate. Reaction conditions: 0.2mol/l phenol; phenol/NaOH/PC 1:1:1 molar ratio; 80°C; 120min; UV detection

NMR analysis

A JEOL JNM-AL 400FT NMR spectrometer was used. ^{13}C-NMR spectra were obtained with the use of deuterium oxide (D_2O) as the solvent and sodium-3-(trimethylsilyl) propionate-2,2,3,3-d_4 (TSP-d_4) as the internal standard.

Results and discussion

Reaction products in the reactions of phenol and HMPs with PC

Figure 1 shows the HPLC chromatograms of the reaction systems of phenol–NaOH, phenol–NaOH–PC, and NaOH–PC. Only one peak assigned to phenol was observed, and no other reaction products could be detected in the phenol–NaOH–PC system. Figure 2 shows the HPLC chromatograms of the reaction systems of THMP with and without PC. There was no difference in the species of reaction products although some difference was observed in the amount of each reaction product. The same features were observed in the reaction systems of 2-HMP and 4-HMP with and without PC. These results indicate that PC or its fragments were not taken into the structures of condensation products. Thus, the mechanism proposed by Pizzi and Stephanou[1–3] and Pizzi et al.[5] is considered to be of no significance.

Change of PC in the reaction systems

Figure 3 shows the HPLC chromatograms of a reaction system of THMP with PC. As seen in Fig. 3b, PC disap-

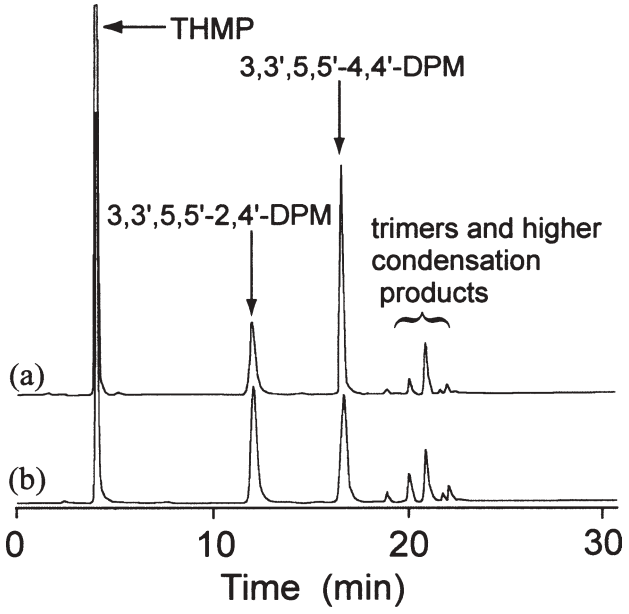


Fig. 2. HPLC chromatograms of the reaction systems of 2,4,6-trihydroxymethyl phenol (*THMP*) with PC (**a**), and without PC (**b**). Reaction conditions: 0.2 mol/l THMP; NaOH/THMP 0.4 molar ratio; PC/THMP 0.1 molar ratio (**a**); 70°C; 30 min (**a**), 60 min (**b**); UV detection

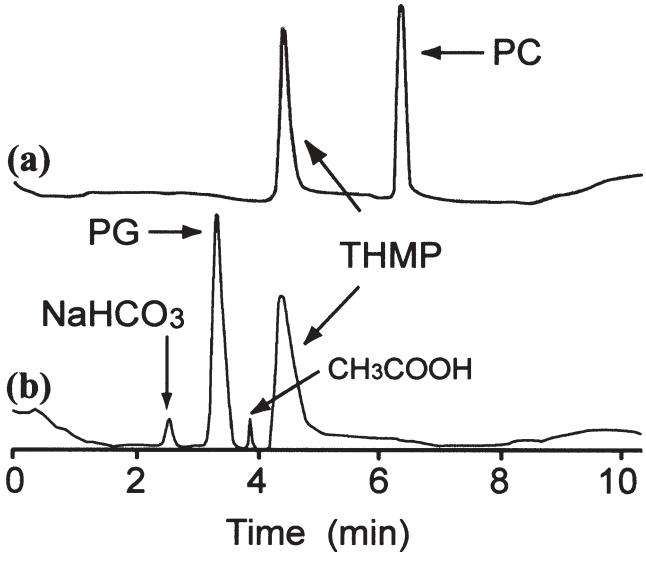


Fig. 3. HPLC chromatograms of the reaction systems of THMP with PC before reaction (**a**), and after 10 s of reaction (**b**). Reaction conditions: 0.2 mol/l THMP; THMP/NaOH/PC 1:0.4:0.1 molar ratio; 70°C; RI refractive index detection. *PG*, propylene glycol

peared in 10 s at 70°C to form propylene glycol (PG) and $NaHCO_3$. The same features were observed in the reaction systems of 2-HMP and 4-HMP with PC. Thus, it is clear that the action of PC is specific to the very early stage of reaction.

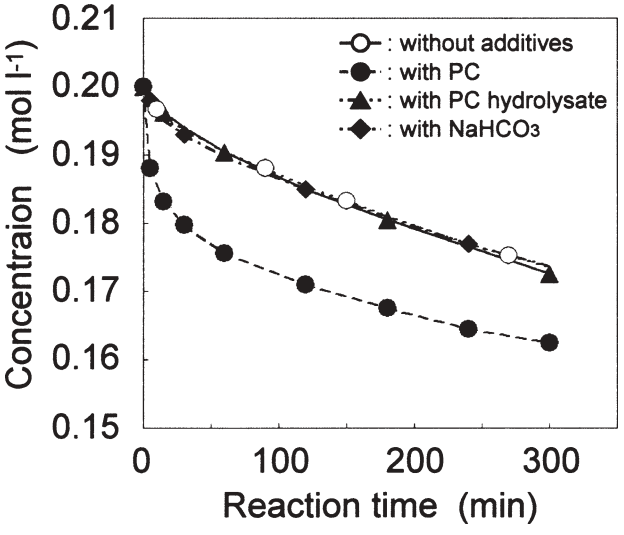


Fig. 4. Time courses of the disappearance of 2-hydroxymethyl phenol (2-HMP) in the reaction systems with and without additives. Reaction conditions: 0.2 mol/l 2-HMP; 2-HMP/NaOH/additive 1:0.2:0.1 molar ratio; 70°C

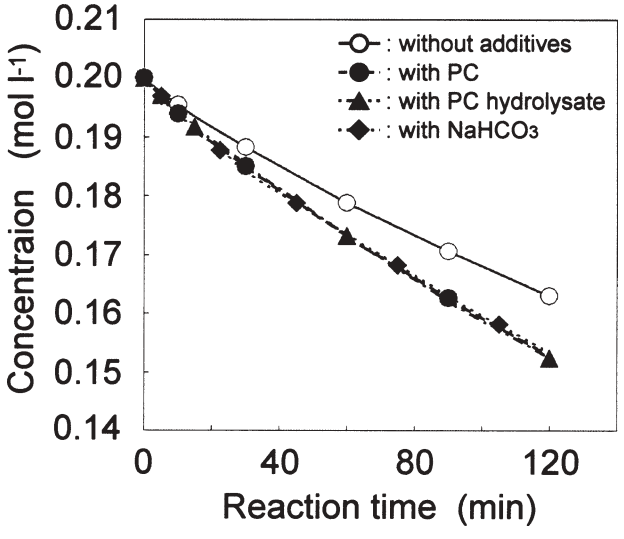


Fig. 5. Time courses of the disappearance of 4-HMP in the reaction systems with and without additives. Reaction conditions: 0.2 mol/l 4-HMP; 4-HMP/NaOH/additive 1:0.3:0.1 molar ratio; 70°C

Effects of PC and PC hydrolysate on the self condensation of HMPs

Figure 4 shows the time courses of the disappearance of 2-HMP. In the 2-HMP–NaOH–PC system, the concentration of 2-HMP significantly decreased immediately after the reaction started. On the other hand, the addition of PC hydrolysate did not affect the rate of decrease in the concentration of 2-HMP.

Figure 5 shows the time courses of the disappearance of 4-HMP. PC and PC hydrolysate increased the rate of decrease in 4-HMP concentration. However, the effects of PC and PC hydrolysate were not so significant as that of PC on

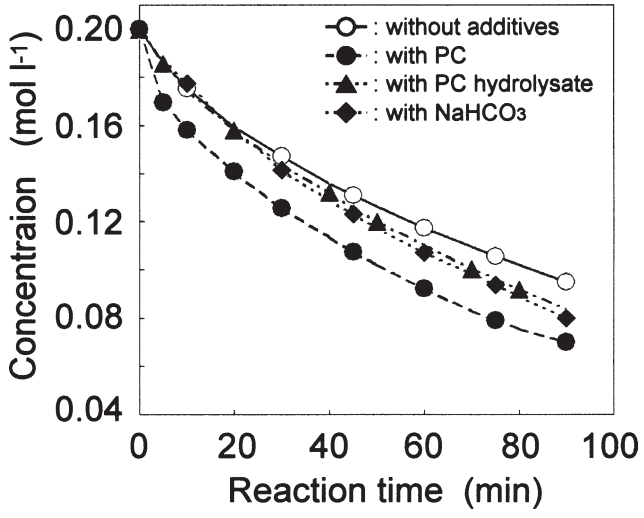


Fig. 6. Time courses of the disappearance of THMP in the reaction systems with and without additives. Reaction conditions: 0.2 mol/l THMP; THMP/NaOH/additive 1:0.4:0.1 molar ratio; 70°C

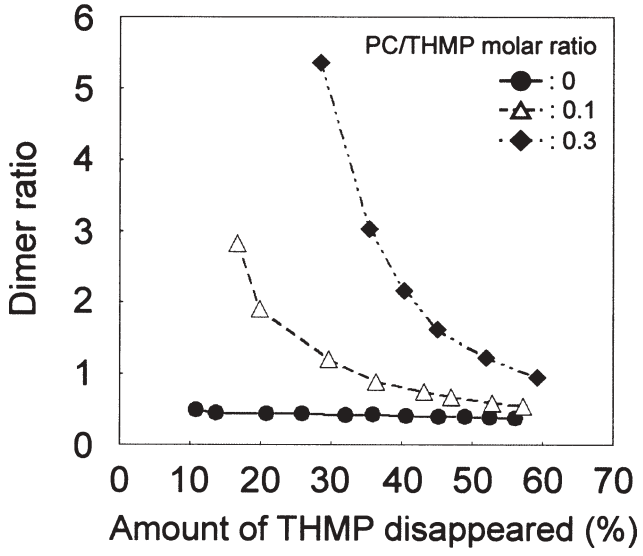


Fig. 7. Effect of PC on THMP dimer formation. Dimer ratio: [*ortho-para* methylene-bonded dimer formed]/[*para-para* methylene-bonded dimer formed]. Reaction conditions: 0.2 mol/l THMP; NaOH/THMP 0.4 molar ratio; 70°C

the condensation of 2-HMP, and they were present for the duration of the reaction. In addition, the effects were very similar to that of $NaHCO_3$.

Figure 6 shows the time courses of the disappearance of THMP. Both PC and PC hydrolysate increased the rate of THMP disappearance. With the addition of PC, the concentration of THMP significantly decreased immediately after the reaction started, as in the case of 2-HMP with PC. On the other hand, the effect of PC hydrolysate was very similar to that of $NaHCO_3$ just as in the case of 4-HMP.

From the above results, it is considered that PC affects the reactivity of the *ortho*-hydroxymethyl group of HMP and that PC hydrolysate, like $NaHCO_3$, affects the reactivity of the *para*-hydroxymethyl group of HMP.

Effects of PC and PC hydrolysate on dimer formation in the self condensation of THMP

In the early stage of self condensation of THMP, two dimers, 3,3′,5,5′-tetrahydroxymethyl-2,4′-dihydroxydiphenylmethane (3,3′,5,5′-2,4′-DPM) and 3,3′,5,5′-tetrahydroxymethyl-4,4′-dihydroxydiphenylmethane (3,3′,5,5′-4,4′-DPM), were formed (Fig. 2). Figure 7 shows the effect of PC on the ratio of the two dimers formed, [3,3′,5,5′-2,4′-DPM]/[3,3′,5,5′-4,4′-DPM]. PC significantly accelerated the formation of 3,3′,5,5′-2,4′-DPM (*ortho-para* methylene-bonded dimer) immediately after the reaction started and the effect increased with the amount of PC added. However, it did not affect the formation of 3,3′,5,5′-4,4′-DPM (*para-para* methylene-bonded dimer). Thus, it can be said that PC increases the reactivity of *ortho*-hydroxymethyl groups.

Figure 8 shows a ^{13}C-NMR spectrum of the reaction system of THMP with PC at the early stage of reaction. No signals for *ortho-ortho* (30.2 ppm) and *para-para* (40.2 ppm) methylene bonds are observed but that for the *ortho-para* methylene bond (34.6 ppm) is observed in this spectrum. It must be noted that propylene glycol, one of the products of PC hydrolysis, is detected in this spectrum. Thus, it is considered that PC accelerates the formation of *ortho-para* methylene bond with the decomposition of itself.

Figure 9 shows the effect of PC hydrolysate on THMP dimer formation. PC hydrolysate accelerated the formation of 3,3′,5,5′-4,4′-DPM (*para-para* methylene-bonded dimer) but it did not affect the formation of 3,3′,5,5′-2,4′-DPM (*ortho-para* methylene-bonded dimer). Thus, it can be said that PC hydrolysate increases the reactivity of the *para*-hydroxymethyl group. Moreover, because the same behavior as that of $NaHCO_3$ was observed, it is said that the substantial action of PC hydrolysate is the catalytic action of $NaHCO_3$ (Fig. 10).

Effects of ethyl formate on the self condensation of THMP

The addition of ethyl formate (EF) accelerated the disappearance of THMP and the formation of the *ortho-para* methylene-bonded dimer immediately after the reaction started. Figure 11 shows the effect of EF on THMP dimer formation compared with that of PC. The effect of EF is similar to that of PC, although the former is more significant. From this similarity, it is considered that PC accelerates the reaction as an ester affecting *ortho*-hydroxymethyl groups. Incidentally, the difference in the acceleration effect between PC and EF may be due to the difference in the steric hindrance in the transesterification reaction: the former is considered to be less reactive owing to its cyclic structure and larger molecular size. However any compounds that indicate the transesterification of HMPs[8,9] were not detected in this study. If the transesterification of HMPs

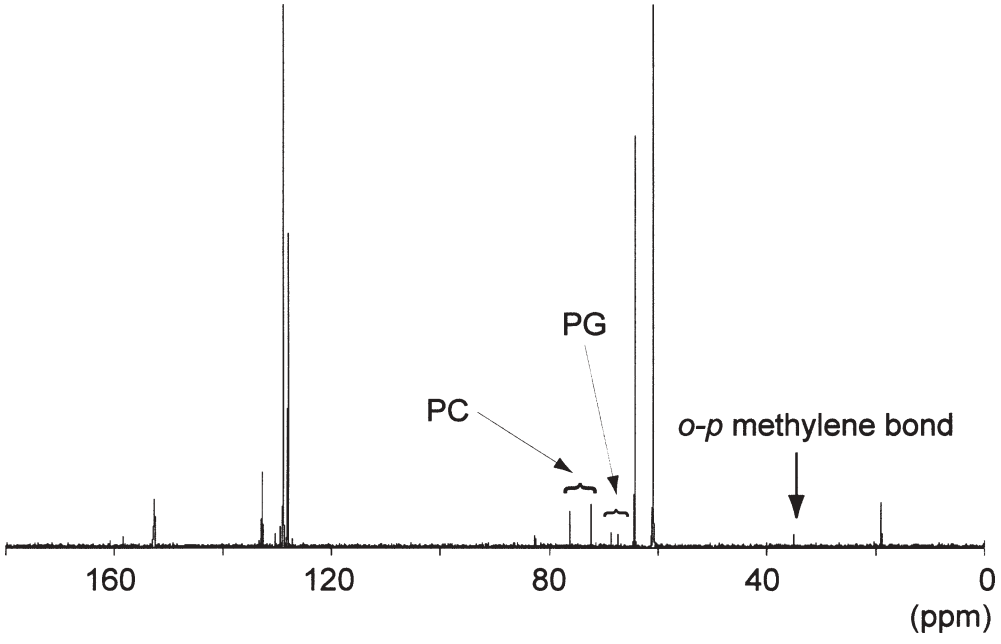


Fig. 8. ^{13}C-NMR spectrum of a reaction system of THMP with PC. Reaction conditions: 0.2 mol/l THMP; THMP/NaOH/PC 1:0.4:0.1 molar ratio; 20°C; 30 min

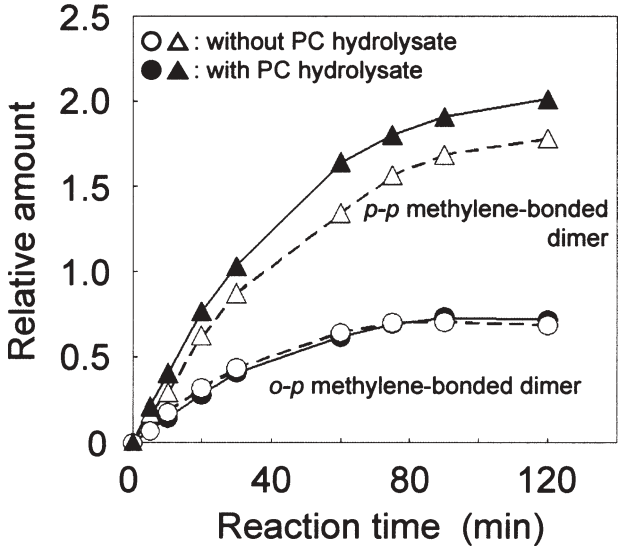


Fig. 9. Effect of PC hydrolysate on THMP dimer formation. Reaction conditions: 0.2 mol/l THMP; *open circles*, *open triangles*, without PC hydrolysate, NaOH/THMP molar ratio 0.3; *filled circles*, *filled triangles*, with PC hydrolysate, THMP/NaOH/PC hydrolysate 1:0.4:0.1 molar ratio; 70°C

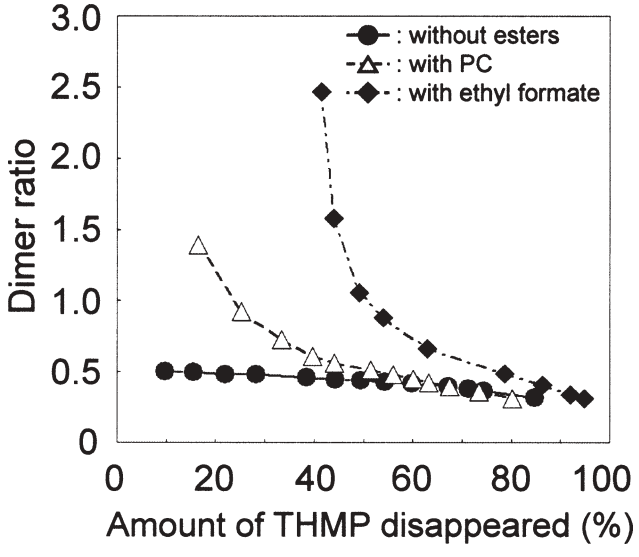


Fig. 11. Effect of ethyl formate on THMP dimer formation compared with that of PC. Reaction conditions: 0.2 mol/l THMP; *filled circles*, without esters, NaOH/THMP 0.3 molar ratio; *filled diamonds*, with ethyl formate, THMP/NaOH/ethyl formate 1:0.4:0.1 molar ratio; *open triangles*, with PC, THMP/NaOH/PC 1:0.4:0.1 molar ratio; 70°C

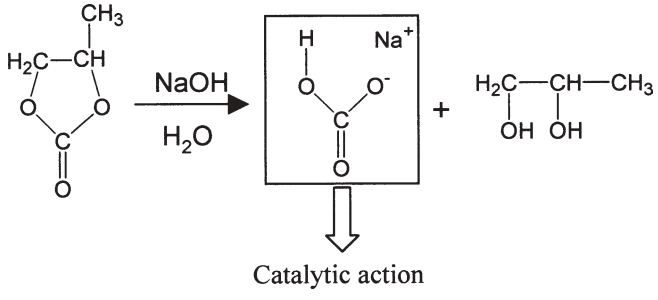


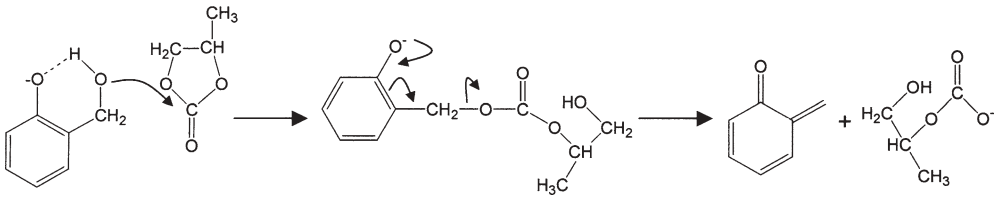
Fig. 10. Formation of $NaHCO_3$ by the hydrolysis of PC

(Fig. 12) occurs, the transesterified HMPs would be very unstable and go into subsequent reactions immediately after formation.

Conclusions

By analyses of the reaction systems of HMPs with and without PC, PC hydrolysate, and $NaHCO_3$, it was confirmed that PC or its fragments were not taken into the structures of condensation products. Immediately after the reaction

Fig. 12. Transesterification of HMP by PC



started, PC, decomposing itself simultaneously, accelerated the disappearance of 2-HMP and THMP, but it did not affect the disappearance of 4-HMP. To the contrary, PC hydrolysate accelerated the disappearance of 4-HMP and THMP, but it did not affect the disappearance of 2-HMP. Although the effect of PC hydrolysate on the disappearance of 4-HMP and THMP was not as significant as that of PC on the disappearance of 2-HMP and THMP, it lasted throughout the course of the reaction. PC accelerated the formation of the *ortho-para* methylene-bonded dimer of THMP, but it did not affect the formation of the *para-para* methylene-bonded dimer. To the contrary, PC hydrolysate accelerated the formation of the *para-para* methylene-bonded dimer of THMP and it did not affect the formation of the *ortho-para* methylene-bonded dimer. This effect of PC hydrolysate was identical to that of $NaHCO_3$. The effect of PC on the formation of THMP dimers was very similar to that of EF. These results indicate that PC increases the reactivity of the *ortho*-hydroxymethyl group, presumably through the transesterification proposed by Miller and Detlefsen.[9] On the other hand, $NaHCO_3$ is formed by the hydrolysis of PC or decomposition of the transesterified HMPs and it increases the reactivity of the *para*-hydroxymethyl group.

References

1. Pizzi A, Stephanou A (1993) On the chemistry, behavior, and cure acceleration of phenol–formaldehyde resins under very alkaline conditions. J Appl Polym Sci 49:2157–2170
2. Stephanou A, Pizzi A (1993) Rapid-curing lignin-based exterior wood adhesives. II. Holzforschung 47:501–506
3. Pizzi A, Stephanou A (1994) Phenol–formaldehyde wood adhesives under very alkaline conditions. II. Holzforschung 48:150–156
4. Tohmura S, Higuchi M (1995) Acceleration of the cure of phenolic resin adhesives VI. Mokuzai Gakkaishi 41:1109–1114
5. Pizzi A, Garcia R, Wang S (1997) On the networking mechanisms of additives-accelerated phenol–formaldehyde polycondensates. J Appl Polym Sci 66:255–266
6. Park BD, Riedl B, Hsu EW, Schields J (1999) Differential scanning calorimetry of phenol–formaldehyde resins cure-accelerated by carbonates. Polymer 40:1689–1699
7. Park BD, Riedl B (2000) ^{13}C-NMR study on cure-accelerated phenol–formaldehyde resins with carbonates. J Appl Polym Sci 77:1284–1293
8. Conner AH, Lorenz LF, Hirth KC (2002) Accelerated cure of phenol–formaldehyde resins. J Appl Polym Sci 86:3256–3263
9. Miller TR, Detlefsen WD (2000) A primer on phenol–formaldehyde resin for the wood products industry. Proceedings of the Wood Adhesives 2000 symposium, NV, USA, pp 455–467
10. Kamo N, Higuchi M, Yoshimatsu T, Ohara Y, Morita M (2002) Condensation reactions of phenolic resins III. J Wood Sci 48:491–496