^{13}C-NMR Study on Cure-Accelerated Phenol–Formaldehyde Resins with Carbonates

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ABSTRACT: Both liquid- and solid-state ^{13}C-NMR spectroscopies were employed to investigate the cure-acceleration effects of three carbonates [propylene carbonate (PC), sodium carbonate (NC), and potassium carbonate (KC)] on liquid and cured phenol–formaldehyde (PF) resins. The liquid-phase ^{13}C-NMR spectra showed that the cure-acceleration mechanism in the PC-added PF resin seemed to be involved in increasing reactivity of the phenol rings, while the addition of both NC and KC into PF resin apparently resulted in the presence of *ortho–ortho* methylene linkages. Proton spin-lattice rotating frame relaxation time ($T_{1\rho H}$) measured by solid-state ^{13}C-CP/MAS-NMR spectroscopy was smaller for the cure-accelerated PF resins than for that of the control PF resin. The result indicated that cure-accelerated PF resins are less rigid than the control PF resin. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 841–851, 2000

Key words: PF resin; carbonates; cure acceleration; solid-state ^{13}C-NMR; $T_{1\rho H}$

INTRODUCTION

Phenolic resins made from the reaction of phenol with formaldehyde were among the first fully synthetic polymers, discovered by Baekeland, and still find very wide commercial applications.[1] Phenol–formaldehyde (PF) resin is classified as an exterior adhesive due to its resistance to water, weathering, and high temperature in the cured glue line. In addition, formaldehyde emission from PF resin–bonded wood products is nearly nonexistent. Because of these aspects, the use of PF resin in these materials as a binder would provide high durability and stability. However, a major drawback that has prevented wider use of PF resins in the manufacture of particleboard and fiberboard is its slow curing speed. Traditionally, urea–formaldehyde (UF) resin has been used for those materials as a binder. In spite of its low cost and proven performance in wood panels, the poor durability and stability of UF-bonded wood panels limits its uses to interior and nonstructural applications such as furniture production and decorative panels. In all, these limitations are evident in strength losses, irreversible swelling of UF-bonded composite panels, and formaldehyde release, especially in high humidity environments.[2]

The slow cure rate of PF resin can be enhanced through cure acceleration. The cure acceleration of very alkaline PF resins for foundry core binders was pioneered in the early 1970s.[3] The addition of considerable amounts of esters such as propylene carbonate, methyl formate, and glycerol triacetate were found to accelerate resin cure to short times.[4,5] The proposed mechanisms are based on the carbanion behavior of aromatic nuclei of phenate ions.[4] In other words, the ester, or residue of its decomposition, attacks the negatively charged phenolic nuclei in a polycondensation re-

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action, resulting in higher functionality (greater than 3) in the addition step to reactive methylol groups. This could lead to much earlier gelling of PF resin. Tohmura and coworkers[6,7] proposed that the catalytic action of the hydrogencarbonate ion produced by the reaction between sodium hydroxide and propylene carbonate is responsible for the cure acceleration of propylene carbonate. Using differential scanning calorimetry (DSC) analysis, in 1999 Park et al.[8] also showed that carbonates have a cure-acceleration effect in PF resole resin systems. They reported that the addition of propylene carbonate into PF resole resin followed autocatalytic reaction kinetics, while the addition of both sodium and potassium carbonates into PF resin followed *n*th-order reaction kinetics.

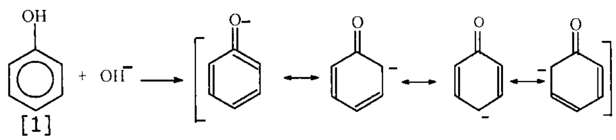
In the last decades many liquid-state ^{13}C-NMR studies have yielded useful information concerning the position of linkages between the phenol rings.[9–16] However, the disadvantages of this technique are the possible influence of solvent and the severe solubility problems for cured resins. The insolubility of the cured resins makes most chemical techniques ineffective for chemical characterization of cured PF resins. However, solid-state carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectroscopy analysis has been used in the study of solid materials. This technique provides an opportunity to directly probe the network structure of the cured resin under nondestructive conditions. In addition, structural information can be obtained from the solid-state spectra while relative molecular mobility can be determined by measuring the proton rotating-frame spin-lattice relaxation time ($T_{1\rho H}$).

In recent years, there have been major advances in solid-state high-resolution ^{13}C-NMR. By a combination of cross polarization with high-power ^{1}H decoupling, accompanied by high-speed magic-angle spinning techniques (CP/MAS), high-resolution ^{13}C-NMR spectra of solid materials can be obtained.[17] The CP technique generates sensitivity-enhanced carbon signals through the transfer of the magnetization from the proton (^{1}H) to the carbon (^{13}C) spins. The MAS method enables the resolving of the resonance of chemically different types of carbons. The probing conditions for solid-state ^{13}C-CP/MAS-NMR vary depending on the authors and purposes of studies. The spinning rates ranged from 2.2 to 5 KHz. The contact times were 0.03 to 2 ms, with a delay time range of from 1 to 30 s. According to the literature, the most often used probing conditions are 3.5–4.0 kHz, 1 ms, and 1 s for the spinning rate, contact time, and delay time, respectively.[18–22]

Using cured novolak and resole PF resins, Fyfe et al.[18] reported that high-resolution CP/MAS techniques reveal the chemical and structural differences in the cured solid resins. They also distinguished nonprotonated carbons from protonated carbon using dipolar dephasing (DD) method, which consists of the insertion of a short delay ($\sim$ 50–100 μs) into the normal cross-polarization sequence between the cross-polarization/spin-locking step and the data acquisition. Subsequently, the magnetization of those carbons with directly bonded protons is rapidly destroyed due to the large proton–carbon dipolar interactions, while that of those carbons with no attached protons is relatively unaffected. The net result is that signals are observed for the latter carbons. Maciel et al.[19] reported $T_{1\rho H}$ to be in the range of 3–10 ms for cured PF resole resins. The authors concluded for the first time that the hydroxyl group of the phenol ring and the methylene bridges were directly involved in the curing process.

Probing neat and substituted PF resins, Shina and Blum[20] showed that the DD method gave better spectral resolution for the substituted compounds. Applying three magnetic fields (1.41, 2.35, and 4.70 T)and using different frequencies (15.1, 25.1, and 50.3 MHz), Bryson et al.[21] reported that there was no real gain in resolution at a higher field, although sensitivity was better at higher fields. They also found that, as the curing process progresses, the peak intensity of the unsubstituted carbon region (115–130 ppm) decreases while the methylene linkage carbons (30–40 ppm) increases in its peak intensity.

According to the literature,[15,19,20–22] the peak assignments of ^{13}C-CP/MAS-NMR spectra of cured PF resins are similar to those of the liquid-phase ^{13}C-NMR spectrum. The hydroxy-substituted carbons (C_1) occur around 152 ppm. The chemical shift of around 130 ppm was assigned to unsubstituted *meta* carbons or substituted *ortho* or *para* carbons of phenolic rings. Both unsubstituted *para* carbons and unsubstituted *ortho* carbons were assigned to 120 ppm and 115–117 ppm, respectively. Dimethylene ether carbons appeared around 73–75 ppm. Hydroxymethyl carbons occur around 58–68 ppm. Methylene carbons of *para–para*, *ortho–para*, and *ortho–ortho* linkages were assigned to 40 ppm, 35 ppm, and 20–27 ppm, respectively.



Scheme 1

The literature above shows that the ^{13}C-CP/MAS-NMR method has been applied and demonstrated its powerfulness and unique benefit for characterizing structural and molecular mobility for various cured PF resins. However, most attempts using solid-state ^{13}C-CP/MAS studies were done to characterize resin's chemistry. The ^{13}C-CP/MAS-NMR method was not used to monitor the chemical and structural characterization of cure-accelerated PF resins with various additives. The use of the ^{13}C-CP/MAS-NMR technique for characterizing cure-accelerated PF resins may provide a powerful tool for both the understanding of curing behavior and the elucidation of the mechanism of cure acceleration by additives. The objective of this study was to investigate the effects of the addition of carbonates on the cured PF resin. Thus, using ^{13}C-CP/MAS-NMR technique, this study looked into differences in the network structure and molecular mobility of cured resins of both the neat and cure-accelerated types by the addition of carbonates.

Chemical Reactions in PF Resole Resin

PF resole polymers are formed through two reaction steps: methylolation and condensation. In order for methylolation to occur, a basic catalyst (usually NaOH) converts phenol into a more reactive (more nucleophilic) phenoxide ion, as shown in Scheme 1.[23]

The above three forms of charged resonance of phenoxide ion illustrate the phenol functionality of the three, with two active *ortho* sites and one active *para* site to the hydroxyl group. For methylolation, the first step is to add formaldehyde to phenol to form various methylolphenols and is an exothermic reaction (Scheme 2).

In consequence, a resole PF resin molecule contains reactive methylol groups. Heating makes the reactive resole molecules condense to form large molecules without hardening agents. As shown in Scheme 3, the second step involves condensation of phenol with methylolphenol units to form a methylene bridge between the unsaturated rings, with a water molecule by-product. The second step is also an exothermic reaction.

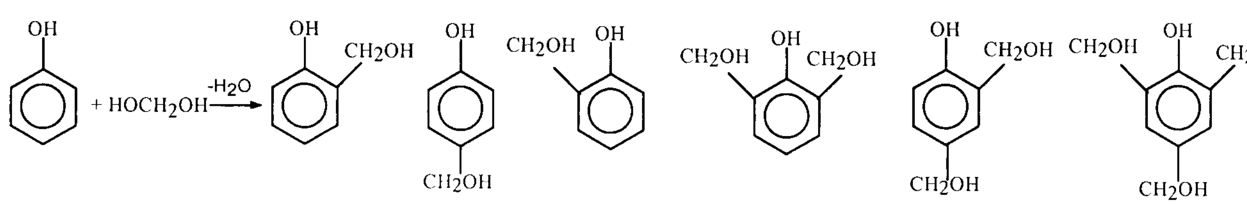
In addition to the formation of methylol phenols, methylol groups may interact with one another and form dimethylene ether links with the liberation of water (Scheme 4). This is particularly prevalent when the ratio of formaldehyde: phenol (F:P) is high.[24] Dimethylene ether links may release one of the bound formaldehydes via disproportion to yield a methylene bridge.

During the initial stages of the alkaline-catalyzed reaction, formaldehyde consumption may also occur through Cannizzaro self-oxidation in competition with methylolation. In the presence of sodium hydroxide, 2 mol formaldehyde react to form 1 mol methanol and 1 mol formic acid.[25]

EXPERIMENTAL

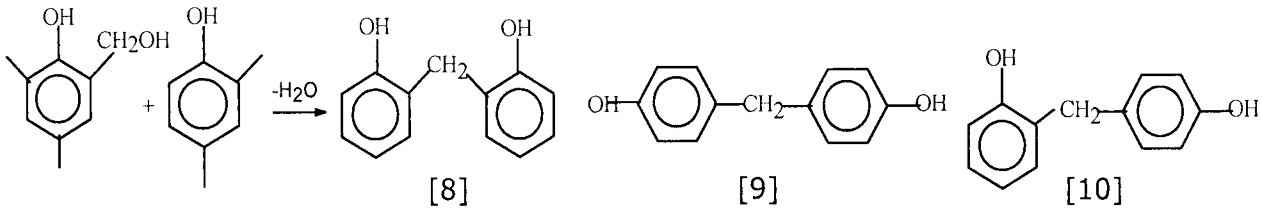
Synthesis of PF Resin

To prepare PF resin for liquid and solid-state ^{13}C-CP/MAS-NMR analysis, liquid phenol (90%) and paraformaldehyde were used as supplied. PF resin was synthesized in a 2:l reaction kettle with a P:F:NaOH molar ratio of 1:2.2:0.3 according to a modified method.[26] The reactor was charged with phenol (90%), paraformaldehyde (45.6%), and water. After heating the components to 40°C in the reactor, the initial sodium hydroxide (50%) was slowly added over 10 min. When the temperature rose to 100°C, the resin was cooked for 2–3 min and then cooled to 65°C, at which point cooking was continued for 65 min. The temperature was



[2] [3] [4] [5] [6] [7]

Scheme 2



Scheme 3

held at 65°C until the Gardner–Holdt viscosity ranking (25°C) reached KL. The resin was then cooled to 30–40°C, and the second portion of sodium hydroxide (50%) was added. The solids content of the synthesized resin was determined to be 40% by a pan solids technique, and alkalinity (pH) was 10.3.

The three carbonates used were propylene carbonate (98%), referred to as PC; sodium carbonate (Na_2CO_3), referred to as NC; and potassium carbonate (K_2CO_3), referred to as KC. All carbonates were diluted in aqueous solutions; propylene carbonate was prepared as a 1*M* solution (10.4 % wt); both sodium carbonate and potassium carbonate were prepared as a 2.5*M* solution (Na_2CO_3: 26.5 % wt; K_2CO_3: 34.5 % wt).

Liquid-State ^{13}C-NMR Spectroscopy

For liquid-phase ^{13}C-NMR analysis, about 5 g of the synthesized PF resin was mixed with the prepared carbonate solutions in a round flask and kept in a drying oven at 120°C for 10 min. The carbonate concentration was fixed as 4 wt % of the nonvolatile solids of the resin. Then powdered PF resins were prepared by freeze-drying the reacted PF resin for 24 h, after which they were finely ground. The ground sample was dissolved in DMSO–d_6 with a PF resin concentration of 30%. The chemical shift of DMSO, which has a chemical peak at 40.5 ppm from TMS, was used for reference. Spectra were obtained with a Varian XL-200 spectrometer with a 5 μs pulse width (30°) and a pulse delay of 10 s. By using the gated decoupling method to minimize the nuclear Overhauser effect, about 5000 scans were accumulated to obtain reliable spectra. All model compounds, including 4-hydroxymethylphenol (4-HMP), 2-hyroxymethylphenol (2-HMP), and 4,4′-dihydroxydiphenylmethane (4,4′-DHDPM) were commercial products (Aldrich Chemical Co.).

Solid-State ^{13}C-CP/MAS-NMR Spectroscopy

For solid-state ^{13}C-CP/MAS-NMR analysis, the reacted PF resin was cured further in an oven at 105°C for 3 h. The three carbonate solutions prepared were added into the liquid PF resin to obtain the 4% carbonate concentration and then cured in the oven under the same conditions. The cured PF resins were ground into fine powder using a small Wiley mill. All CP/MAS NMR experiments were performed on a Bruker ASX 300-MHz spectrometer. The carbon spectra were obtained at 75.47 MHz. The Hartmann–Hahn match was done by tuning ^{1}H and ^{13}C channels with adamantane. The cured PF resin powder was packed into a 7-mm zirconium oxide rotor sealed with Kel-F cap. The rotor was spun at a MAS speed of 4 kHz, with a contact time of 1 ms and a recycle delay of 4 s for spectra acquisitions. A standard cross-polarization pulse with variable contact times at room temperature was used to obtain the proton spin-lattice rotating-frame relaxation times ($T_{1\rho H}$) and carbon-proton cross-polarization rates (T_{CH}). Both $T_{1\rho H}$ and T_{CH} were determined by nonlinear curve-fitting of the signal intensities and delay times to the two components' equation that describes the rise and fall of signal intensity as a function of variable contact time.[27] The equation is expressed as

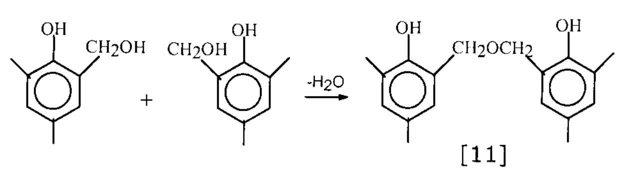
$$I(\tau) = I^*\left(\frac{T_{1\rho H}}{T_{1\rho H} - T_{CH}}\right)(\exp^{\tau/T_{1\rho H}} - \exp^{\tau/T_{CH}}) \quad (1)$$

where I is a peak intensity at a given contact time (τ), and I^* is the corrected intensity. The variable contact times ranged from 0.1 ms to 6 s.

RESULTS AND DISCUSSION

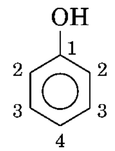
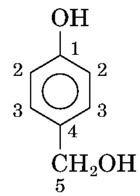
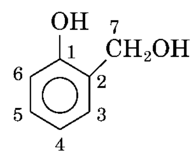
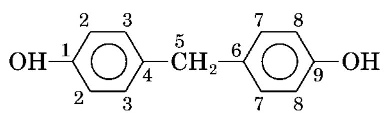
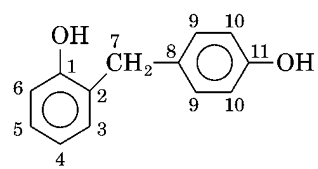
Liquid-Phase ^{13}C-NMR Study

The chemical shifts and chemical structures of model compounds are summarized in Table I. The



Scheme 4

Table I Liquid-Phase ^{13}C-NMR Peak Assignment for Model Compounds Dissolved in DMSO Solvent

Model Compound[a]	Chemical Structure	Chemical Shifts (ppm)										
		C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
Phenol		157.1	115.4	129.3	118.5							
4-HMP		156.2	114.9	128.3	132.5	63.0						
2-HMP		154.4	127.7	128.0	118.9	128.0	114.7	58.8				
4,4′-DHDPM		155.3	115.2	129.5	132.3	b	132.3	129.5	115.2	155.3		
2,4′-DHDPM[c]		154.7	127.1	130.1	118.7	126.9	114.8	35.2	141.0	127.9	128.4	125.4

[a] The model compounds are 4-hydroxymethylphenol (4-HMP); 2-hydroxymethylphenol (2-HMP); 4,4′-dihydroxydiphenylmethane (4,4′-DHDPM); 2,4′-dihydroxydiphenylmethane (2,4′-DHDPM).
[b] Not detected because of overlapping with DMSO solvent.
[c] The peak assignments were cited from Holopainen *et al.* (1997).

Table II Chemical Shifts of Liquid ^{13}C-NMR of Control PF Resin

Chemical Shift (ppm)	Assignment of Carbons
157.1–157.5	Phenoxy
156.2–156.4	Phenoxy, alkylated in *para* position
153.1–153.9	Phenoxy, alkylated in *ortho* position
151.2–152.7	Phenoxy, alkylated in two *ortho* or/and *para* positions
125.1–125.9	Substituted *ortho*
128.3–128.5	Unsubstituted *meta*
129.0–130.4	Substituted *para*
63.3–64.2	*para* methylol
57.4–60.7	*ortho* methyol
34.6–35.1	*ortho–para* methylene bridges

^{13}C-NMR spectra of model compounds were comparable to those of the NMR data reported in the literature.[9–16] The information obtained from the spectra of model compounds was used in the interpretation of the spectra of resins mixed with carbonates.

The chemical shifts of phenoxy carbons (C_1—OH) are 154–157 ppm. The C_1 carbon that is alkylated at *ortho* positions showed lower chemical shift than the ones reacted at *para* positions. Unsubstituted *ortho* and *para* carbons important in the methylolation reaction occur at 114 ppm and 118 ppm, respectively. Substitution of the methylol group (—CH_2OH) causes a downfield shift of the *ortho* and *para* carbon signals to 127 ppm and 132 ppm, respectively. Free *meta* carbons occur between 128 ppm and 130 ppm. The chemical shifts of methylol groups occur at 58 ppm for the *ortho* position and 63 ppm for the *para* position. 2,4′-methylene link groups appeared at 35 ppm, while 4,4′-methylene link groups were not detected because of overlapping with the solvent (DMSO). The peak assignments for the control PF resin are summarized in Table II.

Figure 1 shows a typical ^{13}C-NMR spectrum of the control PF resin used for the modification with carbonates. The signal assignments in Table II were made by comparing those of model compounds with those reported in the literature.[7] The signal range between 151 ppm and 152 ppm was assigned to the C_1 carbons alkylated at two *ortho* (2 and 4) positions, or the 2,4, and 6 positions, which is compatible with the results reported elsewhere.[28] The chemical shifts of 114 ppm and 118 ppm assigned for the unsubstituted *ortho* and *para* carbons were very weak in this resin. This might be the result of the control core resin being advanced quite a lot, as indicated by the final viscosity (275~300 mPa/s). In other words, most *ortho* and *para* positions were reacted with formaldehyde, leading to either methylolated phenols or methylene links.

Methylol group carbons showed three distinctive peaks, corresponding to *ortho* methylols (57 ppm and 60 ppm) and *para* methylols (63 ppm). The two peaks (57 ppm and 60 ppm) of the former might be due to two *ortho* positions reacted to lead to various combinations of methylol phenol such

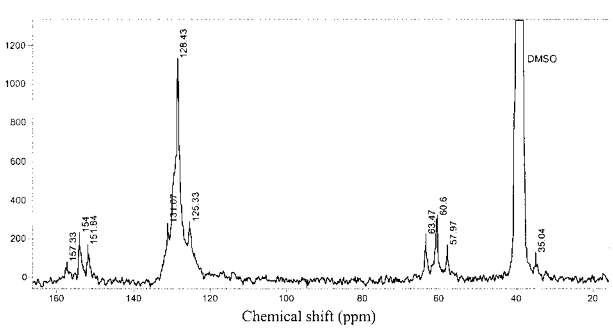


Figure 1 Liquid-phase ^{13}C-NMR spectrum of the control PF resin.

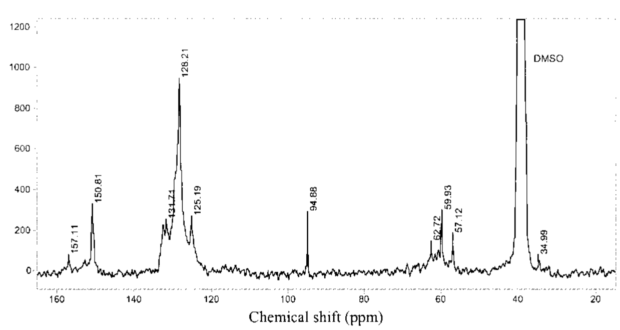


Figure 2 Liquid-phase ^{13}C-NMR spectrum of the cure-accelerated PF resin with PC.

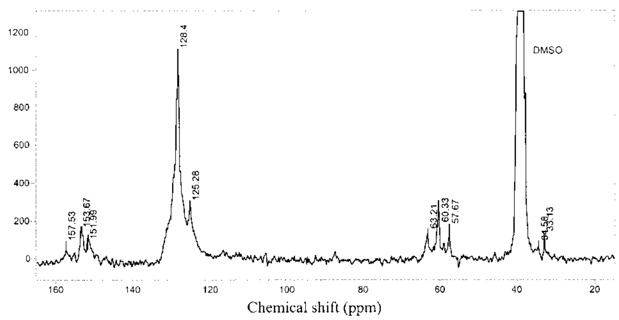
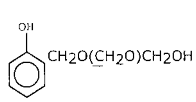


Figure 3 Liquid-phase ^{13}C-NMR spectrum of the cure-accelerated PF resin with NC.

as compounds [2]–[7] (Scheme 2). There are three types of methylene linkage in PF resin: *ortho–ortho* bridges (2,2′-dihydroxydiphenyl methane), *ortho–para* bridges (2,4″-dihydroxydiphenylmethane), and *para–para* bridges (4,4′-dihydroxydiphenyl methane). The first methylene linkages appeared at 35 ppm, which is near the shoulder of the DMSO solvent. However, those signals of the second methylene bridges overlapped with DMSO peaks, making it difficult to assign the chemical shift.

Figures 2–4 are the ^{13}C-NMR spectra of the PF resins that are cure-accelerated with the addition of PC, NC, and KC, respectively. One of the differences between the control PF resin and PC-accelerated PF resin is the appearance of a peak at 150 ppm. This might be due to the acyl group of PC added into the control PF resin.[29] Another possibility might be the phenoxy carbons (C1) alkylated by carbonyl groups (C═O) in *ortho* positions, which is one of the intermediate species of the cure-acceleration mechanism of PC proposed by Pizzi and coworkers.[4,5]

The other difference in the spectrum of the PC-modified PF resin is an additional peak at 132 ppm, which is in the range of the substituted *ortho*, or *para* and *meta,* carbon positions. This chemical shift is very close to that of the substituted para carbons of the model compounds (i.e., 132.5 ppm). Another peak of the spectrum of the PF resin modified with PC occurs at 94 ppm. Werstler[30] reported the presence of a chemical shift at 93 ppm and assigned this peak to hemiformal structure:



[12]

Stack and coworkers[16] also reported hemiformal peaks between 80–95 ppm. In addition, the diether group also has a peak in the range of 90–100 ppm. Therefore, it is not clear whether this peak is due to the ether group or hemiformal species. In addition, study of known hemiformal structures is lacking in the literature, and in general the hemiformal assignments are vague.[30]

For methylol carbons in the 57–64 ppm range, the PC-modified PF resin shows two small peaks occurring at 60.7 and 62.5 ppm, which is different from those of the control PF resin and the other two carbonate- (NC and KC) modified PF resins. These two peaks might be caused by the methylol carbons of unknown species of the intermediates of reactions between PC and PF resin. However, this interpretation requires caution because the full reaction mechanism of cure acceleration has not as yet been explained. The 2,4′-methylene bridges appeared at the chemical shift of 34.9 ppm. This is quite comparable with that of the model compound.

The spectrum of the PF resin modified with NC is shown in Figure 3. In general, the spectrum is quite similar to that of the control PF resin. An interesting peak appears at 33 ppm, which might be from *ortho–ortho* methylene bridges. Others are similar to the reported results.[9,11] Figure 4 is a ^{13}C-NMR spectrum of the PF resin modified with KC. In general, the spectrum is not much different from that of the control PF resin and very similar to that of the PF resin modified with NC (Figure 3).

As in the spectrum of the modified resin with NC, a peak at 33 ppm assigned to *ortho–ortho* methylene bridges was also detected. The presence of *ortho–ortho* methylene linkages might be from the carbonate ions of both NC and KC. The formation of methylene bridges is preferred to *para–para* or *para–ortho* positions under normal

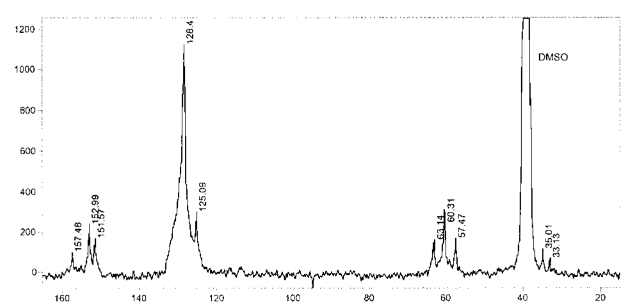


Figure 4 Liquid-phase ^{13}C-NMR spectrum of the cure-accelerated PF resin with KC.

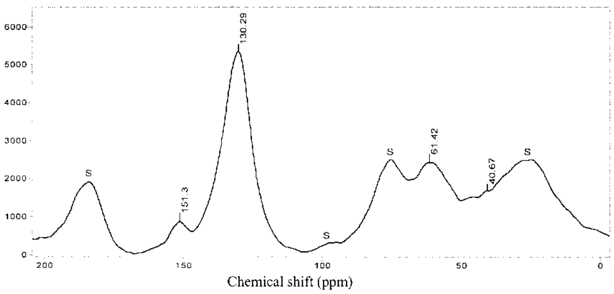


Figure 5 ^{13}C-CP/MAS-NMR spectrum of the control cured PF resin.

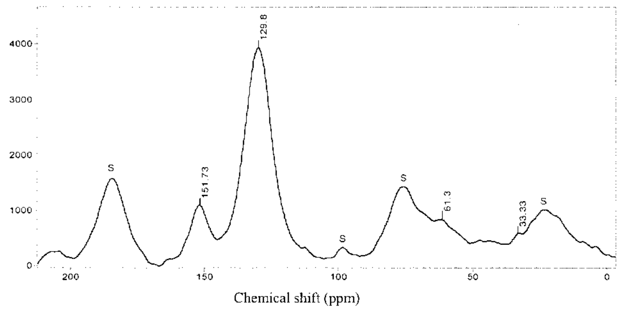


Figure 6 ^{13}C-CP/MAS-NMR spectrum of the cured PF resin cure-accelerated by PC.

reaction condition such as having sodium hydroxide as a catalyst. As suggested by Tomura et al.,[7] however, the carbonate ion facilitates a methylol group to react with another methylol group attached to the *ortho* position of a phenol ring in a competition with the normal reaction process. Another possibility might be that it might be due to the presence of divalent ions of sodium and potassium. A divalent ion such as Ba^{2+} was reported to modify the reaction mechanism and direct reaction paths toward the formation of *ortho*-substituted species like [5] (Scheme 2).[4]

From the liquid-phase ^{13}C-NMR results, it is shown that the three carbonates act differently on the PF resin. As reported in another work,[4] the results of this study also indicate that the added PC might be involved in the reactivity of resole PF resin, leading to increased functionality, while the addition of both NC and KC caused the appearance of the *ortho–ortho* methylene linkages. In order to better understand these points, solid-sate ^{13}C-CP/MAS-NMR was employed for cured PF resole resins accelerated with three carbonates.

Solid-State ^{13}C-CP/MAS-NMR Study

Figures 5–8 show typical spectra of cured PF resins by the CP/MAS method. In general, the chemical shifts are similar to those of liquid NMR. Most peaks are much broader compared to their counterparts in liquid-state NMR because of the heterogeneity and anisotropy of the solid state of cured PF resin. The chemical shifts of all peaks were similar to those of liquid NMR and were assigned with reference to reported results in the literature.[19,22,31,32]

The spectrum of the control PF resin cured is shown in Figure 5. The peak of aromatic carbon (C_1) directly attached to the phenolic hydroxyl occurs at around 151 ppm. Both unsubstituted *meta* and substituted *ortho*, or *para* aromatic carbons, peaks appear at around 130 ppm while unreacted hydroxymethyl carbon peaks occur around 61 ppm. This chemical peak overlaps slightly with a spinning side band (~ 75 ppm). The aliphatic carbons of methylene linkages were assigned the chemical shift of 35–40 ppm. These peaks were assigned with great care because of the overlap with a spinning side band (~ 24 ppm) in most of the spectra. The remaining peaks, labeled *S,* are spinning side bands due to magic-angle spinning.

The CP/MAS spectra of PC-, NC-, and KC-modified PF cured resins are shown in Figures 6–8, respectively. Most chemical shifts were similar. However, PC-modified PF cured resin (Fig. 6) showed a peak at the chemical shift of 33 ppm, which was assigned to *ortho–ortho* methylene bridge carbons in the counterpart of the liquid NMR spectrum (Fig. 4). This is compatible with other reports.[15,18] However, the chemical shift at 33 ppm was severely impaired for the two spectra of both NC- and KC-modified PF resins (Figs. 7 and 8). This peak assignment has to be cautious since the typical line widths of the CP/MAS

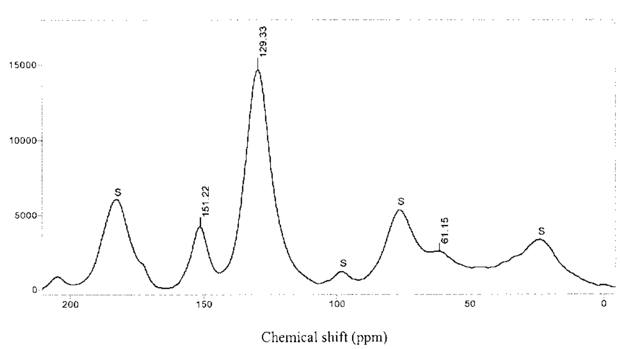


Figure 7 ^{13}C-CP/MAS-NMR spectrum of the cured PF resin cure-accelerated by NC.

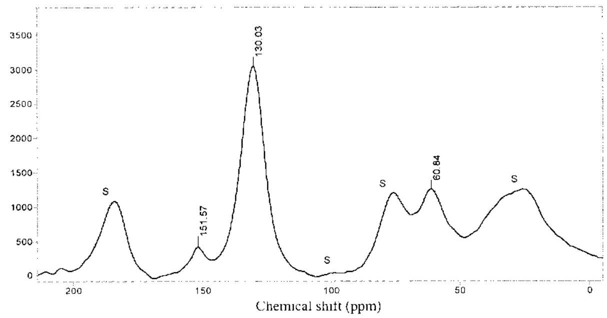


Figure 8 ^{13}C-CP/MAS-NMR spectrum of the cured PF resin cure-accelerated by KC.

method are 15–20 ppm. Therefore, removing the ^{13}C-^{1}H dipolar interactions using deuterium labeling can clear this ambiguity. In addition, the chemical shift of 40 ppm of the control PF resin assigned to *ortho–para* methylene bridge carbons was not identifiable for the spectra of both NC- and KC-modified PF resins (Figs. 7 and 8).

Although spinning side bands around methylene linkages impairs the CP/MAS spectra, the above result indicates that PF resins cure-accelerated by the addition of PC have a tendency to preferably form *ortho–ortho* methylene linkages. This might be the action of either reactivity of PC toward a phenolic ring, proposed by Pizzi and Stephanou,[4] or the catalytic action of hydrogen-carbonate ions, reported by Tohmura and Higuchi.[7] This point should be clarified in future experiments using ^{13}C-isotope-enriched paraformaldehyde for PF resin synthesis. The results reported in the literatures show that the use of isotope-enriched PF resins results in a better resolution for ^{13}C-CP/MAS-NMR spectra.[31,32]

One of the useful spin-relaxation times obtained from solid-state ^{13}C-CP/MAS-NMR is the proton spin-lattice relaxation time in rotating frame, $T_{1\rho H}$. The measurement of $T_{1\rho H}$ enables characterization of molecular dynamics in the mid-kHz frequency range.[33] Nuclear relaxation normally results from two processes: (1) the coupling of local dipolar fields through spin-lattice effects, or motional processes in the solids, and (2) the static transfer of magnetization between nearby protons, known as spin diffusion. Spin diffusion is nonmotional information in origin and can mask the motional contribution to the $T_{1\rho H}$ value.[34] However, it is known that spin diffusion in cured PF resin does not obscure all motional information.[32] The $T_{1\rho H}$ and carbon-proton cross-polarization rate (T_{CH}) results obtained by variable contact times for the CP/MAS-NMR experiment are summarized in Table III.

As shown, the control PF-cured resin showed larger $T_{1\rho H}$ than those of cure-accelerated PF resins with carbonates. For all samples, values of $T_{1\rho H}$ are in the range of a few milliseconds for all samples. According to the results reported in the literature for PF resin, the $T_{1\rho H}$ values are in the ranges of 3 ~ 10 ms,[19] 3.7 ~ 5.9 ms,[31] and 5.28 ~ 5.48 ms.[22] Variations in $T_{1\rho H}$ values might result from the degrees of PF resin advancement during its synthesis procedure, from different cure conditions, or from different probing conditions in the CP/MAS method. In this study the $T_{1\rho H}$ values of the control PF resin are slightly larger than those reported in the literature, while the $T_{1\rho H}$ values of the cure-accelerated PF resins are in the range. The slightly higher $T_{1\rho H}$ values of the control PF resin might be attributed to fairly high advancement of the resin, as indicated by the final viscosity after its synthesis (275~300 mPa/s at 25°C).

In general, mobile rubbery polymer exhibits a smaller $T_{1\rho H}$ than rigid, glassy, or crystalline polymers.[34] For example, the $T_{1\rho H}$ for hydroxymethyl carbons increases with increasing cure time and temperature.[31,32] Thus, the above results indicate that carbonate-accelerated PF resins are less rigid than the control PF resin. This might be related to the cure-acceleration actions of carbonates during PF resin curing. However, it is not clear from this study whether the added carbonates created any additional mobile phase in the cured PF resins. Nevertheless, there is an interesting result relevant to this point. Our previous DSC work[8] on cure-accelerated PF resins with carbonates showed that cure-accelerated PF resins have a rapid transition from chemical-controlled reaction to diffusion-controlled reaction. The diffusion-controlled reaction might cause a less rigid phase in the cure-accelerated resin in a way that would increase free volume. In addition,

Table III Results of T_{CH} and $T_{1\rho H}$ Measurement for Different Carbonate-Modified PF Resins

Carbonate Type	$T_{1\rho H}$ (ms)	T_{CH} (ms)
Control	18.6 ± 0.13	0.22 ± 0.05
PC	3.01 ± 0.38	0.15 ± 0.02
NC	7.19 ± 1.79	0.19 ± 0.03
KC	5.71 ± 0.85	0.20 ± 0.04

[a] Both measurements were based on the chemical shifts of 129 ppm.

it was shown that substitution with an alkyl group on the phenolic ring could soften PF resins, since substituted alkyl chains remain fairly flexible in the crosslinked state.[20]

The results of T_{CH} are also summarized in Table III. The T_{CH} values of the peak around 130 ppm ranged from 150 to 220 μs. Compared with the reported result,[19] the T_{CH} values measured in this study are in a similar range. In this study the main mechanism of cross polarization was the internuclear dipolar interaction between the nuclei involved: ^{13}C and nearby proton(s). In fact, the strength of an internuclear dipolar interaction in a rigid solid state is inversely proportional to the cube of the relevant internuclear distance. A larger internuclear distance usually corresponds to a larger T_{CH} value. In other words, the stronger the dipolar interactions between ^{13}C and a nearby proton, the smaller the T_{CH} value will be. In addition, mobile rubbery polymers give rise to longer values of T_{CH} than do rigid polymers because of the dipolar interaction.[34] The results of T_{CH} measurements in this study were not sufficiently consistent to draw any conclusive statement.

CONCLUSIONS

The chemical shift assignments and spectra of liquid-phase ^{13}C-NMR spectra were in good agreement with results reported in the literatures. The liquid-phase ^{13}C-NMR spectra showed that the cure-acceleration mechanism in the PC-modified PF resin is different from the cure acceleration actions of NC and KC. The addition of PC into PF resin seemed to be involved in the increasing reactivity of phenol rings. In contrast, the addition of both NC and KC into PF resin apparently caused the appearance of *ortho–ortho* methylene linkages. Solid-state ^{13}C-CP/MAS-NMR was also successfully applied to investigating cured PF resins accelerated by the addition of carbonates, and it provided information on the molecular mobility of cured PF resins through the measurement of both $T_{1\rho H}$ and T_{CH}. The cure-accelerated PF resins showed a smaller $T_{1\rho H}$ value than that of the control PF resin. This result indicated that the cure-accelerated PF resins are less rigid than the control PF resin.

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