

Effect of Synthesis Parameters on Thermal Behavior of Phenol–Formaldehyde Resol Resin

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ABSTRACT: Differential scanning calorimetry (DSC) was used to investigate the influence of resin synthesis parameters on the thermal behavior of low molecular weight phenol–formaldehyde (PF) resol resins prepared with different formaldehyde/phenol (F/P) molar ratios, different sodium hydroxide/phenol (NaOH/P) molar ratios, and different catalysts. As the F/P molar ratio increased, the molecular weight and activation energy increased while the gel time, peak temperature, resin pH, and nonvolatile solids content decreased. By contrast, the molecular weight, gel time, resin pH, resin solids content, and peak temperature increased with an increasing NaOH/P molar ratio. However, the activation energy decreased with an increasing NaOH/P molar ratio. The polydispersity increased with both F/P and NaOH/P ratios. Calcium hydroxide gave a faster curing resin compared to sodium and potassium hydroxides. All DSC thermograms of this study showed just a single exothermic peak for the resins that were used. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1415–1424, 2002

Key words: phenol–formaldehyde resol resin; formaldehyde/phenol ratio; sodium hydroxide/phenol ratio; catalysts; differential scanning calorimetry; molecular weight

INTRODUCTION

Phenol–formaldehyde (PF) resins are used as adhesives for wood-based composite products such as plywood, oriented strandboard (OSB), and laminated veneer lumber. The PF resins formulated by Baekeland in 1907 are synthetic polymers and are derived from the reaction of phenol with formaldehyde. The principal PF resins used for wood binders are alkaline-catalyzed resols and, to a

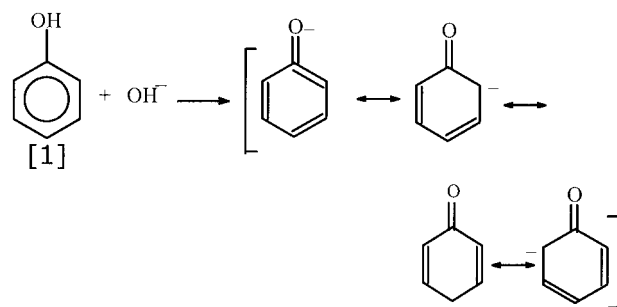
lesser extent, acid-catalyzed novolacs. Novolacs are made with a formaldehyde to phenol molar ratio of <1.0 (typically 0.75–0.85) whereas resols usually have formaldehyde/phenol (F/P) molar ratios between 1.6 and 2.6.

Phenols condense initially with formaldehyde in the presence of either acid or alkali to form a methylolphenol and then dimethylphenol. A novolac resin obtained with acid catalysis has no reactive methylol groups and thus is incapable of condensing with other novolac molecules when heated without hardening agents. Resols are obtained under alkaline catalysis and an excess of formaldehyde and contain reactive methylol groups that enable the resin to cure by itself when heated, forming large molecules without hardening agents.

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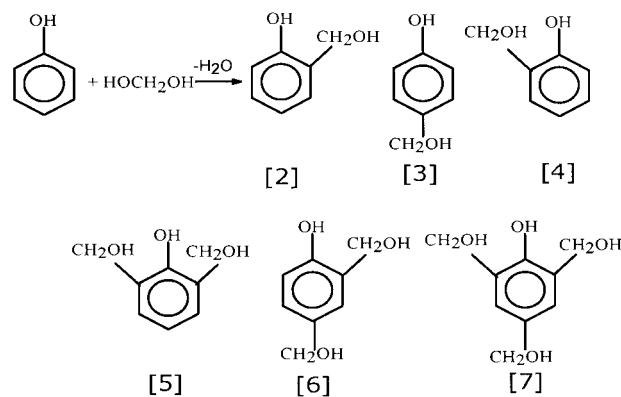
Scheme 1 Under alkaline conditions a base catalyzes the reaction by converting phenol into the more reactive phenoxide ion.

Under alkaline conditions a base (e.g., NaOH) catalyzes the reaction by converting phenol into the more reactive (more nucleophilic) phenoxide ion as shown in Scheme 1.¹

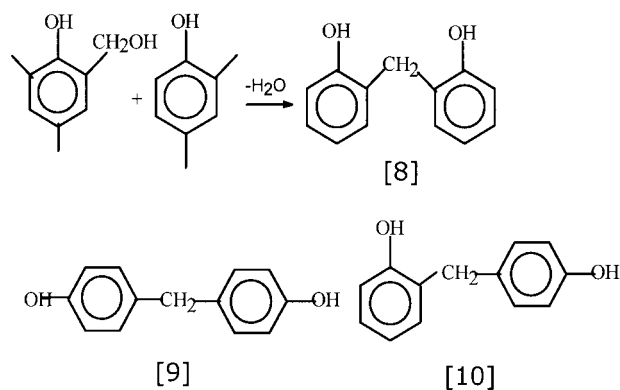
The three resonance forms of a charged phenoxide ion illustrate a phenol functionality of 3 with two active ortho sites and one active para site to the hydroxyl group. PF resol polymers are formed through two reaction steps. The first step is methylation, which adds formaldehyde to phenol to form various methylolphenols; it is an exothermic reaction (Scheme 2).

The second step involves condensation of phenol with the methylolphenol unit and the production of a water molecule to form a methylene bridge between the unsaturated rings (Scheme 3). The second step is also an exothermic reaction.

In addition, in the formation of methylolphenols, methylol groups may interact with one another and form dimethylene ether links with the



Scheme 2 The first reaction step is methylation, which adds formaldehyde to phenol to form various methylolphenols.

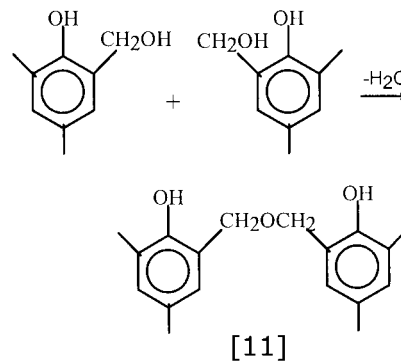


Scheme 3 The second reaction step involves condensation of phenol with the methylolphenol unit and the production of a water molecule to form a methylene bridge between the unsaturated rings.

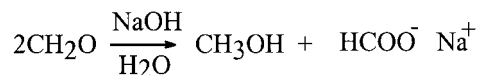
liberation of water (Scheme 4). This is a prevalent reaction path when the F/P ratio is high.² The dimethylene ether links may release one of the bound formaldehydes via disproportionation to yield a methylene bridge.

During the initial stages of the alkaline-catalyzed reaction, formaldehyde consumption may also occur by the Cannizzaro self-reaction in competition with methylation. Two molecules of formaldehyde react in the presence of sodium hydroxide to form one molecule of methanol and 1 mol of formic acid as shown in Scheme 5.³

Because polyfunctional phenol reacts with formaldehyde in both the ortho and para position to the hydroxyl group, the reaction is accomplished through polycondensation of prepolymers. Thus, the PF resin represents a mixture of polymer molecules differing in molecular weights,



Scheme 4 Methylol groups interact with one another and form dimethylene ether links with the liberation of water.



Scheme 5 Two molecules of formaldehyde react in the presence of sodium hydroxide to form one molecule of methanol and 1 mol of formic acid.

shapes, and degree of substitution with methylol groups or methylene linkages. The ingredient ratios and parameters of the resin formulation are frequently adjusted empirically to tailor the resin properties to specific production requirements such as the resin reactivity, formaldehyde emissions, board resistance to water swelling, dimensional stability, and so forth.

The ultimate performance of a fully cured PF resin largely depends on its synthesizing parameters, including the F/P molar ratio, sodium hydroxide/P (NaOH/P) molar ratio, viscosity, reactivity, and so on. On a macromolecular level, an understanding of the curing properties and thermal stability of PF resins provides insight into the overall quality and durability of a glue line.

The F/P and NaOH/P molar ratios affected the cure shrinkage⁴ and surface tension of PF resol resins.⁵ Various F/P ratios were inversely related to wood failure of parallel-laminated panels, which was attributed to poor flow of the resin at long assembly times.⁶ Another work showed that the percentage of wood failure increased up to a F/P ratio of 1.4 and then was relatively stable.⁷ Both ratios also affected the rigidity of the cured resins, showing that high F/P and NaOH/P ratios gave high relative rigidity.⁸

It was reported that the resin with a higher NaOH/P ratio gave a higher cure reactivity, which was indicated by faster aging, a lower differential scanning calorimetry (DSC) peak temperature, and a higher heat of cure.⁹ However, this result is incompatible with other results, showing that the higher exothermic peak temperatures had occurred when the F/P ratio was low or the NaOH/P ratio was high.¹⁰ The results of a dynamic thermal analysis (DTA) study reported that F/P ratios of 0.75–2.4 showed two endothermic peaks, the second of which increased in magnitude with an increasing molar ratio.⁷ The other conclusion of this work was that higher NaOH/P levels required higher temperatures to cure.⁷

Chow and Steiner¹¹ compared novolac with resol resins and reported an interesting DSC result showing an endothermic peak at about 150°C

for the resol reaction and an exothermic peak at about 160°C for the novolac reaction. Their results provided an explanation about the nature of the inconsistencies of exothermic or endothermic reactions, depending on the types of resin systems (i.e., resol or novolac) and the states of the resins (liquid or solid). However, Christiansen and Gollob¹⁰ reported the presence of two exothermic peaks for PF resol resins using DSC and concluded that the first peak occurring between 98 and 129°C is an addition reaction while the second peak occurring at 139–151°C is a condensation reaction.

In addition to the F/P and NaOH/P ratios, the type of catalyst also affects the final properties of the PF resol resin. For example, most electropositive bivalent metallic ions are known to accelerate the PF reaction.² The extent of the reaction rate depends on the type of metal ion and its concentration. For example, Grenier-Loustalot et al.¹² reported a positive relationship between the characteristics of a catalyst (size and valence of the cation) and the reaction rate. In other words, the greater the radius of the hydrated cation, the faster the disappearance of formaldehyde in the reaction. However, trivalent metal ions such as chromium have an inhibiting effect, retarding the reaction rate of the PF resin.¹³

As shown in the literature, many researchers tried to understand the influences of resin synthesis parameters on the subsequent properties of prepared PF resol resins. However, few DSC works were done so far compared to other techniques. Furthermore, the results of thermal analyses like the DTA and DSC techniques showed inconsistency about the existence of two exothermic peaks for the PF resol resin, and little work was done for low molecular weight PF resol resins that were being used for face layers. Therefore, this work was conducted to study the influence of the synthesis parameters of low molecular weight PF resol resins on their thermokinetic properties using a DSC technique.

EXPERIMENTAL

Resin Synthesis

To prepare the PF resol resins, liquid phenol (90%) and paraformaldehyde were used as supplied. The PF resin was synthesized in a 1-L reaction kettle according to the following proce-

Table I Synthesis Parameters and Their Levels for PF Resol Resins

Batch No.	F/P Ratio	OH ⁻ /P Ratio	Resin Solids (%)	Viscosity (mPa s)	pH	Free CH ₂ O (%)	Catalyst Type
1	1.9	0.3	51.4	24	10.8	0.20	NaOH
2	2.2	0.3	50.8	44	10.6	0.24	NaOH
3	2.5	0.3	50.8	48	10.4	0.59	NaOH
4	2.2	0.2	50.7	32	10.1	0.23	NaOH
5	2.2	0.4	51.9	56	11.3	0.23	NaOH
6	2.2	0.5	52.2	60	11.7	0.24	NaOH
7	2.2	0.4	45.7	40	10.1	0.23	KOH
8	2.2	0.4	46.6	44	9.5	0.22	Ca(OH) ₂

ture.¹⁴ 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, cooled to 65°C, and then cooked for 65 min. The temperature was held at 65°C until the Gardner–Holdt viscosity ranking (25°C) was AB. The resin was then cooled to 40–30°C, and the second portion of sodium hydroxide (50%) and ammonium hydroxide (28–30%) were added. The solids content of the prepared resins was determined by a pan solids technique.¹⁵

Resin Characterization Methods

A gel time meter, size exclusion chromatography (SEC), and DSC were employed to characterize the prepared resins. The gel time was measured with a Sunshine gel time meter with 1 g of resin at 120°C. The SEC system configuration was a Waters WISP710B injection system, a Waters M45B pump, a Waters TCM column temperature controller, a Waters R401 differential refractometer, and a Waters programmable system controller with a data module. The column was packed with styrene–divinylbenzene gels, and *N,N*-dimethylformamide (DMF) was used as a solvent for the PF resins. A small amount of 0.1M lithium bromide (LiBr) was added to the solvent to keep the ionic strength of the eluent constant. The solvent and samples were filtered through a 0.45- μ m filter before injection. The concentration of each sample was 0.5% (w/v) and the flow rate was 0.8 mL/min. The column was calibrated with poly(ethylene glycol) molecular weight standards under the same conditions. All DSC measurements were made on a Mettler DSC 20 with a

Mettler TA400 thermal analysis system, using a large sealed capsule (ME-29889/V). The capsule with a volume of 270 μ L can withstand a vapor pressure up to 10 MPa. The temperature range scanned was from 30 to 240°C with a heating rate of 10°C/min.

The Borchardt–Daniels method¹⁶ was used for all samples of this work. This method is based on a single heating rate run to analyze a curing reaction and assuming the *n*th-order kinetics expressed by eq. (1).

$$d\alpha/dt = Z \exp(-E_a/RT)(1 - \alpha)^n \quad (1)$$

where *Z* is the preexponential factor or the Arrhenius frequency factor (s⁻¹), *E_a* is the activation energy (J/mol), *R* is the gas constant (8.314 J/mol K), and *T* is the absolute temperature (K). Taking logarithms of eq. (1) gives

$$\ln(d\alpha/dt) = \ln Z - E_a/RT + n \ln(1 - \alpha) \quad (2)$$

Equation (2) can be solved with a multiple linear regression, and *Z* and *E_a* can be obtained from the intercept and slope of the regression line. This method is attractive because it provides abundant information potentially contained in a single temperature-programmed experiment. However, it is not consistently reliable when used to predict the course of a reaction over a wide time–temperature range.¹⁷

RESULTS AND DISCUSSION

The characteristics of the prepared PF resins are summarized in Table I. In general, the PF resol resins prepared for this study are relatively lower

molecular species as indicated by their lower viscosity. This kind of resin is being used as the face resin for the manufacture of OSB panels because face strand layers are exposed to the platens of a hot press at high temperatures.

The nonvolatile resin solids of the prepared resins ranged from 46 to 52%. As the F/P molar ratio increased, the nonvolatile resin solids slightly decreased. This might be due to the inherent chemical reaction as shown in Schemes 2, 3, and 4. In other words, as the chemical reaction progresses, the amount of water produced increases, which results in lower resin solids. The other reason would be the content of free formaldehyde in the resins. As shown in Table I, the free formaldehyde content increased with increasing F/P molar ratios. Some of this free formaldehyde would have evaporated in the process of drying the resin to obtain resin solids. However, the resin solids increased with an increasing NaOH/P molar ratio. Obviously, this would be due to the increased amount of sodium for the higher NaOH/P ratio.

The alkalinity of the prepared resin measured as the resin pH decreased and increased with increasing F/P and NaOH/P ratios, respectively (Table I). This result shows that the resol resin becomes more acidic as the F/P ratio increases. As shown in Scheme II, the methylolphenols are produced by the addition reaction of formaldehyde to a phenol ring prior to starting the condensation reaction. Because methylolphenols and formalde-

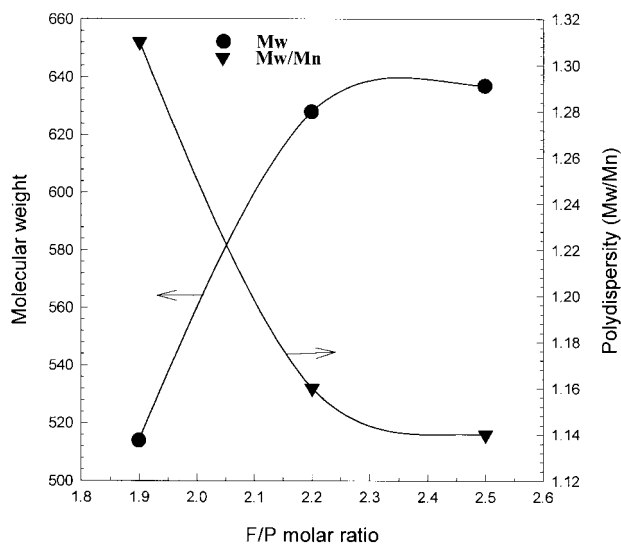


Figure 1 The weight-average molecular weight (M_w) of PF resol resins as a function of the F/P molar ratio.

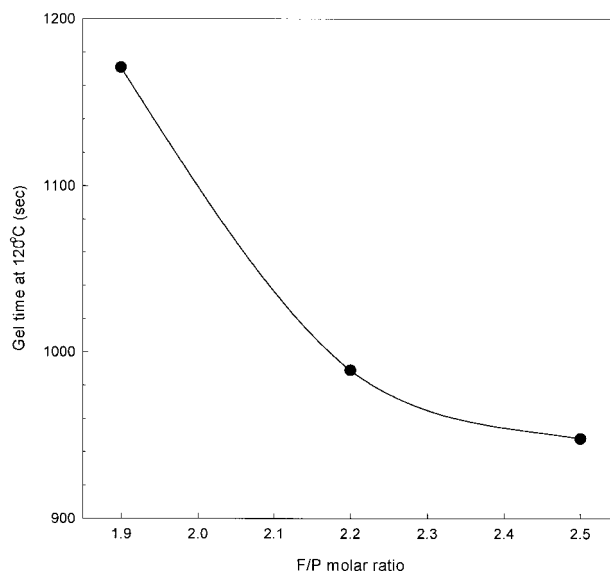


Figure 2 The gel time of PF resol resins as a function of the F/P molar ratio.

hyde are essentially acidic, the higher F/P ratio could produce more methylolphenols and thus reduce its alkalinity. This interpretation is also supported by the result of the weight-average molecular weight (M_w) measurement (Fig. 1). As expected, the alkalinity of the resin increased with increasing NaOH/P ratio.

The viscosity of the prepared resins also shows the dependence on the F/P ratio (Table I). As the F/P ratios increased, the viscosity also increased. A higher degree of methylation and the resulting solution of more crosslinked and sterically hindered oligomers explain the increased viscosity with the higher F/P ratio.

The amount of free formaldehyde determined increased with an increasing F/P ratio while it did not change much with an increasing NaOH/P ratio. The higher free formaldehyde content from the highest F/P ratio (2.5) might be due to the saturation of methylolated phenols that consumed formaldehyde in the reaction. As the NaOH/P ratio increases, a relatively small change in the amount of free formaldehyde content might be attributed to the fixed F/P ratio of 2.2. The free formaldehyde content also did not change much among the three catalysts used [NaOH, KOH, and $\text{Ca}(\text{OH})_2$].

Figure 2 shows the gel times of the synthesized PF resol resins as a function of the F/P ratio. The gel time decreased with increasing F/P molar ratios. This might be attributed to an increased

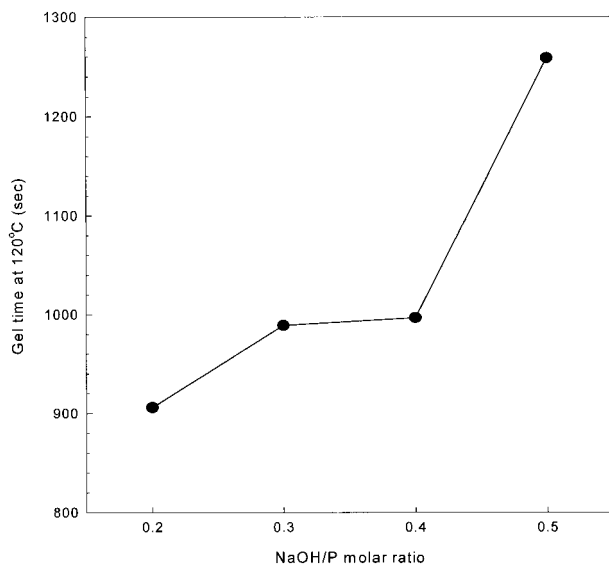


Figure 3 The gel time of PF resol resins as a function of the NaOH/P molar ratio.

reactivity of the resin due to the increased formaldehyde content. Under the high F/P molar ratio, more methylol groups that are reactive are formed in the resin. In other words, a higher F/P molar ratio results in higher methylation. Thus, a higher F/P molar ratio makes the resin cure faster than a lower F/P molar ratio does.

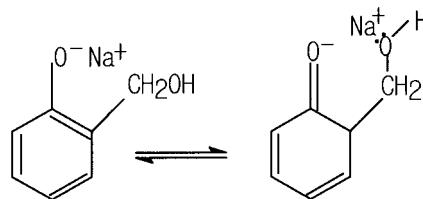
Figure 3 also shows the gel time of PF resins prepared as a function of the NaOH/P molar ratios. The gel time increased with an increasing NaOH/P molar ratio. This result indicates that the resin reactivity decreases with an increasing NaOH/P molar ratio. In synthesizing the PF resol resin the catalyst NaOH (or generally known as caustics) changes phenol into an ionized state to form a sodium phenoxide ion as shown Scheme 1, which is more reactive than phenol. The mechanism for the progressive retardation of the PF resol resin with increasing alkalinity (either the resin pH or NaOH/P ratio) was originally proposed by Caesar and Sachanen¹⁸ and was also supported by Pizzi.¹⁹ They postulated that an intermolecular chelate group holding the Na⁺ is formed between the phenolic ring and the *o*-methylolhydroxyls of a PF resin as shown in Scheme 6.

This ring complex mechanism would explain the progressive retardation of PF resins when increasing the resin pH. There are two possible factors that affect the reactivity of *O*-hydroxybenzyl alcohol molecules in the resin as soon as the Na⁺ ring complex is formed. First, the methylol

group is blocked, which decreases its mobility and its capacity to react to methylene linkages. Second, the strong inclusion of Na⁺ in the complex decreases the electron density on the phenol ring, which reduces the carbanion negative charge that is the main driving force for the PF condensation reaction under alkaline conditions. However, this mechanism is based on a pure PF resin itself. Therefore, the acidic nature of wood might affect the retardation of the PF resin cure under higher pH levels because the process of adhesion includes the interaction between the wood and the PF resol resin in panel manufacture.

The results of the molecular weight measurement of the PF resol resin are shown in Figure 1 and Table II. The M_w , number-average molecular weight (M_n), and polydispersity (M_w/M_n) of the prepared resins were obtained from gel permeation chromatography measurements. As the F/P molar ratio increased the M_w increased while the M_w/M_n of the resin decreased with increasing F/P molar ratio. The M_n also increased with increasing F/P molar ratio. This result indicates that the M_w increases more rapidly than the M_n does. In general, the M_w is sensitive to the admixture of molecules of high molecular mass while the M_n is sensitive to the admixture of molecules of low molecular mass.²⁰ The polydispersity gives a measure of the range of molecular sizes in the resin. In other words, the higher the M_w/M_n the resin has, the wider range of molecular sizes it has. Thus, the decreased M_w/M_n ratio indicates that the range of molecular sizes is reduced as the F/P ratio increases. The present results indicate that the amount of lower molecular weight species decreases with a higher F/P molar ratio.

Figure 4 shows the change of the M_w and M_w/M_n as a function of the NaOH/P ratio. As the NaOH/P ratio increased, the M_w increased while the M_w/M_n generally decreased. This result is not



Scheme 6 The reactions showing that an intermolecular chelate group holding the Na⁺ is formed between the phenolic ring and the *o*-methylolhydroxyls of a PF resin.

Table II Molecular Weights of PF Resol Resins

Batch No.	F/P Ratio	OH ⁻ /P Ratio	M_w	M_n	M_w/M_n
1	1.9	0.3	514	390	1.31
2	2.2	0.3	628	540	1.16
3	2.5	0.3	637	555	1.14
4	2.2	0.2	457	360	1.27
5	2.2	0.4	634	525	1.20
6	2.2	0.5	701	607	1.15
7	2.2	0.4	598	498	1.20
8	2.2	0.4	486	390	1.24

in agreement with other results.¹⁰ This might be ascribed to a difference in the hydrodynamic volume of the PF resol resin in the different mobile phases between the hexafluoroisopropanol and DMF used in this study. In fact, it was reported that the hydrodynamic volume of a PF resol resin depends on the types of mobile phases (i.e. solvents, and cosolvents, especially salts such as lithium chloride), as well as its molecular weight.²¹

DSC was used to characterize the thermal behavior of the prepared PF resins at a heating rate of 10°C/min according to the dynamic heating method. Table III is a summary of the DSC results, including the heat of reaction (ΔH), preexponential factor (or Arrhenius frequency factor) ($\ln Z$), E_a , reaction order (n), and exothermic peak temperatures. Figure 5 also shows the activation energy of the resins as a function of the F/P ratio. The activation energy increased with an increas-

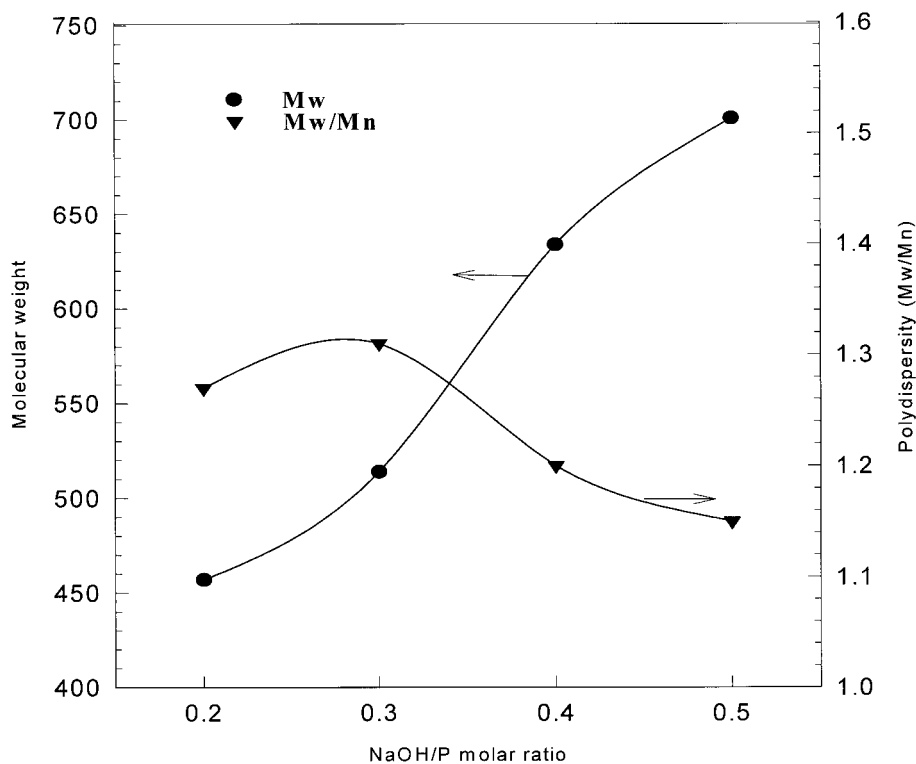


Figure 4 The weight-average molecular weight (M_w) of PF resol resins as a function of the NaOH/P molar ratio.

Table III DSC Results of PF Resol Resins

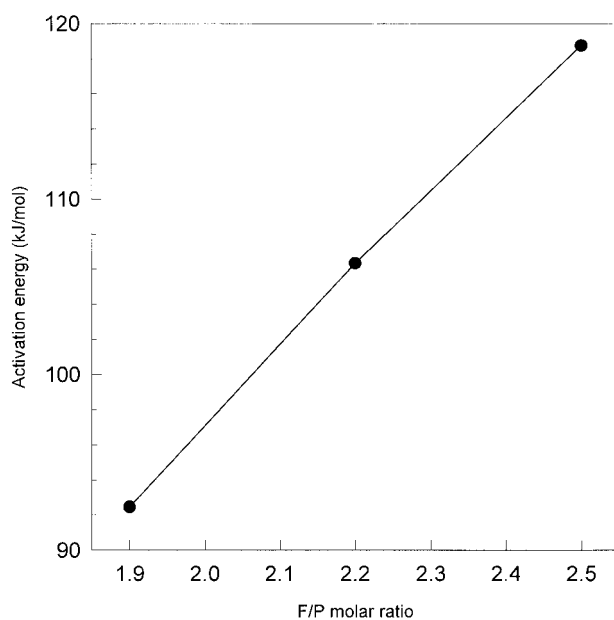
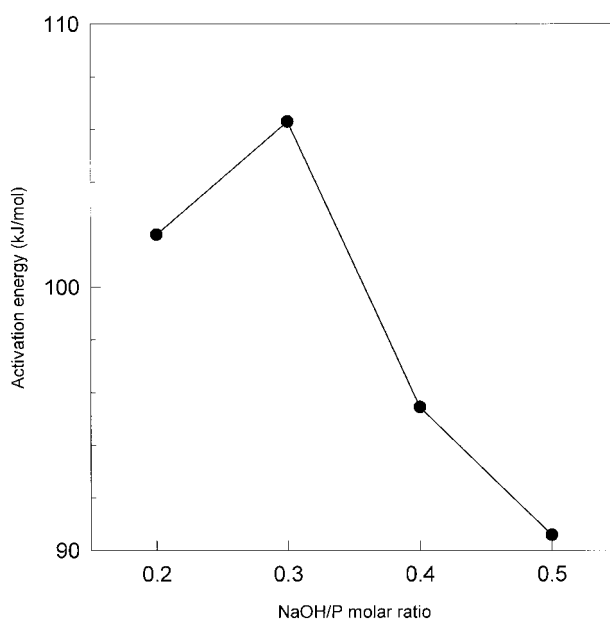
Batch No.	F/P Molar Ratio	OH ⁻ /P Ratio	ΔH (J/g)	$\ln Z$ (s ⁻¹)	E_a (kJ/mol)	n	Peak Temp. (°C)
1	1.9	0.3	654.2	21.4	92.4	1.3	154
2	2.2	0.3	773.4	25.6	106.3	2.0	153
3	2.5	0.3	761.5	29.4	118.7	2.1	151
4	2.2	0.2	742.1	24.3	102.0	1.6	154
5	2.2	0.4	726.2	22.3	95.5	1.6	153
6	2.2	0.5	725.5	20.8	90.5	1.5	156
7	2.2	0.4	689.5	26.4	109.6	1.6	155
8	2.2	0.4	634.4	40.6	156.4	3.0	148

ing F/P ratio. This is quite understandable because the larger molecules produced by the higher F/P ratio require more energy to begin the spontaneous condensation reaction.

Figure 6 also shows the activation energy of the resins for different NaOH/P molar ratios. In general, the activation energy decreased with an increasing NaOH/P ratio, even though there was a slight increase at the NaOH/P ratio of 0.3. This result indicates that less energy is required to spontaneously start the condensation reaction for the resin prepared with a higher NaOH/P ratio. The activation energy generally decreased with an increasing NaOH/P molar ratio. However, this result conflicts with the previous result that the

activation energy decreases as the PF resol resin cures faster.²² In other words, the reactivity of the PF resol resin decreases under high alkaline conditions as explained by the ring complex mechanisms. Thus, this result might be due to an instability of the Bocharadt–Daniels method of DSC.¹⁶ It is known that this method overestimates the activation energy.²³

As the NaOH/P ratio increases, the peak temperature obtained from DSC thermograms is slightly decreased up to the NaOH/P ratio of 0.4 and then is increased thereafter (Table III). This result is in agreement with the results of Christiansen and Gollob,¹⁰ but is not compatible with other results.⁹ Myers et al.⁹ ascribed the reason to

**Figure 5** The activation energy of PF resol resins as a function of the F/P molar ratio.**Figure 6** The activation energy of PF resol resins as a function of the NaOH/P molar ratio.

lower free formaldehyde and lower ring substitution yielded by higher NaOH/P ratio resins. However, the free formaldehyde content of this work did not change much with an increasing NaOH/P molar ratio.

All of the DSC thermograms obtained from this study showed a single exothermic peak for all the samples. This result is not compatible with the results of other work.¹⁰ Christiansen and Gollob¹⁰ reported the presence of two exothermic peaks for liquid PF resol resins and attributed this to the relatively high molecular weight of the PF resins. In addition, Holopainen et al.²³ reported two exothermic peaks for low molecular weight PF resins with various F/P molar ratios. The authors showed that two exothermic peaks overlapped at lower F/P molar ratios from 1.9 to 2.3 while the peaks were well separated from each other at higher F/P ratios. They attributed the reason for the two peaks to the condensation of methylolphenols and the condensation of the dibenzyl ether bridges to methylene bridges. However, Park et al.²⁴ reported a single exothermic peak for liquid PF resol resins. The difference of these conflicting results might be attributed to the difference in the weight-average molecular weight of the PF resins. The molecular weights of the PF resins used by Holopainen et al.²³ ranged from 2717 to 3113, which were much greater than those of this work, which ranged from 486 to 701. This is also the case for other work.¹⁰ Thus, the single exothermic peak in this work is probably due to the lower molecular weight of the resin synthesized. Nevertheless, further works are required to determine whether or not PF resol resins inherently possess two exothermic peaks.

The activation energy and peak temperatures of the resins prepared with different catalysts are also shown in Table III. The resin prepared with Ca(OH)₂ showed the highest activation energy, the highest reaction order ($n = 3.0$), and the lowest peak temperature among the three catalysts [NaOH, KOH, and Ca(OH)₂]. However, the order of the three is much greater than normal ($n = 2.0$). This result suggests that calcium hydroxide provides the resol resins with a faster curing system and is also supported by the shortest gel time among the three catalysts. It was reported that a greater radius of a hydrated cation gives a faster disappearance of formaldehyde in the reaction.¹² It is recognized that ortho-substitution is considerably enhanced if the metal hydroxides of the first and second main group in the series have

the following order: $K < Na < Li < Ba < Ca < Mg$.²⁴ The more ortho-substitution is favored, the higher the chelating strength of the cation. Thus, future work is needed to detect the possibility of increased ortho-substitution for the calcium hydroxide-catalyzed resin using ¹³C-NMR spectroscopy.

CONCLUSIONS

Three synthesis parameters of a PF resol resin (F/P molar ratio, NaOH/P molar ratio, and types of catalysts) were selected to investigate their influence on the synthesized resin properties and the thermal behavior of lower molecular weight PF resol resins. A DSC technique was employed to observe the thermal behavior of the low molecular weight PF resol resins that were prepared. The following conclusions were obtained. As the F/P molar ratio increased, the molecular weight and activation energy increased while the gel time, peak temperature, resin pH, and nonvolatile solids content decreased. In contrast, the molecular weight, gel time, resin pH, resin solids content, and peak temperature increased with an increasing NaOH/P molar ratio. However, the activation energy decreased when increasing the NaOH/P molar ratio. The polydispersity increased as both the F/P and NaOH/P ratios increased. Calcium hydroxide gave a faster curing resin when compared with sodium and potassium hydroxides. All the DSC thermograms of this study showed just a single exothermic peak for the resins used.

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