Controlled Synthesis of High-Ortho-Substitution Phenol–Formaldehyde Resins

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ABSTRACT: The relationship between the use of 19 kinds of metal catalysts and the proportion of ortho–ortho links of novolac resins was studied. The proportion of ortho–ortho links of novolac resins was characterized with Fourier transform infrared, ^{1}H-NMR, and ^{13}C-NMR. The effects of different catalysts and different reaction conditions, such as the molar ratio of phenol to formaldehyde, the pH value of the reaction, and the reaction time, were examined. Phenol–formaldehyde resins were synthesized with a certain proportion of the ortho position through the adjustment of the reaction conditions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 652–658, 2005

Key words: resins; novolac; high ortho

INTRODUCTION

In 1907, phenolic resins were the first thermosetting resins to be synthesized. Today, phenolic resins are still widely used, especially in thermal insulation materials and wood products. However, the relationship between the synthesis conditions, the structure, and the mechanical properties has not yet been completely clarified. One of the reasons for this is that the polymerization of the resins has a complicated reaction mechanism.[1]

Bender[2] showed that a resin in which a high proportion of ortho–ortho links was formed in the phenol–methylene chains could be cured by hexamethylenetetramine at a higher rate than resins made with conventional acid catalysts. It has been reported that if the reaction of phenol and formaldehyde is carried out within the pH range 4–7 in the presence of salts of bivalent metals, an ortho-directing effect occurs, and this results in the production of high-ortho-substitution phenolic resins.[3] However, the relationship between the metal catalyst and the proportion of the ortho–ortho links has not been studied in detail.

This article discusses the controlled synthesis of high-ortho-position phenol–formaldehyde resins with different catalyst types under different reaction conditions, such as the molar ratio of phenol to formaldehyde, the pH value, and the reaction time. This research should help manufacturers in designing and controlling novolac resins that have higher ortho ratios.

EXPERIMENTAL

Synthesis of the novolac resin

Phenol (>98%), formaldehyde (37%; aqueous solution), and the catalyst were commercial products and were used without further purification.

The reference high-ortho novolac resin used in the curing experiments was prepared through the reaction of phenol with a formaldehyde solution in the pH range 3–7 and in the presence of a bivalent metal-ion catalyst and dimethylbenzene. The reactor was a three-necked flask equipped with a stirrer, a cooling condenser, a thermometer, and a heating mantle. The mixture reacted at different temperatures for different times. After cooling to room temperature, the resin was washed several times with water and subjected to a vacuum at 75°C until the total extraction of water.

Curing of the novolac resin

The novolac resin was cured with hexamethylenetetramine (5 wt % equivalent of the resin) as a hardening agent under atmospheric pressure at different temperatures to measure the gel time. The gel time was determined with a second chronograph with the resin sample in a jar partly immersed in a preheated oil bath and measured from the start of the addition of the hardening agent to the resin.
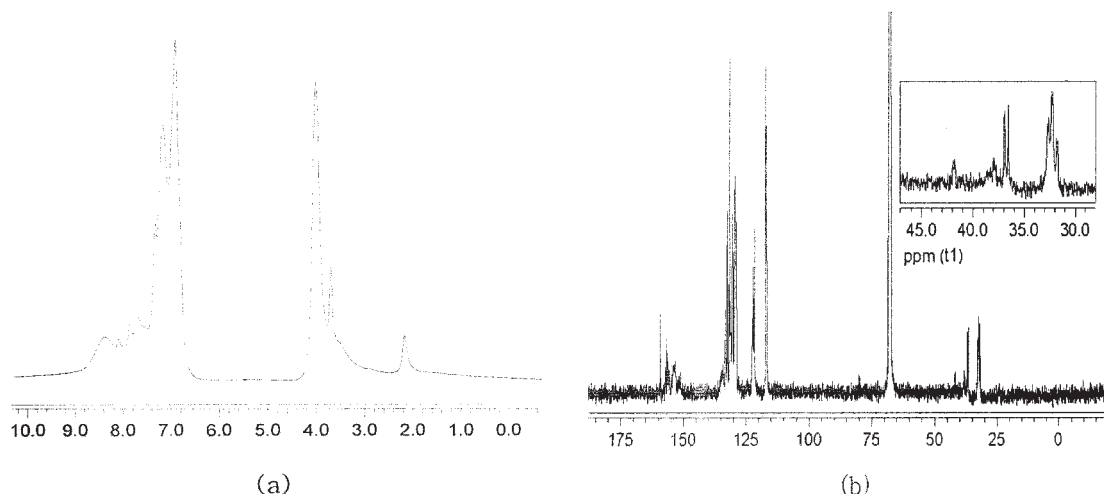
Figure 1 (a) ^{1}H-NMR (500 Hz) and (b) ^{13}C-NMR (125 Hz) spectra of the high-ortho resin.

NMR experiments

The structures of the novolac resins were analyzed with 500-Hz ^{1}H-NMR and 125-Hz ^{13}C-NMR spectroscopy. The spectra were recorded on a Varian Unity Plus-500 spectrometer (Palo Alto, CA) for a polymer solution in dioxane-d_6 at 298 K.

Fourier transform infrared (FTIR) spectroscopy experiments

A Nicolet Avatar 360 reaction analyzer (Waltham, MA) was used to collect FTIR spectra of the novolac resins with a spectral width of $4000-400$ cm^{-1}. The novolac resins were dissolved in acetone and spread onto KBr windows.

Differential scanning calorimetry (DSC) experiments

DSC analysis with a Netzsch DSC-204 (Selb, Germany) equipped with a thermal analysis data station enabled the curing exotherms of the resins to be determined. The series of novolac resins was mixed with hexamethylenetetramine (5 wt % equivalent of the resin). A 2.900–7.400-mg droplet of the mixture was sealed in each aluminum capsule pan under a nitrogen atmosphere at 20°C/min between 30 and 250°C.

RESULTS AND DISCUSSION

^{1}H-NMR and ^{13}C-NMR spectra

Typical ^{1}H-NMR and ^{13}C-NMR spectra of the high-ortho resin that we synthesized, taken in dioxane-d_6, are shown in Figure 1. The spectral peak assignments were made according to the method of Park et al.[4] Figure 1(a) is the ^{1}H-NMR spectrum. Under these experimental conditions, the signals of the aromatic ring protons (Ar**H**) were at 8.6–6.9 ppm, the signals of the methylene protons in o,o'- and o,p'-diphenylmethane-type methylene bridges (o,o'- and o,p'-RArC**H**$_2$ArR′) were at 4.2–3.8 ppm, and the signals of the methylene protons in p,p'-diphenylmethane-type methylene bridges (p,p'-RArC**H**$_2$ArR′) were at 3.7 ppm. The peak at 2.2 ppm originated from the residual phenol.

The high-ortho resin is also identified by ^{13}C-NMR in Figure 1(b). The band at 159 ppm was attributed to the residual phenol. Particular attention was paid to the zone at 45–30 ppm of the methylene bridges between two aromatic rings. In particular, the bands around 42, 35, and 32 ppm were attributed to the methylene protons in p,p'-, o,p'-, and o,o'-diphenylmethane-type methylene bridges. The peaks at 42 ppm were very weak in the resin. The relative quantities of various methylene linkages, as estimated from the ^{13}C-NMR spectrum, were in agreement with the values calculated from the ^{1}H-NMR spectrum. In the high-ortho resin, the o,o'-linkages were formed dominantly, and the ratio of p,p'-linkages was low.

FTIR studies of the novolac resins with different catalysts

The chemical structures of the conventional novolac resin and high-ortho novolac resin were confirmed with FTIR. IR spectra (Fig. 2) showed the characteristic absorptions of a benzene structure for the conventional novolac resin and high-ortho novolac resin at 1596 (aromatic C=C stretching), 1231 (asymmetric stretching of C—O—C), 1103 (symmetric stretching of C—O—C), 1352 (—CH$_2$— wagging), and 1509 cm^{-1} (1,2,6-trisubstituted benzene ring). Characteristic absorption bands assigned to the allyl group appeared at 3048 cm^{-1} (stretching of =C—H). Additionally, the

conventional   novolac

"high-ortho" novolac resin

1509cm^{-1}

812cm^{-1}

753cm^{-1}

3500   3000   2500   2000   1500   1000   500
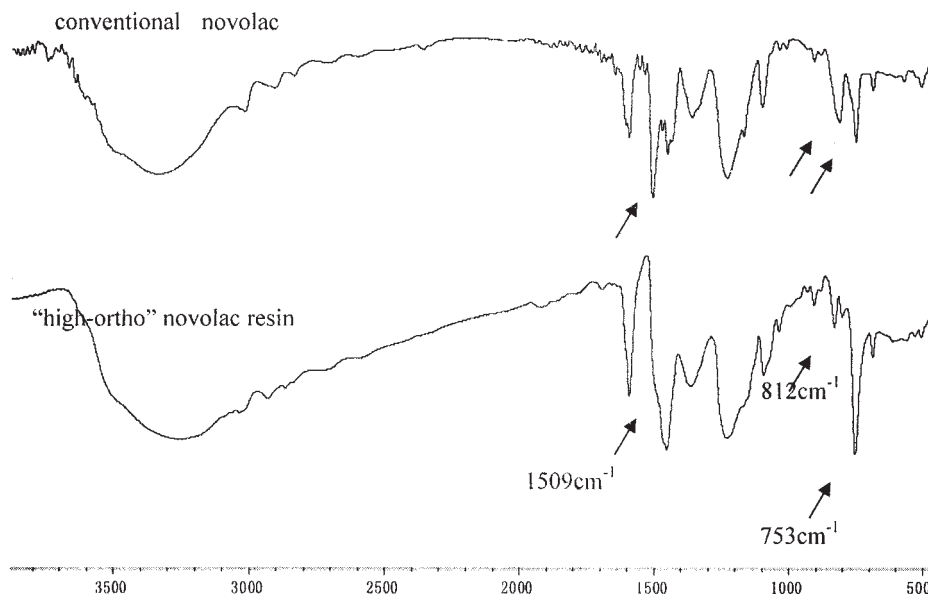
Figure 2   IR spectra of the conventional novolac resin and high-ortho novolac resin.

out-of-plane bending vibrations of olefinic C—H were observed at 890 cm^{-1} and indicated the allyl group. The out-of-plane C—H deformation in the monosubstituted benzene ring appeared at 691 cm^{-1}. The peak around 753 cm^{-1} corresponded to 1,3- and 1,2,3-substituted benzene rings. The peak at 812 cm^{-1} was attributable to 1,4- and 1,2,4-substitution, and the 888-cm^{-1} peak was identified with the 1,2,4,6-substituted benzene ring.

Roczniak and coworkers[5] identified the region between 1500 and 1400 cm^{-1} as characteristic for the deformation vibrations of the —CH— bonds on —CH$_2$— groups, and some differences can be noticed. These differences can yield information on the structure of the methylene bridge.

We assigned the different wavelengths in the spectra of the different compounds according to spectroscopic studies of substituted benzene.[6] We configured

TABLE I
Effects of the Catalysts on the High-Ortho Novolac Resins

Polymer	Catalyst	R ($[l]_{753}/[l]_{812}$)	Proportion of ortho–ortho links (%)
0	Hydrochloric acid (HCl)[a]	1.14	43.1
1	Ferric chloride (FeCl$_3$)	1.22	48.7
2	Stannic chloride (SnCl$_2$)	1.34	52.3
3	Ferrous sulfate (FeSO$_4$)	1.60	58.0
4	Cobalt chloride (CoCl$_2$)	1.70	60.0
5	Strontium chloride (SrCl$_2$)	1.75	61.1
6	Nickel chloride (NiCl$_2$)	1.76	61.5
7	Calcium chloride (CaCl$_2$)	1.85	63.0
8	Barium chloride (BaCl$_2$)	1.93	64.5
9	Calcium acetate (CaAc$_2$)	2.39	70.6
10	Cobalt acetate (CoAc$_2$)	2.56	72.1
11	Aluminum hydroxide [Al(OH)$_3$]	2.67	72.8
12	Zinc oxide + Hydrochloric acid (ZnO + HCl)	3.08	75.6
13	Calcium oxalate (CaC$_2$O$_4$)	3.32	77.0
14	Cadmium chloride (CdCl$_2$)	3.37	77.4
15	Copper acetate (CuAc$_2$)	4.74	82.0
16	Boric acid (H$_3$BO$_3$)	4.98	82.5
17	Manganese acetate (MnAc$_2$)	5.90	84.5
18	Magnesium acetate (MgAc$_2$)	6.80	87.0
19	Zinc acetate (ZnAc$_2$)	9.07	90.8

The high-ortho novolac resins (polymers 1–19) were synthesized at a molar ratio of P/F = 1.26. The molar ratio of catalyst to phenol was 4% at 125°C for 4 h.
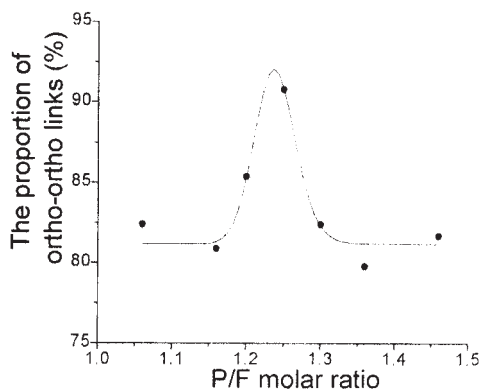   [a] Polymer used HCl as a catalyst and was conventional novolac resin.

Figure 3 Proportion of ortho–ortho links of the synthesized resins versus the P/F molar ratio. The polymers were synthesized with a molar ratio of $ZnAc_2$/phenol = 4% at 125°C for 4 h.

the different ratios of 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene to observe the changes in the characteristic absorption band intensities. In all cases, the reference bands of 753 and 812 cm^{-1} were used. This corresponds to the 1,2,3- and 1,2,4-substitution of the aromatic ring, which seems to be invariant. The relative intensives (I) of the absorptions at 812 and 753 cm^{-1} ($R = [I]_{753}/[I]_{812}$) of the novolac resins were considered a measure of the extent of benzene ring substitution.[6,7] The effect of the isomeric composition on the novolac resins was evaluated by the study of the substitution of the benzene ring. We established a working curve of the characteristic peaks of different substituted benzenes. The assignment of each peak permitted the quantification of each compound. Using this working curve, we could obtain the ortho–ortho ratio of the novolac resin, and the results with the different catalysts are shown in Table I.

As shown in Table I, the proportions of ortho–ortho links of all the high-ortho resins (polymers 1–19) were higher than that of the conventional novolac resin (polymer 0), and this indicated that most bivalent metallic ions are beneficial for increasing the proportion of high-ortho links.

The proportion of ortho–ortho links obtained from FTIR indicates that the metal catalyst effect is probably valid for most phenols with a free ortho position to the hydroxyl group. In Table I, we list two sorts of catalysts: inorganic salts (polymers 1–8, 12, and 14) and organic salts (polymers 9–10, 13, 15, and 17–19). Comparing them, we found that the effect of most inorganic salt catalysts was inferior to that of the organic salt catalysts. The proportion of ortho–ortho links of the former was below 70% mostly, whereas that of the latter was always greater than 70%.

The order of the metals corresponding to the proportions of ortho–ortho links can be obtained from Table I. The extent of the effects of the metal-ion catalysts can be expressed as follows:

For chloride, $Cd^{2+} > Ba^{2+}, Ca^{2+} > Ni^{2+}, Sr^{2+}, Co^{2+} > Fe^{2+} > Sn^{2+} > Fe^{3+}$.

For acetate, $Zn^{2+} > Mg^{2+} > Mn^{2+}, Cu^{2+} > Cd^{2+} > Co^{2+}, Ca^{2+}$.

For the same bivalent metal ions, we found that the effect of the organic salt catalysts was better than that of the inorganic salt catalysts. The proportions indicating the extent of the effect of the various anions were as follows:

For Zn^{2+}, $ZnAc_2$ (90.8%) > ZnO + HCl (75.6%).

For Ca^{2+}, CaC_2O_4 (77.4%) > $CaAc_2$ (70.6%) > $CaCl_2$ (63.0%).

For Co^{2+}, $CoAc_2$ (72.1%) > $CoCl_2$ (60.0%).

Therefore, we can conclude that the effect of a bivalent metal-ion catalyst depends on not only the metals but also the anion. According to the aforementioned scale, with the exception of the higher proportions of ortho–ortho links, a more organic orientation should be noticeable.

Synthesis

Of various catalysts, $ZnAc_2$ has an outstanding effect on obtaining high-ortho novolac resins. Therefore, we chose $ZnAc_2$ as a catalyst to study other factors during the synthesis.

Fraser et al.[3] found that a molar excess of phenol in the original condensation is necessary for high-ortho novolac resins. We altered the P/F ratio from 1.06 to 1.46. Figure 3 shows the proportions of ortho–ortho links of the synthesized resins with different P/F molar ratios. The proportion reached the peak when the P/F ratio was 1.26. In the system with $ZnAc_2$ as the catalyst, the best P/F molar ratio was 1.2–1.3.
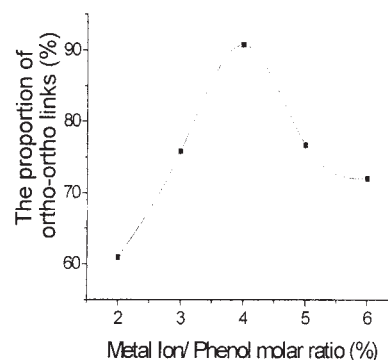

Figure 4 Proportion of ortho–ortho links of the synthesized resins versus the metal-ion/phenol molar ratio. The polymers were synthesized with a molar ratio of P/F = 1.26 at 125°C for 4 h.
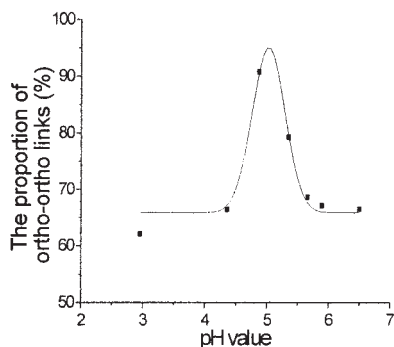
Figure 5 Proportion of ortho–ortho links of the synthesized resins versus the pH value. The polymers were synthesized with molar ratios of P/F = 1.26 and ZnAc$_2$/phenol = 4% at 125°C for 4 h.

Figure 4 presents a curve of the proportions of ortho–ortho links of the synthesized resins versus the metal-ion/phenol molar ratio. The extent of the effect was directly proportional to the quantity of metallic ions present, and the proportion reached the peak when the metal-ion/phenol molar ratio was 4%. When the metal-ion/phenol ratio was less than 4%, some phenol lacked metal ions to form the chelate rings, so the proportion was increased with an increasing metal-ion/phenol ratio. When the metal-ion/phenol ratio was greater than 4%, the amount of the metal was relatively excessive in comparison with that of phenol, and the superfluous metal ions destroyed the chelate rings that formed; therefore, the proportion was decreased with an increasing metal-ion/phenol ratio. This result indicated that the formation of chelate rings between the metal, formaldehyde, and phenol should have appropriate conditions. The complex formed by the bivalent metal and phenol demanded an appropriate range of metal-ion/phenol molar ratios. Under the metal-ion/phenol ratio of 4%, we obtained a high-ortho novolac resin that had the highest proportion of ortho–ortho links.

The pH value and the reaction time are also important parameters for the synthesis of high-ortho novolac resins. The effect of the pH value is shown in Figure 5. Hydrochloric acid and sodium hydroxide were used to adjust the pH value of the system. When the pH was 4–7, the proportion of ortho–ortho links of the synthesized resins was greater than 65%. When the pH value was around 5, the catalyst (ZnAc$_2$) had the best catalysis effect. The decrease in the effect at lower and higher pH values could be ascribed to the reduction of the metal-ion effect by the increased reactivity of the phenol–formaldehyde system.[8]

The effect of the reaction time is shown in Figure 6. When the system reacted too long, the high-ortho novolac resin with ortho–ortho links continued reacting at the para position of phenol, so the proportion was reduced. For a higher proportion of ortho–ortho links, the reaction time had to be between 4 and 6 h.
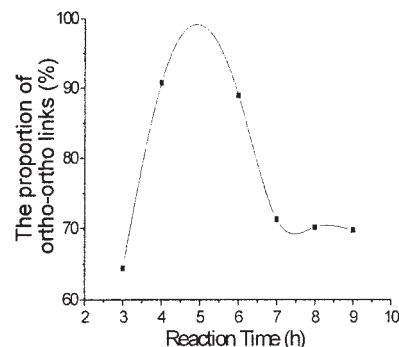

Figure 6 Proportion of ortho–ortho links of the synthesized resins versus the reaction time. The polymers were synthesized with molar ratios of P/F = 1.26 and ZnAc$_2$/phenol = 4% at 125°C for certain times.

Curing

High-ortho resins can be cured by hexamethylenetetramine at a much higher rate than resins made with conventional acid or alkali catalysts.[2] We chose various resins with different proportions of ortho–ortho links to measure the gel time. The plots in Figure 7 indicate that the gel time was in inverse proportion to the proportion of ortho–ortho links. The faster curing rate of the high-ortho resin was ascribed to the higher proportion of free more highly reactive para positions available for further reaction during the curing of the resin.

In Figure 8, we compare the gel times for different high-ortho resins at different cure temperatures. As we expected, a shorter gel time was needed for a higher proportion of ortho–ortho links of the resin at any cure temperature. The gel time was linear with the cure temperature for various high-ortho novolac resins. For various high-ortho novolac resins, the lines were parallel. In other words, whatever the proportion was, we could choose a temperature to cure the resin within the expected time.

DSC

A useful technique for DSC analysis is model-free kinetics, as described by Vyazovkin and coworkers,[9]
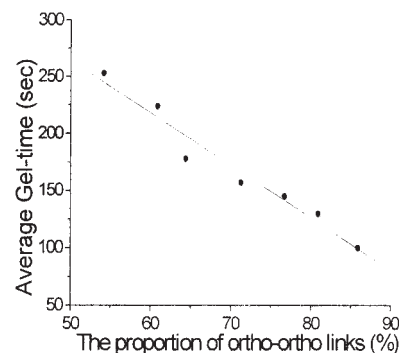

Figure 7 Average gel time versus the proportion of ortho–ortho links of the synthesized resins at 155 °C.

which is based on the realization that the function of the degree of conversion [$f(\alpha)$] and the activation energy at a given degree of conversion (E_α) depend on the degree of the reaction conversion (α) but are always the same at a particular value of α, being independent of the heating rate used. The basis used for this technique is the activation energy curve as a function of α. This new formulation requires no knowledge of the reaction model. For the cure of thermosetting systems, the general method ignores the complexity of the cure in kinetic calculations. The basic reaction rate equation is as follows:

$$d\alpha/dt = k \times f(\alpha) \qquad (1)$$

where k is the rate constant and t is the reaction time. In general, k is dependent on the temperature through an Arrhenius-type equation. Equation (1) can thus be rewritten as follows:

$$d\alpha/dt = f(d\alpha/dt) \times A \times \exp(-E/RT) \qquad (2)$$

where E is the activation energy and A is the preexponential factor. It is assumed that function $f(\alpha)$ and parameters A and $E\alpha$ in this equation are constant at a particular value of α. Therefore, we can obtain a differential equation from eq. (2):

$$d \ln(d\alpha/dt)_\alpha/dT^{-1} = E_\alpha/R \qquad (3)$$

The model-free method follows every point of conversion, obtaining the activation energy at each point. Therefore, it can reveal the dependence of $E\alpha$ on α and the complexity of the curing process.

The curing behavior of the high-ortho novolac resin with hexamethylenetetramine was examined with DSC. A sharp exotherm was observed for every resin. For all the resins, the DSC curves had one exothermic peak, and they were analyzed for the total curing enthalpy (ΔH) and individual curing temperatures
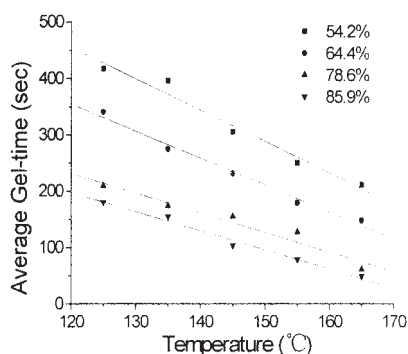

Figure 8 Average gel time versus the temperature for different proportions of ortho–ortho links of the synthesized resins.

TABLE II
DSC Results of the High-Ortho Novolac Resins

Proportion of ortho–ortho links (%)	Peak temperature (°C)	ΔH (J/g)	E_α (kJ/mol)
54.2	133	35.05	43.42
64.4	140	43.58	27.99
71.3	141	64.80	22.75
76.7	146	54.54	16.16
80.9	153	46.59	14.34
85.9	162	27.55	13.39

(see Table II). None of the variables had a statistically significant effect on ΔH and the peak temperature. The activation energy for curing showed a decreasing trend with an increase in the proportion of ortho–ortho links of the resins, and this indicated that the high-ortho novolac resin needed less energy than the conventional novolac resin.

CONCLUSIONS

We undertook this study to investigate the effects of various conditions on high-ortho novolac resins and to control the special proportion of ortho–ortho links of the resins by adjusting the conditions.

We reached the following conclusions:

1. To obtain a higher proportion of ortho–ortho links of the resins, we should choose the bivalent metal salt of an organic acid as the catalyst, especially the salts of Zn^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+}, Cd^{2+}, and Ca^{2+}.
2. $ZnAc_2$ is an excellent catalyst for enhancing the proportion of ortho–ortho links of the resins. When the P/F molar ratio is 1.2–1.3, the metal-ion/phenol ratio is 3–5%, the pH value of the system is adjusted to around 5, and the reaction time is 4–6 h, the catalysis effect of $ZnAc_2$ will be optimal, and we can obtain a resin whose proportion of ortho–ortho links is above 90% easily.
3. A higher proportion of ortho–ortho links needs a lower activation energy, a lower cure temperature, and a shorter cure time. During the curing of the resins, there is a linear relation between the time and temperature for various proportions of ortho–ortho links of the resins.

We can choose the catalyst and the synthesis conditions to control the proportion of ortho–ortho links of the resins. For the curing, we also can choose the temperature or time.

References

1. Knop, A.; Pilato, L. A. Chemistry and Application of Phenolic Resins; Springer-Verlag: Berlin, 1979; p 28.

2. (a) Bender, H. L. Wood Plast 1953, 30, 136; (b) Bender, H. L. Wood Plast 1954, 31, 115.

3. (a) Fraser, D. A.; Hall, R. W.; Raum, A. L. J. J Appl Chem 1957, 7, 676; (b) Fraser, D. A.; Hall, R. W.; Raum, A. L. J. J Appl Chem 1957, 7, 689.

4. (a) Park, B. D.; Riedl, B. J Appl Polym Sci 2000, 77, 841; (b) Park, B. D.; Riedl, B. J Appl Polym Sci 2000, 77, 1284.

5. (a) Roczniak, C.; Biernacka, T.; Skarzynski, M. J Appl Polym Sci 1983, 28, 531; (b) Scariah, K. J.; Usha, K. M.; Narayanaswamy, K.; Shanmugam, K.; Sastri, K. S. J Appl Polym Sci 2003, 90, 2517.

6. Grenier-Loustalot, M. F.; Larroque, S.; Screnier, P. Polymer 1996, 37, 639.

7. Rama, R. M.; Alwan, S.; Scariah, K. J.; Sastri, K. S. J Therm Anal 1997, 49, 261.

8. Pizzi, A. Wood Additives: Chemistry and Technology; Marcel Dekker: New York, 1983; p 118.

9. (a) Vyazovkin, S.; Lesnikovich, A. Thermochim Acta 1990, 165, 273; (b) Vyazovkin, S. Thermochim Acta 1992, 194, 221; (c) Vyazovkin, S.; Sbirrazzuoli, N. Macromolecules 1996, 29, 1867.