

The Curing of Novolacs with Paraformaldehyde

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Synopsis

The curing of novolacs with paraformaldehyde is analyzed with several experimental techniques (DSC, IR, sol fraction) as well as statistical arguments. Results for typical novolacs show that a maximum crosslinking density is attained at a mass ratio m_P/m_N close to 0.20. However, at m_P/m_N greater than 0.10, hemiformals appear in the cured product, increasing the amount of extractable formaldehyde. The heat of reaction increases linearly from $m_P/m_N = 0$ to 0.15, attaining a maximum value of $-\Delta H = 98$ cal/g novolac at $m_P/m_N \sim 0.20$. The curing kinetics follows an overall second-order law with an activation energy $E = 32.5$ kcal/mol and a preexponential factor $A = 1.1 \times 10^{15}$ min⁻¹ (both for $m_P/m_N > 0.1$).

INTRODUCTION

Novolac resins, which are thermoplastic in nature, must be cured with the addition of a crosslinking agent. Hexamethylenetetramine (HMTA) is the most widely used, other reagents such as paraformaldehyde (PF) or trioxane being of only limited importance. However, for some applications, the use of HMTA may be the cause of severe problems. For example, ammonia can be split off from HMTA-cured novolacs under influence of moisture and temperature, resulting in corrosion of copper and brass parts.¹ Also, the presence of nitrogen in the coated sand used in shell molding is the cause of blow holes and subsurface porosity, particularly in low- to medium-carbon and low-alloy steel casting.²⁻⁴ In this case, lower HMTA levels may be used with ortho-linked novolacs. However, for thin sections, nonnitrogen resin is often essential, paraformaldehyde having been suggested as a convenient alternative hardener.³

The aim of this report is to provide information related to the energetics, kinetics, and kinds of reactions taking place in the curing of novolacs with paraformaldehyde. Results should enable the definition of suitable operating conditions for the curing process.

EXPERIMENTAL

The novolac was obtained⁵ by reacting phenol and paraformaldehyde in a stainless steel reactor with oxalic acid as catalyst. The formaldehyde/phenol molar ratio was $F/P = 0.8$, temperature = 100°C, and reaction time = 4 h. Water was evacuated under reduced pressure during 4 h at 120°C. The product was discharged, dried in air, and heated to 160°C under vacuum in order to distil off free phenol (IR spectra confirmed the product being distilled to be pure phenol). Cryoscopy in dioxan gave a number-average molecular weight (\bar{M}_n) of 745 for the resulting novolac. Paraformaldehyde was a technical-grade reagent with 92% CH₂O. Both oligomers were ground and thoroughly mixed in mass ratios (m_P/m_N): paraformaldehyde/novolac ranging between 0.005 and 0.27.

Differential scanning calorimetry (DSC) thermograms were obtained with a du Pont 990 Thermal Analyzer provided with a pressure DSC cell. Runs were carried out in a nitrogen atmosphere at 650 psi and heating rates ranging between 5 and 20°C/min.

Mixtures of novolac and paraformaldehyde were reacted in closed steel tubes (15 cm length, 1.1 cm diameter), increasing the temperature in two steps: 1 hr at 150°C and 1 h at 190°C. Cured samples were extracted from the reactors and pulverized.

Pellets prepared from mixtures of the cured samples with KBr were monitored on a Perkin-Elmer 599 IR spectrophotometer. The sol fraction of cured samples was measured with Soxhlet devices using acetone (technical grade) as solvent.

RESULTS AND DISCUSSION

Energetics

Figure 1 shows a DSC thermogram of a sample containing a paraformaldehyde (PF) mass fraction, $w_P = m_P/(m_P + m_N) = 0.10$, cured at a 10°C/min heating rate. A broad exothermic peak with a maximum at 200°C is observed. Cure begins at ~140°C, at which PF decomposition showed an incipient rate increase when heated alone. This band lies in exactly the same range as that of the one reported by Sebenik et al.⁶ for the uncatalyzed curing of phenol with PF using a 1:1 phenol/formaldehyde molar ratio. As discussed by these authors, both formaldehyde addition to a free *o*-, *o'*- or *p*-position of a phenolic ring in the novolac and condensation of the resulting methylolated novolac with another free position take place simultaneously at this temperature range.

The heat of reaction is related to the area under a DSC curve. Carrying out the corresponding calculations for samples containing different PF amounts, the curve plotted in Figure 2 is obtained. Each experimental point corresponds to an average of at least four runs. Different scanning rates gave the same values within experimental error. The increase in the heat released per unit mass of novolac is related to an increase in the substitution of free *o*-, *o'*-, and *p*-positions

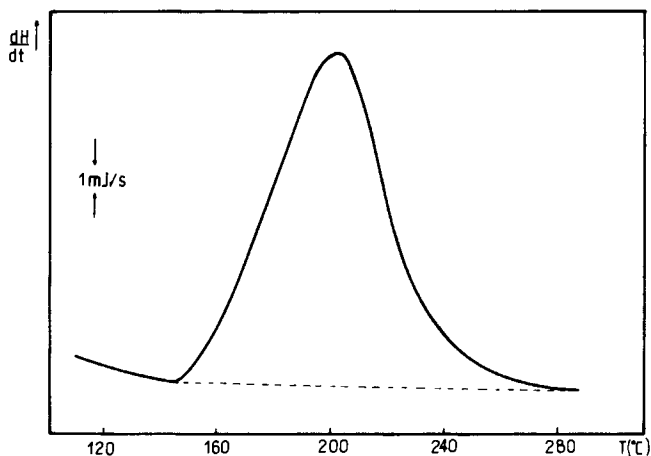


Fig. 1. DSC thermogram of a sample containing a PF mass fraction, w_P 0.10, cured at a 10°C/min heating rate.

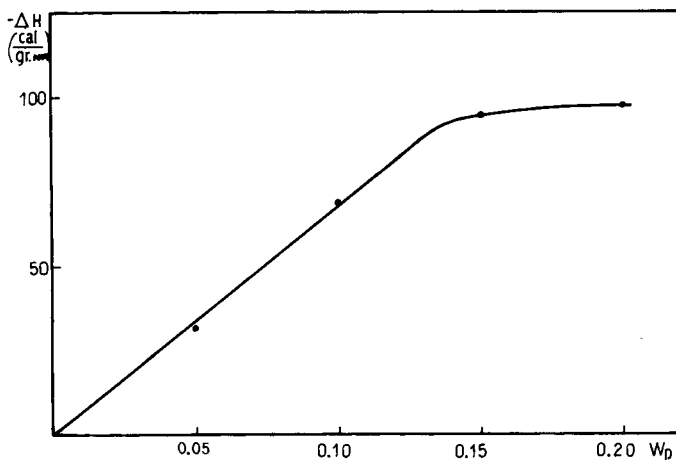


Fig. 2. Heat of reaction per unit mass of novolac as function of the PF mass fraction w_P .

of phenolic rings in the novolac. Thus, saturation of novolac functionalities is apparently accomplished at w_P close to 0.15 (or at a mass ratio $m_P/m_N = 0.176$).

Kinetics

A phenomenological kinetic expression for the curing reaction was obtained by applying the analysis of Barrett⁷ to the DSC curves. A second-order kinetic expression gave a very good fitting for all the conversion range and different PF mass fractions:

$$\frac{dx}{dt} = A \exp\left(\frac{-E}{RT}\right) (1-x)^2 \quad (1)$$

where x is the overall conversion (fraction of area under the DSC curve), and values of A and E are shown in Table I as a function of w_P . Each one of the rows of Table I is an average of at least four runs. The high A value for samples with $w_P = 0.05$ is the result of a compensation effect with the corresponding high E value.

For the NaOH-catalyzed phenol-PF system, Sebenik et al.⁶ reported a second-order reaction for the addition step and a first-order reaction for the condensation step. Reported activation energies, at 0.25% NaOH catalyst level, were $E_a = 23.7$ kcal/mol and $E_c = 22.9$ kcal/mol. A decrease in both E_a and E_c

TABLE I
Kinetic Parameters for the Curing Reaction

A (min^{-1})	E (kcal/mol)	Mass fraction w_P	Correlation coefficient
$3.9 \cdot 10^{17}$	37.3	0.05	0.993
$1.0 \cdot 10^{15}$	32.3	0.10	0.998
$1.1 \cdot 10^{15}$	32.3	0.15	0.998
$1.1 \cdot 10^{15}$	32.8	0.20	0.995

with increasing NaOH amounts was also reported. Our results agree with a controlling addition step and an activation energy greater than the one corresponding to the catalyzed reaction.

IR Spectra

Figure 3 shows IR spectra of the novolac, PF, and a cured sample with $w_P = 0.15$. In spite of the partial overlapping of PF and novolac peaks, no evidence of the presence of PF in the cured product arises from the figure. Thus, most of the ether linkages, C—O—C, are broken during the curing reaction. The band located at 1500 cm^{-1} is assigned to a phenolic ring substituted in the *o*-, *p*-, and (*o,p*)-positions.⁸ The disappearance of this band in the cured sample shows the depletion of mono- and disubstituted phenolic rings due to crosslinking. The band at 1470 cm^{-1} is due to (*o,o'*)- and (*o,o'*)-substitutions of the phenolic ring and methylene linkages, —CH₂—. The relative intensity increase of this band in the cured product is also associated with the crosslinking increase. Besides, the absorption band at 820 cm^{-1} , which can be assigned to *o*- and *p*-substituted phenolic rings,⁸ shows a strong intensity decrease in the cured sample due to crosslinking. Thus, for the most part the free available positions of phenolic rings are joined by methylene linkages.

The increase in crosslinking when increasing the PF mass fraction (w_P) from 0.0054 to 0.15 is shown in Figure 4. The band at 1500 cm^{-1} practically disappears, while the band at 1470 cm^{-1} becomes dominant. This is in perfect agreement with calorimetric results (Fig. 2), showing that saturation of novolac functionalities was accomplished at w_P close to 0.15. There is, however, one small band which gives a hint of an efficiency loss in the crosslinking process; this is the peak at 1000 cm^{-1} , which may be assigned to the stretching vibration of a

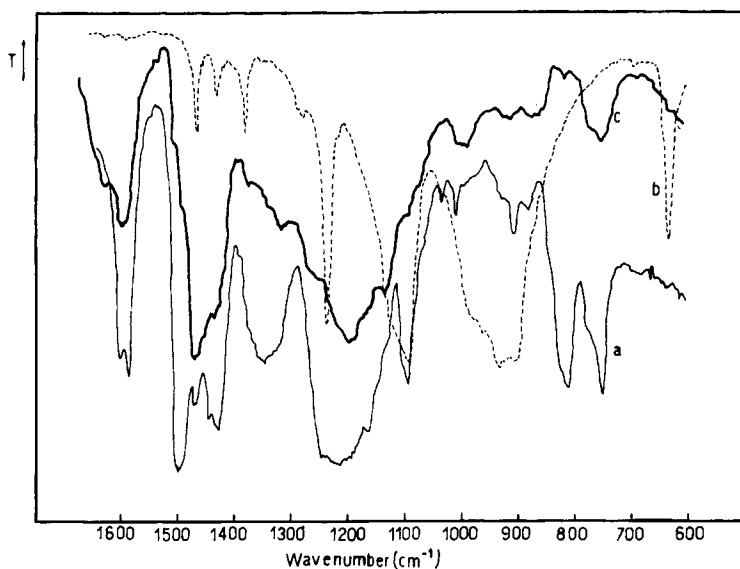


Fig. 3. IR spectra of novolac (a), paraformaldehyde (b), and a cured sample with a PF mass fraction w_P of 0.15 (c).

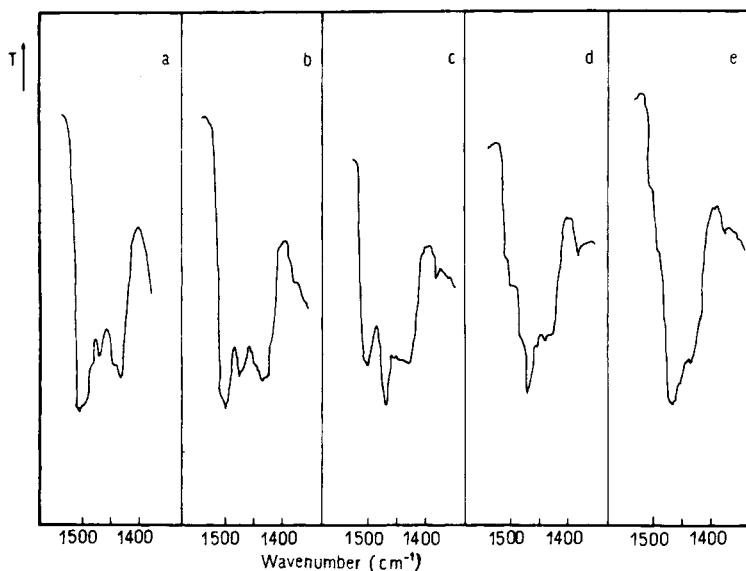


Fig. 4. IR spectra in wave number range 1400–1550 cm^{-1} for samples cured with different PF mass fractions: (a) $w_P = 0.0054$; (b) $w_P = 0.023$; (c) $w_P = 0.060$; (d) $w_P = 0.100$; (e) $w_P = 0.15$.

C—OH linkage in a methylol group⁶ ($-\text{CH}_2\text{OH}$). This band is absent for $w_P < 0.10$, incipient for $w_P = 0.10$, and definitely present for $w_P = 0.15$ (Fig. 3). Thus, when reactive positions of the novolac have been highly depleted, the methylolated product resulting from the addition step does not condense easily with the few remaining reactive positions of the novolac, possibly due to steric hindrances. In these conditions, both methylol groups and reactive positions of the novolac compete for the remaining $-\text{CH}_2\text{O}-$ groups. This may lead to the presence of hemiformals, $\text{R}-\text{CH}_2-\text{O}-\text{CH}_2\text{OH}$, in the cured product.^{1,9,10} Then a complete conversion of the available theoretical functionalities cannot be attained.

Soluble Fraction

Figure 5 shows the sol fraction of the cured products as a function of the mass ratio of PF to novolac, m_P/m_N . The gel point (reaction extent from which w_s begins to be less than 1) is reached for a very low PF amount. The curve passes through a minimum for $m_P/m_N \sim 0.08$ and then increases. Thus, for m_P/m_N ratios between 0.08 and 0.18, where the crosslinking density increases as shown by IR and calorimetric results, there is an abnormal increase in the sol fraction. This may be explained by accepting that hemiformals appear at $m_P/m_N > 0.08$ and are decomposed by the boiling solvent during the sol fraction determination (technical-grade acetone contained water). To prove this, cured samples were immersed in boiling water for several hours and formaldehyde qualitatively detected in the resulting solutions with the chromotropic acid color test.¹¹ This test was positive for $m_P/m_N \geq 0.10$, confirming the presence of hemiformal compounds which were hydrolyzed by boiling water.

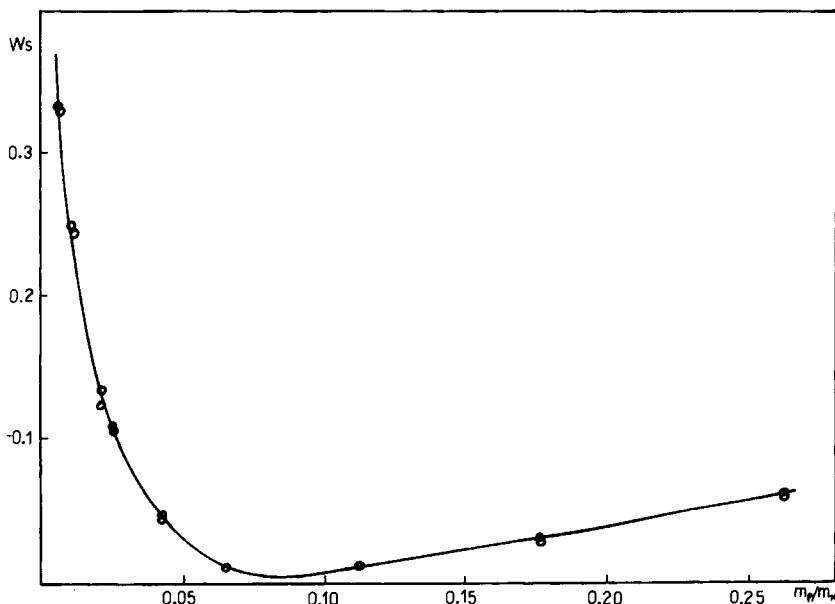


Fig. 5. Sol fraction of cured products as function of mass ratio of paraformaldehyde to novolac, m_P/m_N .

Statistics

Statistical calculations may be carried out by assuming the curing reaction to take place between a generic novolac molecule, N_i , with i phenolic rings and functionality f_i , and a formaldehyde molecule, CH_2O , with a functionality of 2. The main reaction may be represented as



where $(\text{NOV})-\text{H}$ represents any active hydrogen associated to the novolac (i.e., any one occupying an *o*-, *o'*-, or *p*-position in a phenolic ring). As each one of the i phenolic rings of the novolac had originally three reactive positions, there were $3i$ initial reactive positions, from which $2(i-1)$ were converted into linkages between rings. The remaining free positions are

$$f_i = 3i - 2(i-1) = 2 + i \quad (2)$$

If the system has polymerized until some fraction x_F of the formaldehyde functionalities and some fraction x_N of the novolac functionalities have reacted, it must be verified that

$$2F_0x_F = (\sum_i f_i N_i)x_N \quad (3)$$

where $2F_0$ is the initial number of formaldehyde functionalities (related to the initial mass of paraformaldehyde, m_P) and $\sum_i f_i N_i$ is the initial number of novolac functionalities.

The gel point is reached when¹²

$$(x_F x_N)_{\text{gel}} = \frac{1}{(f_e - 1)(2 - 1)} \quad (4)$$

where

$$f_e = \frac{\sum_i f_i^2 N_i}{\sum_i f_i N_i} \quad (5)$$

If the paraformaldehyde is the limiting reactant and the reaction is carried out to $x_F = 1$, from eqs. (3) and (4)

$$\left(\frac{\sum_i f_i N_i}{2F_0} \right)_{\text{gel}} = f_e - 1 \quad (6)$$

The statistics involved in the production of novolacs have been reported elsewhere.¹³ For a novolac prepared with F/P = 0.8 ($x_F = 1$) and containing no free phenol, the predicted number-average molecular weight is 757.5, and the corresponding weight-average molecular weight is 2087.7. The experimental \bar{M}_n value was equal to 745, in good agreement.

The molecular weight of a generic novolac containing i phenolic rings is

$$M_i = 106i - 12 \quad (7)$$

From eqs. (2) and (7),

$$f_i = 9.43 \times 10^{-3} M_i + 2.113 \quad (8)$$

Taking into account the definitions of \bar{M}_n and \bar{M}_w ,

$$\sum_i f_i N_i = \left(9.43 \times 10^{-3} + \frac{2.113}{\bar{M}_n} \right) m_N \quad (9)$$

$$\sum_i f_i^2 N_i = \left(8.89 \times 10^{-5} \bar{M}_w + 3.985 \times 10^{-2} + \frac{4.465}{\bar{M}_n} \right) m_N \quad (10)$$

where m_N is the mass of novolac.

By replacing the values of \bar{M}_n and \bar{M}_w ,

$$\sum_i f_i N_i = 1.222 \times 10^{-2} m_N; f_e = 18.93 \quad (11)$$

On the other hand, a mass m_P of 92% PF contains m_P (0.92/30) moles of formaldehyde. Thus,

$$F_0 = 3.067 \times 10^{-2} m_P \quad (12)$$

By replacing eqs. (11) and (12) into eq. (6), we get

$$\left(\frac{m_P}{m_N} \right)_{\text{gel}} = 0.011$$

a value which is greater but lying in the same range as the experimental one,

$$\left(\frac{m_P}{m_N} \right)_{\text{gel}} (\text{exp}) \sim 0.004-0.005$$

Let us now analyze the theoretical condition for maximum crosslinking density. This is achieved when both reagents are used in stoichiometric amounts. From eq. (3), $x_N = 1$ when $x_F = 1$, for

$$\sum_i f_i N_i = 2F_0 \quad (13)$$

From eqs. (11), (12), and (13),

$$\left(\frac{m_P}{m_N} \right)_{\text{max. crosslinking}} = 0.20$$

or

$$w_P = \left(\frac{m_P}{m_N + m_P} \right)_{\text{max. crosslinking}} = 0.17$$

These values are in very good agreement with calorimetric results (Fig. 2) and infrared spectra (Fig. 4). However, at $m_P/m_N > 0.10$, the formaldehyde begins to lose efficiency as a crosslinking agent due to the formation of hemiformals, as revealed by the increase in the sol fraction (Fig. 5). Thus, depending on the required characteristics of the cured product, the PF proportion must be varied. If the probability of formaldehyde evolution from the cured product must be kept at a minimum, the mass ratio m_P/m_N should not exceed 10% for a typical novolac. In this way, the crosslinking density would be half of the maximum theoretical value, with corresponding variations in mechanical properties. Increasing the PF amount in the m_P/m_N range 0.10–0.20 will increase both the crosslinking density and the amount of extractable formaldehyde.

CONCLUSIONS

Typical novolacs may be cured with paraformaldehyde giving highly cross-linked products, mainly through methylene bridges. The maximum crosslinking density is attained at m_P/m_N close to 0.20. However, if m_P/m_N is greater than 0.10, hemiformals begin to appear in the cured product, increasing the amount of extractable formaldehyde. The optimum PF amount depends on the required characteristics of the cured product.

The temperature range where the curing reaction may be accomplished lies between 140 and 200°C. The heat of reaction increases linearly from $m_P/m_N = 0$ to 0.15, attaining a maximum value of $-\Delta H = 98$ cal/g novolac at $m_P/m_N \sim 0.20$. The curing kinetics follows an overall second-order law with an activation energy $E = 32.5$ kcal/mol, and a preexponential factor $A = 1.1 \times 10^{15} \text{ min}^{-1}$ (for a PF mass fraction $w_P \geq 0.1$).

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