

# Kinetic Investigation on the Curing of Phenol-Furfural Resin by Differential Scanning Calorimetry

RAVJI D. PATEL, RANJAN G. PATEL and VITHAL S. PATEL,  
*Chemistry Department, Sardar Patel University, Vallabh  
Vidyanagar-388120, India, and E. M. PEARCE, Polytechnic  
University, Brooklyn, New York, 11201*

## Synopsis

Curing reactions of phenol-furfural (PFu) resin with hexamethylene tetramine (Hexa) have been studied by differential scanning calorimetry technique both dynamically as well as isothermally. The curing exotherms obtained have been analyzed to derive the kinetic parameters associated with the curing process. The effect of the concentration of hexa and the temperature on the curing characteristics have been investigated. The optimum concentration of hexa and the optimum temperature for curing are observed to be 12% and 160°C, respectively.

## INTRODUCTION

Among the thermosetting resins, phenolics have attracted special attention because of their wide range of applications in adhesives, castings, mouldings, and in structural parts, etc.<sup>1</sup> Due to its industrial importance, it is worthwhile that the curing chemistry of phenolics be understood in detail. Differential scanning calorimetry (DSC) has proved to be a valuable technique to follow the curing kinetics of thermosetting resins.<sup>2</sup> A number of studies have reported on the curing of phenol-formaldehyde (PF) resins.<sup>3-5</sup> However, no systematic study has been made on the curing of phenol-furfural (PFu) resins, which are in ever increasing demand due to their good flow property and the superior electrical properties of the cured product.

In the present paper, DSC technique is applied to study the curing kinetics of a novolac-type phenol-furfural resin using hexamethylene tetramine (Hexa) as a curing agent. DSC study was carried out both dynamically at a heating rate of 10°C/min and isothermally at 150, 160, 170, and 180°C using hexa, in amounts of 8, 10, 12, and 14% (wt% of resin). The overall kinetic parameters for the curing reaction are estimated using various relations reported in the literature, based on a single dynamic scan as well as on isothermal scan. The effect of the variation of concentration of hexa in resin-hexa mixture and the temperature on the characteristic parameters is investigated.

## EXPERIMENTAL

### Materials

The resin used for the study was a novolac-type phenol-furfural resin, which was prepared by the method reported in literature<sup>6</sup> with some modifications.

Molten phenol (400 g, 4.25 mol) was placed in the reaction flask. To this potassium carbonate (8 g dissolved in 20 mL water) was added and the temperature of the reaction mixture was raised to 135°C. Furfural (408 g, 4.25 mol) was added dropwise during a period of 30 min. The temperature was kept at 135°C for 4 h. After the reaction was completed, the reaction mixture was evacuated at 20 mm pressure and at maximum temperature of 135°C. The solid product obtained on cooling was ground to powder and washed several times with water, and dried in air.

The curing agent, hexa was an Analar-grade reagent.

**Analysis of the Resin.** The resin was a dark-colored amorphous powder having softening temperature in the range 98–105°C. The intrinsic viscosity in acetone at 30°C, as determined using Ubbelohde suspended level-type viscometer was observed to be  $[\eta] = 4.0 \times 10^{-2}$  dL/g. The number-average molecular weight determined by vapor pressure osmometry was about 1080. The ratio of reacted furfural to phenol was  $\sim 0.87$ , which was determined by measuring the amount of phenol and furfural separated out during the reaction, during vacuum distillation and during the washings of the resin.

**DSC Measurements.** Ambient pressure DSC was performed on Dupont 990 differential scanning calorimeter. The dynamic scans were taken at a heating rate of 10°C/min in the range 30–280°C. For the isothermal scans the DSC cell was first heated to the elevated temperature at a predetermined rate (200°C/min) and maintained at the required temperature while a cure exotherm was monitored as a function of time. The cell was calibrated with samples of known heat of fusion according to the instrument manual. For DSC sample preparation  $\sim 2$  g of the exact weight of the resin was taken in a small capsule and the required amount of hexa was mixed thoroughly with it. The mixture was heated at 110°C for 5 min to ensure the complete mixing of the components. About 5–8 mg of the prepared sample was cured in the DSC cell using the empty cell as a reference. The DSC runs were made in triplicate and the reproducibility of the kinetic data was observed to be  $\sim 98\%$ . The kinetic parameters were computed for each of the runs and the values were averaged and reported with statistical variations.

**Analysis of the Dynamic DSC Run.** The heat flow data and the area under the curve obtained from the DSC exotherm were processed to obtain the degree of conversion,  $\alpha$ , and the rate of the reaction,  $\frac{d\alpha}{dt}$ . The rate constant  $k$  was determined, using the Barrett relation<sup>7</sup> [Eq. (1)], for a series of temperatures. Also the data were analyzed to evaluate activation energy and order of the reaction using Freeman-Carroll relation<sup>8</sup> [Eq. (2)], Ellerstein relation<sup>9</sup> [Eq. (3)], and Kay-Westwood relation<sup>10</sup> [Eq. (4)].

**Analysis of the Isothermal DSC Scan.** The exotherms obtained in the isothermal scans were analyzed for their heat flow data as a function of time for a particular scan obtained at a specified temperature. The results were used to derive certain kinetic parameters using the reported relations.

## RESULTS AND DISCUSSION

The phenol-furfural resin is a novolac-type resin and requires some formaldehyde-generating curing agent for crosslinking reactions. In the present

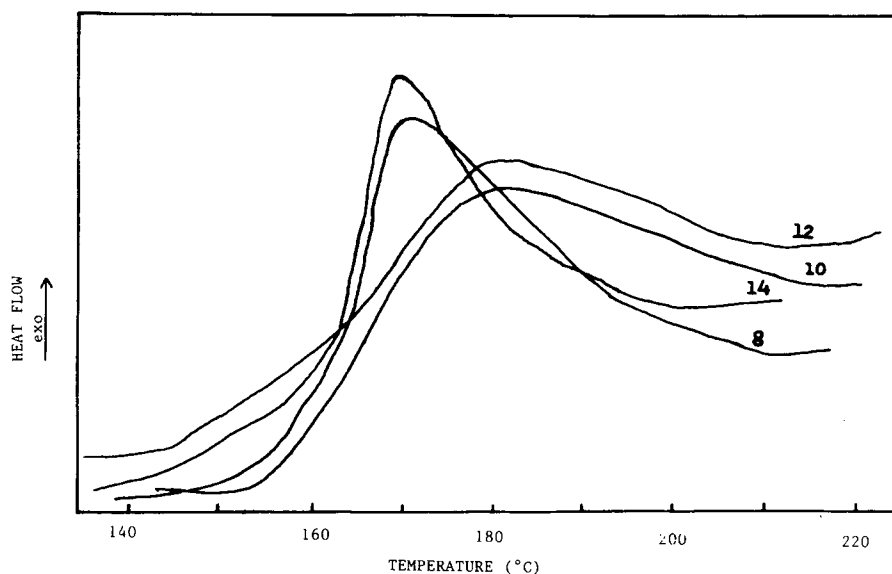


Fig. 1. Dynamic DSC scans obtained using 8, 10, 12, and 14% of hexa.

case, hexamethylene tetramine was used as a curing agent, the amount of which was selected in the range 8–14% by weight of resin on the basis of the reported amount of hexa in the range 10–15% for the curing of phenol-formaldehyde resin.<sup>3,4</sup> The amount of hexa was selected as 8, 10, 12, and 14% by weight of resin in order to determine optimum hexa content. The curing of PFu resin with hexa is a condensation-type reaction and may lead to the emission of some volatile products. Hence the DSC cells were hermetically sealed after filling with sample.

No detectable curing reaction was observed on heating the resin-hexa mixture in a separate experiment at 110°C for about 20 min, while curing exotherms in the range 150–210°C were observed during DSC cure studies. Selected dynamic DSC scans obtained using 8, 10, 12, and 14% of hexa are shown in Figure 1. The exotherms obtained are analyzed to determine the temperatures suggesting the starting ( $T_i$ ); the maximum ( $T_m$ ), and the completion ( $T_f$ ) of the curing. They are listed in Table I along with the curing time and the heat of reactions. The area under the curve and the heat flow were measured from the exothermic curve at certain temperature intervals and the data was fitted to four different relations<sup>7-10</sup> to obtain the kinetic

TABLE I  
Curing Characteristics of PFu-Hexa Systems from Dynamic Scan

PFu-Hexa	$T_i$ (°C)	$T_m$ (°C)	$T_f$ (°C)	Cure Range (min)	$\Delta H$ (J/g)
100:8	152	170	212	12.2	32.6
100:10	148	178	210	12.8	36.5
100:12	146	182	208	13.4	40.8
100:14	143	170	202	11.2	37.2

parameters. The computational methods using these relations are rapid and simple for determining the kinetic parameters from a single DSC dynamic scan. Also the major advantage is that the relations are interrelated in the sense that the quantities to be measured to derive the rate data are more or less similar. The relations are described by the Eqs. (1) to (4).

$$k = \frac{d\alpha/dt}{A - \alpha} = \frac{dH/dt}{A - \alpha} \quad (1)$$

$$\frac{\Delta \ln(dH/dt)}{\Delta \ln(A - \alpha)} = n - \frac{(E/R)\Delta(1/T)}{\Delta \ln(A - \alpha)} \quad (2)$$

$$T^2(S/h) = E/R - nT^2(h/r) \quad (3)$$

$$\frac{(1 - H/H_T)d/dt(dH/dt)}{\beta(dH/dt)^2} = \frac{E(1 - H/H_T)}{R dH/dt \cdot T^2} - \frac{n}{H_T \cdot \beta} \quad (4)$$

In the above mentioned equations the terms involved are defined as  $k$  = rate constant,  $\alpha$  = fractional conversion,  $\frac{d\alpha}{dt}$  = rate of reaction,  $\frac{dH}{dt}$  = rate of heat generation,  $a = H$  = heat of reaction (J/g) at a given temperature (time) = area under DSC curve at a particular temperature,  $A = H_T$  = total heat of reaction (J/g) = total area under DSC curve,  $n$  = order of the reaction,  $E$  = Arrhenius activation energy (kJ/mole),  $R$  = gas constant,  $T$  = temperature ( $^{\circ}$ K),  $S = d^2H/dt^2$ ,  $h = dH/(\beta) dt$ ,  $\beta$  = heating rate ( $^{\circ}$ C/min), and  $r$  = unreacted fraction =  $H_T - H$ .

For the purpose it was assumed that the reactions can be described as being simple  $n$ th order Arrhenius-type temperature-dependent reactions. The assumption is fairly valid as the reactions appeared to follow Arrhenius-type kinetics over the range studied through at least 70–80% of the completion, as the plots of  $\ln k$  against  $1/T$  gave a fairly good straight line. The values of the activation energy,  $E$  and the frequency factor  $\ln A$  obtained from the regression plots of the data fitted to the Barrett relation<sup>7</sup> [Eq. (1)] are listed in Table II. The kinetic parameters, the activation energy,  $E$  and the order of the reaction,  $n$  as determined by using Freeman-Carrol relation<sup>8</sup> [Eq. (2)], Ellerstein relation<sup>9</sup> [Eq. (3)], and the Kay-Westwood relation<sup>10</sup> [Eq. (4)], are listed in Table III along with the regression coefficients of the analysis.

TABLE II  
Data Evaluated Using Barrett Relation

PFu-Hexa	$E \pm 2$ (kJ/mol)	$\ln A \pm 1$ (min)	$r^a$
100 : 8	151.3	28.7	0.996
100 : 10	141.7	34.5	0.981
100 : 12	119.9	28.9	0.995
100 : 14	130.4	32.7	0.988

<sup>a</sup> $r$ : The regression coefficient.

TABLE III  
Kinetic Parameters Evaluated Using Eqs. (2)–(4)

PFu-Hexa	Eq. (2)			Eq. (3)			Eq. (4)		
	E <sup>a</sup>	n <sup>b</sup>	r <sup>c</sup>	E <sup>a</sup>	n <sup>b</sup>	r <sup>c</sup>	E <sup>a</sup>	n <sup>b</sup>	r <sup>c</sup>
100 : 8	167.2	0.93	0.998	165.5	1.27	0.985	160.5	1.05	0.988
100 : 10	131.2	1.15	0.999	140.0	1.23	0.960	137.1	0.97	0.989
100 : 12	113.7	1.06	0.986	123.3	0.87	0.964	122.0	0.99	0.992
100 : 14	132.1	1.18	0.983	140.0	0.86	0.983	135.8	1.23	0.985

<sup>a</sup>The activation energy,  $E \pm 2$  kJ/mole.

<sup>b</sup>n, the order of the reaction.

<sup>c</sup>r, the regression coefficient.

The data listed in Table I show that on increasing the concentration of the curing agent, the temperature of the start and completion of curing is lowered, as expected. However, the time taken for the curing reaction does not fit this trend. The time taken from start to completion of the curing is highest when the curing agent used is 12%. This indicates that when the curing agent is taken in the proportion 12% by weight of the resin, the resin remains in the gel state for a longer time compared to situations where the curing agent is used in 8, 10, or 14% by weight of resin. The activation energy listed in Table II indicates the reverse type of dependance of the curing on the concentration of curing agent. The activation energy is lowest for the 100 : 12 resin-hexa system. On increasing concentration of hexa from 12 to 14%, the activation energy is further found to increase. The increase in activation energy on increasing the concentration of hexa beyond 12% indicates the somewhat complex nature of the reaction, which may be due to the contamination of the excess of curing agent (hexa) or the degradation products of hexa remained in the system.

The exothermic curves obtained in the case of the isothermal scans indicated their peak maxima at the extent to  $\sim 20$ – $30\%$  of the reaction. This shows that the reaction is an autocatalytic one. The autocatalytic effect may be due to the degradation products of hexa (ammonia and formaldehyde) or to absorbed water or to some intermediate species formed during the reaction. The exotherms obtained using 100 : 8, 100 : 10, 100 : 12, and 100 : 14 resin-hexa mixtures at 150, 160, 170, and 180°C are analyzed to obtain the curing characteristics using the reported relation [Eq. (5)] for such type of autocatalytic reactions.<sup>11</sup>

$$\frac{d\alpha/dt}{(1-\alpha)(B-\alpha)} = \alpha k_1 + k_2 \quad (5)$$

where  $\alpha$  = fractional conversion,  $d\alpha/dt$  = rate of reaction,  $B$  = concentration of curing agent/concentration of resin,  $k_1$  = autocatalyzed rate constant and  $k_2$  = rate constant of catalyzed reaction (free of autocatalysis).

This relation shows that the plot of the terms on the left of the relation, known as reduced reaction rate, versus the degree of conversion,  $\alpha$  gives the values  $k_1$  and  $k_2$  from the slope and intercepts, respectively. The values evaluated for  $k_1$  and  $k_2$  by the regression plots are listed in Table IV along

TABLE IV  
 Curing Characteristics of PFu-Hexa Systems from Isothermal Scans

Temperature °C	PFu-Hexa	$t_p$ (min)	$t_{50}$ (min)	$t_f$ (min)	$\alpha_p$	$\alpha'_p$ (s)	$k_1$ (s)	$k_2$ (s)
150	100 : 8	2.96	6.40	10.0	0.211	0.0039	0.057	0.0025
160		2.19	5.20	9.5	0.227	0.0093	0.064	0.0055
170		1.50	2.63	9.2	0.258	0.0126	0.085	0.0100
180		1.21	2.20	8.9	0.291	0.0139	0.126	0.0155
150	100 : 10	2.83	5.80	9.8	0.145	0.0026	0.078	0.0044
160		2.01	4.95	8.6	0.189	0.0069	0.103	0.0062
170		1.47	2.25	8.0	0.192	0.0086	0.157	0.0125
180		1.08	1.98	6.5	0.209	0.0144	0.207	0.0185
150	100 : 12	2.20	5.60	9.5	0.140	0.0024	0.092	0.0065
160		2.00	4.50	8.8	0.198	0.0058	0.117	0.0088
170		1.40	2.13	7.8	0.214	0.0104	0.168	0.0150
180		1.05	1.72	6.0	0.232	0.0158	0.218	0.0215
150	100 : 14	2.06	4.28	9.0	0.168	0.0023	0.112	0.0085
160		1.84	4.00	8.0	0.212	0.0048	0.156	0.0105
170		1.71	1.70	6.2	0.228	0.0112	0.255	0.0180
180		1.00	1.42	4.0	0.254	0.0162	0.357	0.0255

with the values of  $t_p$ , the time required to attain the peak maximum,  $t_{50}$ , the time required for 50% of conversion, and  $t_f$ , the time required for completion of the reaction. The values of the corresponding activation energy  $E_1$  and  $E_2$  are also determined from the regression plots of  $\ln k_1$  vs.  $1/T$  and  $\ln k_2$  vs.  $1/T$ , respectively. The values of  $E_1$  and  $E_2$  are 56.5 and 84.8 for 100 : 8, 52.3 and 78.4 for 100 : 10, 44.8 and 58.3 for 100 : 12, and 55.2 and 59.3 kJ/mole for 100 : 14 resin-hexa systems, respectively. The values of  $\alpha_p$ , the degree of conversion at peak, and  $\alpha'_p$ , the rate of conversion at the peak are also presented in Table IV.

One more relation<sup>12</sup> [Eq. (6)],

$$\ln \left( \frac{1}{H_T} \frac{dH}{dt} \right) = n \ln \left( \frac{H_{T-H}}{H_T} \right) + \ln k \quad (6)$$

where  $H_T$  = total heat of reaction (J/g) = total area under DSC curve,  $dH/dt$  = rate of heat generation,  $n$  = order of the reaction,  $H$  = heat of reaction at a particular temperature, and  $k$  = rate constant, was used to estimate the values of  $\ln k$ . The values of  $\ln k$  determined at four different temperatures were used to estimate the activation energy by the regression analysis using the Arrhenius relation. The values of activation energy obtained were 85.0, 83.0, 79.6, and 100.6 kJ/mol, respectively for the PFu-Hexa systems when 8, 10, 12, and 14% hexa was used. The activation energy determined using Eq. (6) from the isothermal scans has a small range. However, the trend observed is similar to that observed in the case of dynamic experiments. The values of activation energy obtained by isothermal experiments are observed to be lower than those obtained by dynamic experiments. This may be due to variations in the order of the reaction with temperature.

However, the variations in  $n$  have no detectable effect on the linearity of the plot of  $\ln k$  vs.  $1/T$  in the range studied for a dynamic scan. In the dynamic study the curing reaction of PFu with hexa can be regarded to follow simple first-order kinetics.<sup>13</sup> The values of the activation energy determined from the dynamic study are also in good agreement with reported values of activation energy for the curing of PF with urotropin.<sup>14</sup>

The results of the dynamic and isothermal DSC study strongly suggest that the amount of hexa has a marked effect on the curing characteristics. Hexa in the amount of 12% is the optimum level for curing, as it gives the system having the lowest activation energy and the highest heat of reaction which are essential for easy cure of the resin. Also, the time for cure cycle is maximum when 12% hexa is used as curing agent. The phenol-furfural resins are known for their flow times for a given curing speed,<sup>15</sup> which is required for transfer moulding. In this respect the 12% hexa may be considered as a more suitable curing agent. The isothermal study revealed that the probable optimum temperature may be regarded as 160°C, as the heat of reaction at this temperature was found to attain a maximum.

### References

1. N. M. Bikales, *Encyclopedia of Polymer Science and Technology*, Interscience Publ. John Wiley and Sons, New York, 1969, Vol. 10, p. 56.
2. R. B. Prime, in *Thermal Characteristics of Polymeric Materials*, E. A. Turi, Ed., Academic Press, New York, 1981, Ch. 5.
3. R. Burns and E. W. Orrel, *J. Mater. Sci.*, **2**(1), 72 (1967).
4. V. I. Kurachenkov and L. A. Igonin, *J. Polym. Sci.*, **9**, 2283 (1971).
5. S. Chow and P. R. Steiner, *J. Appl. Polym. Sci.*, **23**, 1973 (1979).
6. L. H. Brown, *Ind. Eng. Chem.*, **44**(11), 2673 (1952).
7. K. E. J. Barrett, *J. Appl. Polym. Sci.*, **11**, 1617 (1967).
8. E. S. Freeman and B. Carrol, *J. Phys. Chem.*, **62**, 394 (1958).
9. L. W. Crane, P. J. Dynes, and D. H. Kaelable, *J. Polym. Sci., Polym. Lett. Edn.*, **11**, 533 (1973).
10. R. Kay and A. R. Westwood, *Eur. Polym. J.*, **11**, 25 (1975).
11. S. Sourour and M. R. Kamal, *Thermochim. Acta.*, **14**, 41 (1976).
12. P. Peyser and W. D. Bascom, *J. Appl. Polym. Sci.*, **21**, 2359 (1977).
13. L. M. Debing, G. E. Murray, and R. J. Schatz, *Ind. Eng. Chem.*, **44**, 354 (1952).
14. N. I. Basov, Yu. V. Kazankov, A. I. Leonov, V. A. Lyubartovich, and V. A. Mironov, *Khim. Technol.*, **12**(11), 1578 (1969); *C. A.* **72**, 122279c (1970).
15. R. E. Kirk, *Encyclopedia of Chemical Technology*, The Encyclopedia Inc., New York, 1953, Vol. 10, p. 364.

Received January 5, 1987

Accepted March 31, 1987