

# THERMOCHEMICAL CHARACTERIZATION OF PHENOLIC RESINS

## Thermogravimetric and pyrolysis-GC studies

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### Abstract

Phenol-formaldehyde resins (I and II), synthesised at a monomer feed ratio of F/P=1.0 and 1.5, were cured at 130°C for 48 h without any catalyst (Ia, IIa), with 0.1% ferric acetyl acetate (Ib, IIb) and with 0.1% *p*-toluenesulphonic acid (Ic, IIc). Thermogravimetric studies indicate that the decomposition of the cured products takes place in two distinct stages: The first stage ( $T=340\text{--}480^\circ\text{C}$ ;  $\alpha=0.045\text{--}0.16$ ;  $\Delta E_1=140\pm 10\text{--}239\pm 24$  and  $60\pm 3\text{--}65\pm 2$  kJ mol<sup>-1</sup> for series I and II respectively) was attributed to the predominant cleavage of formal linkages. The main stage decomposition ( $T=460\text{--}640^\circ\text{C}$ ;  $\alpha=0.114\text{--}0.393$ ;  $\Delta E_2=115\pm 8\text{--}169\pm 8$  and  $91\pm 6\text{--}103\pm 7$  kJ mol<sup>-1</sup> for series I and II respectively) was attributed to reactions leading to graphitisation.  $\Delta E_2$  values were correlated to the extent of cure as measured by IR spectroscopy and pyrolysis-GC. The effect of catalysts on the extent of cure and on the activation energy was evaluated.

**Keywords:** kinetics, phenol-formaldehyde resins, pyrolysis-GC, thermal degradation

### Introduction

Structural features like isomeric composition and average chain length of phenol-formaldehyde (PF) resins have a substantial effect on the nature, extent of cross-linking and end-use properties [1-3]. Thus an understanding of the structure - property relationship of the resin and its cured analog becomes essential to meet the intended applications as composites and ablative materials [4-6]. Studies based on IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies [7-12] provided many details of PF reactions, but are limited to solution state. Attempts have also been made to elucidate the structural features of the cured resins by solid state <sup>13</sup>C NMR spectroscopy [13] and pyrolysis-GC-MS techniques [14], but there is paucity of information in this regard. Hence, in this communication we report on the characterization of cured phenolic resins by thermogravimetric, pyrolysis-GC, IR and solid state <sup>13</sup>C NMR techniques.

## Experimental

### Materials

Resole-type phenol-formaldehyde resins **I** and **II** were prepared with a formaldehyde to phenol ratio (F/P) of 1.0 and 1.5 respectively using sodium hydroxide catalyst at a *pH* of 8.5–8.6 as per the details described elsewhere [15]. The resins **I** and **II** were cured in an inert atmosphere of nitrogen at 130°C for 48 h without any catalysts (**Ia**, **IIa**), with 0.1% ferric acetyl acetonate (FAA) (**Ib**, **IIb**) and with 0.1% *p*-toluenesulphonic acid (*p*-TSA) (**Ic**, **IIc**).

### Thermogravimetric studies

Thermal curves were recorded under nitrogen atmosphere using a Du Pont 2000 in combination with a 951 thermogravimetric analyser with a sample size of about 5 mg.

### Pyrolysis-GC

About 0.5–0.6 mg of samples were pyrolysed in a Shimadzu PYR-2A furnace type pyrolyser coupled to Shimadzu GC-9A Chromatograph. The GC conditions used were pyrolysis temperature: 750°C; column: OV-17 (Shimadzu), 1 m×4 mm i.d.; column temperature: 60–150°C at a programmed heating rate of 15°C min<sup>-1</sup> [60(5)-15-150(15)]; injection port temperature: 250°C; detector: FID; carrier gas: He at a flow rate of 90 mL min<sup>-1</sup>. A Shimadzu data processor (Shimadzu CR 3A) was used for computation of peak areas.

## Results and discussion

### Characterisation of cured resins

The cured resins were characterized by their IR spectra and the relative intensities of absorptions at 818 and 754 cm<sup>-1</sup> ( $R = [I]_{818}/[I]_{754}$ ) which can be assigned to the C–H out-of-plane deformations, were considered as a measure of the extent of ring substitution [16]. In addition, the intensity of the peak at 1595 cm<sup>-1</sup> (aromatic C=C stretching) is expected to be nearly constant and its ratio to the intensities of peaks at 818 and 754 cm<sup>-1</sup> were also considered to determine the extent of cure. The results, shown in Table I, indicate that: (i) the extent of cure is higher for **I** series compared to **II** series; and (ii) incorporation of catalysts decreases the extent of cure in **I** series but enhances it in series **II**. These differences might be arising due to the inherent structural differences in **I** and **II** resins. The catalysts might be promoting the decomposition of the formal linkages liberating formaldehyde which in turn partially reacts with aromatic ring leading to increased aromatic substitution. In addition, the catalysts may complex with methyloxyl groups preventing further substitution reactions. These two opposing factors contribute to the catalytic activity and depend on the relative amounts of methyloxyl and formal linkages in the sample. Consequently, the presence of more of formal bridges in series **II** com-

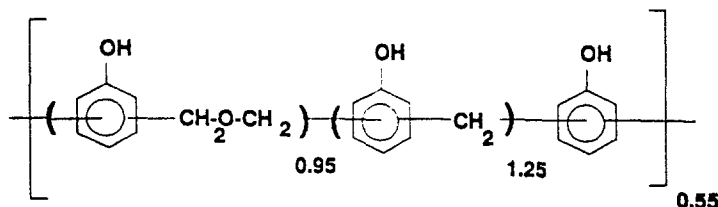
pared to series I, lead to further ring substitution reactions and increased extent of cure for series II. However, in the case of I series, the net effect is such that the extent of cure decreases in the presence of catalysts compared to the non catalysed case.

These results were further confirmed by the solid state  $^{13}\text{C}$  NMR spectrum of IIa. The presence of absorption at  $\delta=114.8$  ppm clearly indicates incomplete substitution at the carbon atom ortho to the carbon bearing OH group.

### Thermal stability of cured phenolic resins

The thermal stability as measured by char yields at  $800^\circ\text{C}$  are shown in Table 1. It is seen that I series in which F/P ratio=1.0 gave higher char yields compared to II series in which F/P ratio =1.5. This can be attributed to the higher proportion of thermally labile formal linkages in II series compared to I series. This is also consistent with the IR data which shows lower aromatic substitution in the II series as discussed earlier.

Also, it may be noted that the average structure of I neat resin as determined by  $^1\text{H}$  NMR spectrum could be represented as



Assuming that during complete decomposition of the cured product, loss of  $-\text{OCH}_2-$ ,  $-\text{CH}_2-$ , and  $\text{H}_2\text{O}$  fragments occurs, the above structure indicates that the total mass loss would be about 36% leaving a char yield of 64%, in excellent agreement with the observed value of 63–67%. This suggests that the structure of the char is essentially graphitised carbon. In the case of II series in view of the higher percentage of formalin, the weight fraction of the aromatic rings would be less and therefore the char yield would be less.

Further, it is seen that the decomposition takes place essentially in two stages in agreement with the data reported earlier [17]. The temperature range and mass loss for the two stages are given in Table 1. In the case of I series, the mass loss in the first stage is 11–14% whereas it is slightly higher in the II series. This could be rationalised as follows: It is envisaged that the first stage of decomposition involves the cleavage of the formal linkages ( $\text{ArCH}_2\text{OCH}_2\text{Ar} \rightarrow \text{ArCH}_2\text{Ar} + \text{CH}_2\text{O}$ , a low energy process). The mass percentage of the formal linkages in the I series is approximately 15.5% which agrees reasonably well with the mass loss of 11–14% in the first stage. Therefore, the first stage of decomposition involves predominant loss of formal units. The second stage of decomposition would involve a further 20% mass loss due to the loss of methylene and water fragments leaving a graphitised residue. The II series also behave in a similar fashion with weight loss in the first stage being greater (16%) due to the higher formal content.

Table 1 Properties of cured phenolic resins

Sample	Relative optical density				Thermal stability				Char/% 800°C
	$[I]_{1595}$		$[I]_{818}$		$T^{\circ}\text{C}$		$T^{\circ}\text{C}$		
	$[I]_{1595}$	$[I]_{754}$	$[I]_{1595}$	$[I]_{754}$	First stage	Second stage	$\alpha$	$\alpha$	
Ia	1.444	1.050	0.7267	0.7106	340-450	460-620	.052-.118	.123-.318	64
Ib	1.784	1.268	0.7106	0.5857	340-450	460-620	.047-.110	.114-.288	67
Ic	1.756	1.029	0.5857	0.4558	340-450	480-640	.045-.139	.152-.332	63
IIa	5.961	2.731	0.4558	0.6173	340-470	470-580	.066-.160	.160-.393	45
IIb	3.060	1.889	0.6173	0.5370	360-470	490-620	.080-.151	.167-.314	63
IIc	4.483	2.407	0.5370		350-480	480-590	.068-.149	.149-.316	58

Table 2 Thermal degradation kinetics of phenolics by Chatterjee-Conrad's method

Sample	Stage 1				Stage 2			
	$T_{\text{range}}$	$\alpha_{\text{range}}$	$\Delta E_1 / \text{kJ mol}^{-1}$	corr. coeff.	$T_{\text{range}}$	$\alpha_{\text{range}}$	$\Delta E_2 / \text{kJ mol}^{-1}$	corr. coeff.
Ia	345-390	.05-.07	184±6	.996	465-505	.13-.17	169±8	.992
Ib	340-380	.05-.07	140±10	.993	450-510	.11-.17	138±9	.991
Ic	340-390	.05-.07	239±24	.990	460-520	.14-.21	115±8	.989
IIa	340-430	.07-.12	65±2	.995	470-530	.16-.28	91±6	.989
IIb	360-440	.08-.13	60±3	.990	490-540	.17-.24	103±7	.992
IIc	350-440	.07-.12	62±1	.997	480-540	.15-.24	94±3	.997

### Kinetic parameters of decomposition

The kinetic parameters of Ia was studied in detail. The thermal curves were recorded in three different heating rates (5, 10 and 20°C min<sup>-1</sup>). The thermal curves were analysed by two different methods: (i) Ozawa's method [18], and (ii) Chatterjee-Conrad's method [19]. The isoconversional plots of Ozawa's method are shown in Fig. 1. The results indicate that the global activation energy of decomposition is essentially constant and is equal to 150.9±8.2 kJ mol<sup>-1</sup> and log A = 12.2± 0.4 min<sup>-1</sup>.

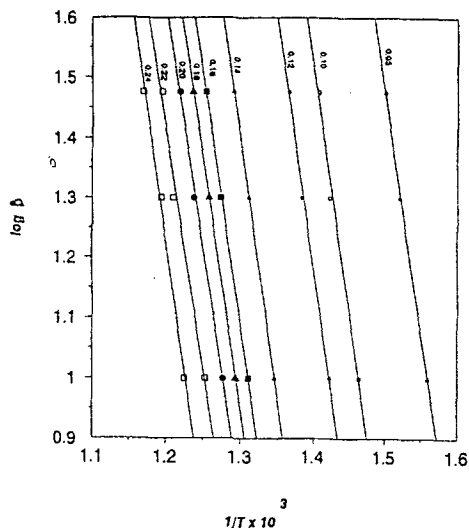


Fig. 1 Isoconversional plots of log  $\beta$  vs.  $1/T$  (Ozawa's method) for Ia

The treatment of the mass loss data according to Chatterjee-Conrad's method shows two stages of decomposition. Assuming a pseudo first order reaction, the activation energies for the first and second stages of decomposition were found to be 184±6 and 169±8 kJ mol<sup>-1</sup> in reasonable agreement with Ozawa's method. Consequently, Chatterjee-Conrad's method which uses only a single heating rate was chosen for kinetic analysis of other samples. The results obtained are given Table 2. It is seen from the results that: (i) the activation energy for the first stage decomposition for II series is considerably lower compared to the corresponding values of the I series; (ii) the activation energies for the main stage decomposition for II series are higher than the corresponding first stage; and (iii) the activation energies for the first and main stages are not considerably different for the I series except for Ic which appears to be an anomaly.

These observations were rationalised as follows: The magnitudes of the activation energies are expected to reflect the extent of cross-linking of the cured samples. As discussed earlier, the values of  $R$  obtained from IR spectra were considered as a measure of extent of cure. Therefore, the activation energies  $\Delta E_2$  for the main stage decomposition were plotted against  $R$  as shown in Fig. 2 and confirms the expected trend that activation energy increases with increase in the extent of cross-linking.

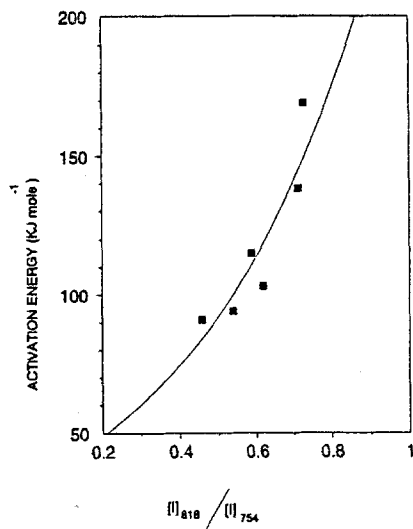


Fig. 2 Plot of activation energy vs.  $[I]_{818}/[I]_{754}$

However, it is to be noted that the activation energy for the decomposition of phenolic resins was reported to be about  $9 \text{ kJ mol}^{-1}$  by Komoreva *et al.* [20] whereas for glass-phenolic composites, a value of  $270 \text{ kJ mol}^{-1}$  was reported by Henderson *et al.* [17] and  $42\text{--}77 \text{ kJ mol}^{-1}$  by Ninan [21]. This indicates clearly that the extent of cure greatly influence the calculated activation energy values. Consequently, the results obtained in the present study can be considered as adequate for the intended purpose of comparison of samples prepared under different conditions.

### Pyrolysis-GC studies

Since the cured phenolic resins are intractable, an attempt was made to characterize the resins by their products of decomposition on pyrolysis. A pyrolysis temperature of  $750^\circ\text{C}$  was chosen to obtain reproducible pyrograms with sharp peaks. Lower temperatures of pyrolysis resulted in broad and poorly resolved peaks due to slow decomposition of the resin. About  $0.6\text{--}0.7 \text{ mg}$  of cured phenolics were pyrolysed at  $750^\circ\text{C}$  and phenol, formaldehyde, benzene and toluene are some of the peaks identified in the pyrogram. The results indicate that P/F ratio in the pyrolyzates differs considerably for both I and II series indicating that the ratio is dependent on the extent of cure reactions. Thus, the plot of  $\Delta E_2$  vs. P/F ratio shown in Fig.3 indicates the dependence of activation energy on the extent of cure. I and II series show different extents of dependence since the F/P ratios in the virgin resins are different. Thus, the pyrolysis-GC results are also in consistence with the conclusions drawn from the IR and thermogravimetric data.

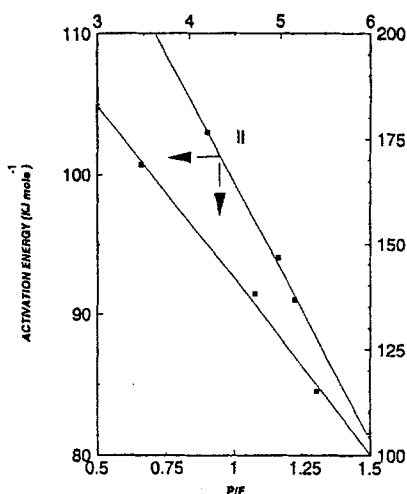


Fig. 3 Plots of activation energy vs. P/F ratio in the pyrolyzates

## Conclusions

The main conclusions that can be drawn from the present study are: (i) the extent of cure of a phenol-formaldehyde resin depends on the feed ratio of the monomer; (ii) the effect of the catalysts used FAA and *p*-TSA on the extent of cure is dependent on the extent of formal linkages present in the resin; (iii) phenol-formaldehyde resin decomposition is in two stages, the first step involving predominantly the cleavage of formal ( $-\text{CH}_2-\text{O}-\text{CH}_2-$ ) linkages and the second stage involves reactions leading to graphitisation and (iv) the extent of cure depends on the nature of the PF resin and can be ascertained from the optical densities ratio of peaks at 818 and  $754\text{ cm}^{-1}$  in IR spectra, the P/F ratio in the pyrolyzates and also activation energies for decomposition.

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## References

- 1 A. A. K. Whitehouse, E. G. K. Pritchett and G. Barnett, Phenolic Resins, Iliffe, London 1967.
- 2 A. Knop and W. Scheib, Chemistry and Applications of Phenolic Resins, Springer-Verlag, New York 1979.
- 3 Chem. Eng. News, 31 (1953) 2771.
- 4 D. O. Newling and E. J. Walker, Proc. Int. Conf. carbon fibres, Plastic Institute, London 1971, p. 142.
- 5 D. W. Meker, Carbon, 24 (1987) 551.

- 6 E. Fitzer and R. Gadoor, *Am. Cer. Soc. Bull.*, 65 (1986) 326.
- 7 M. I. Aranguren, J. Borrajo and R. J. J. Williams, *J. Polym. Soc., Polym. Chem. Ed.*, 20 (1982) 311.
- 8 J. C. Woodbrey, H. P. Higginbottom and H. B. Culbertson, *J. Polym. Sci., A*, 3 (1965) 1079.
- 9 P. W. Kopf and E. R. Wagner, *J. Polym. Sci., Polym. Chem. Ed.*, 11 (1973) 939.
- 10 E. Dradi, G. Casiraghi, G. Sartori and G. Casnati, *Macromolecules*, 11 (1978) 1295.
- 11 C. A. Fyfe, A. Rudin and W. Tchir, *Macromolecules*, 13 (1980) 1320.
- 12 C. A. Fyfe, M. S. McKinnon, A. Rudin and W. J. Tchir, *Macromolecules*, 16 (1983) 1216.
- 13 G. E. Maciel, I. S. Chuang and L. Gallot, *Macromolecules*, 17 (1984) 1081.
- 14 M. Blazso and T. Toth, *J. Anal. Appl. Pyrol.*, 10 (1986) 41.
- 15 K. M. Usha, T. R. Balakrishnan, S. Alwan and K. S. Sastri, *Macromolecules-Current Trends*, Eds. S. Venkatachalam et al., Allied Publishers, New Delhi 1995, p. 42.
- 16 C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York 1963.
- 17 J. B. Henderson, M. R. Tant, G. R. Moore and J. A. Wiebelt, *Thermochim. Acta*, 44 (1981) 253.
- 18 T. Ozawa, *Bull. Chem. Soc. Jpn.*, 38 (1965) 1881.
- 19 P. K. Chatterjee and C. M. Conrad, *J. Polym. Sci., A-1*, 6 (1968) 3217.
- 20 T. V. Komorova, S. D. Fedoseev, O. M. Petrova, A. N. Seleznev and L. V. Polevaya, *Zh. Prikl. Khim.*, 50 (1977) 1666; *C.A.*, 87 (1977) 118513u.
- 21 K. N. Ninan, *J. Space Craft and Rockets*, 23 (1986) 347.