Thermal degradation kinetics of phenol–crotonaldehyde resins

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A series of base catalysed phenol–crotonaldehyde and phenol–formaldehyde resins of different mole ratios were synthesized and their thermal behaviour was studied. The non-isothermal procedures of Coats–Redfern and Horowitz–Mitzger were applied to study the thermal degradation kinetics of these resins in air. The softening temperature of phenol–crotonaldehyde resins after curing was found to be in the range of 143–158°C and phenol–formaldehyde resins of similar type exhibited infusible thermoset behaviour. Phenol–crotonaldehyde resins in the presence of a cross-linking agent, after curing at elevated temperatures, yielded infusible thermosets. The initial, final, 10% and 20% degradation temperatures (DT) of cured phenol-crotonaldehyde resins were higher than those observed for uncured as well as cured phenol–formaldehyde resins. The estimated activation energy for the cured phenol–crotonaldehyde resins is higher (102.5 kJ mole^{-1}) compared to cured phenol–formaldehyde resins (57.3 kJ mole^{-1}). © 1998 Elsevier Science Limited. All rights reserved

1 INTRODUCTION

Phenolic resins were the first commercially successful synthetic resins. These resins have been extensively studied[1–5] for over 85 years. Phenolics are still among the best available commercial heat-resistant resins. Therefore, they are used particularly as ablative and friction materials and high temperature mouldings.

Recent studies[6,7] on thermal degradation of ortho-novalacks by differential thermogravimetric (DTG) analysis established that, while substitution in the phenol ring reduced the thermal stability, an increase in the aromatic content led to an increase in the thermal stability of these resins. Despite the extensive studies[8–16] conducted on thermal stability of phenolic resins, no data from thermal studies of phenol–crotonaldehyde resins is available in the literature.

A study of thermal properties and thermal degradation of crotonaldehyde based resins was conducted to understand their thermal behaviour

compared with phenol–formaldehyde resins (PF) with respect to their softening and kinetics of degradation. The knowledge of the effect of propanoic units between phenolic aromatic rings on thermal behaviour is essential when considering the development of new polymeric material for commercial use. In this communication, the kinetics of thermal degradation of phenol–crotonaldehyde resins (PC) are reported.

The effect of mole ratio on curing characteristics, softening and degradation temperatures and the activation energy of the thermal degradation is discussed and the results are compared with those obtained for PF resins of similar composition.

2 EXPERIMENTAL

Phenol was a product of Hindustan Organic Chemicals with a purity of > 99% and crotonaldehyde was obtained from Somaya Organics and Chemicals. Crotonaldehyde was distilled before use and purity was checked by GC and found to be 99.5%. Analytical reagent grade sodium hydroxide and hexamethylenetetraamine(hexa) were used.

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The mole ratio of crotonaldehyde to phenol was varied from 1.2 to 3.0. The poly-condensation reactions were carried out as per standard procedure[5] in base catalysed medium and all reactions were monitored by means of refractive index and percentage of free crotonaldehyde in the reaction mixture. Similar experiments were also carried out for phenol-formaldehyde resin synthesis. The synthesized resins were purified and dried before use for thermal studies.

Both uncured and cured PC resins, with and without hexa, were examined for thermal behaviour and compared with cured PF resins synthesized under identical experimental conditions. The softening temperatures were estimated in sealed glass capillaries using a melting point apparatus. The thermal behaviour of the resins was studied in air, using a Perkin-Elmer Delta series TGA7 thermoanalyser. The approximate sample size was 5–10 mg. The resins were heated at a constant rate of $10°C\,min^{-1}$. Thermograms were obtained in the range 25–900°C.

3 RESULTS AND DISCUSSION

3.1 Softening temperature studies

The effect of curing temperature and addition of a conventional cross-linking agent, hexa, on the softening point of PC resins was examined and the results are given in Table 1.

PC resins showed a behaviour markedly different from that of PF resins.The former were exhibited thermoplastic even with the addition of hexa in low temperature curing. Interestingly the PC resin, without addition of hexa, cured at elevated temperature ($\geq$180°C) retains the thermoplastic characteristics. Post-curing of these resins with the addition of hexa at temperature ($\geq$180°C yielded thermoset

behaviour. PF resins of similar type cured faster and showed thermoset behaviour.

The softening points were found to be independent of the phenol-crotonaldehyde ratio and there was no appreciable increase in the softening temperature for PC resins prepared without hexa and cured at lower temperatures. However, the softening temperatures increase with the addition of hexa indicating that PC resins do react with hexa as in the case of conventional PF resins. The incorporation of the methyl group in the aromatic ring seemes to increase the softening temperature.

3.2 Degradation studies

The degradation study was conducted by dynamic TGA methods using thermogravimetric analyser to obtain the reaction order, pre-exponential factor (A), and the energy of activation (E).[17] Differential thermogravimetry (DTG) was used to estimate[18] the temperature of maximum degradation rate (T_{max}), the initial degradation temperature (T_i) and the final degradation temperature (T_f). The superimposed plots of the rate of change in mass of the uncured and cured PC are presented in Fig. 1. As can be seen from this figure, both resins showed a two stage degradation. In uncured resins the intial degradation rate starts relatively rapidly and goes up to 380°C. The weight loss is 45–58% and it arises from the volatilization of bound water and other low molecular weight species.[19] The final degradation stage is observable from 400°C and is complete at 900°C. The degradation of cured resins starts intially at a very low rate, and increases after 350°C continuing to 500°C. The final degradation starts at 500°C and goes to completion at 800°C. The final stage, being the most significant, was selected for comparison in terms of the effect of composition and structure on the energy of activation.[20]

Table 1. Thermal behaviour of PC and PF resins

Sample	Aldehyde–phenol mole	Before curing	Softening temperature range (°C)		After post-curing at 180°C for 30 min Without hexa*
			After curing at 140°C for 30 min		
			Without hexa	With 10% hexa	
PC1R	1.2	96–100	150–154	175–179	220–225
PC2R	1.6	98–101	150–155	173–177	218–222
PC3R	2.0	103–108	154–158	185–190	235–240
PC4R	2.5	98–103	147–152	163–166	210–215
PC5R	3.0	97–102	143–148	158–163	220–225
PF3R	2.0	63–67	Infusible	Infusible	Infusible

*With 10% hexa after post-curing at 180°C for 30 min, all PC samples have shown infusible behaviour.
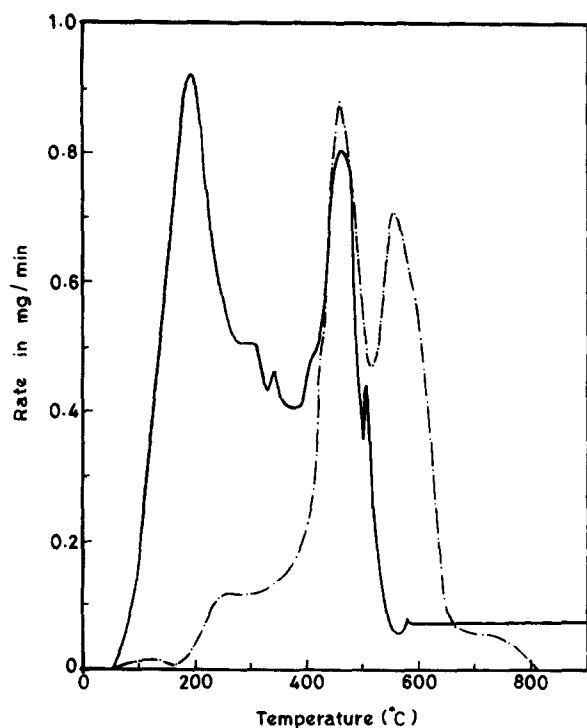
Fig. 1. Thermograms for the degradation of phenol–crotona-ldehyde (1:2) resin. Uncured (—) and cured (- · · -).

Degradation studies of PF resins and alkyl sub-stituted phenol-formaldehyde resins by TGA and DTG methods have been reported[8–16] earlier. For example, Jeffrey[15] reported that a large peak can be observed for the alkyl substituted phenols in the temperature range 430–470°C. This sharp peak is absent in the case of the unsubstituted phenol-for-maldehyde resins. The reason for the development of a sharp peak in former resins is due to the pre-sence of bulkier side chains, (alkyl substitution), leading to an increase in the mass loss giving rise to sharp peaks.

PC resins showed a similar degradation beha-viour (second stage) and a sharp peak was obser-vable in the temperature range 400–500°C for the uncured and 530–630°C for the cured PC resins. The bridging group in PC resins consists of four carbon atoms and thus plays a similar role as the

side chain resulting in a sharp peak. Several possi-ble explanations were offered[15] for these sharp peaks, but the main important factor is that the resins degrade at the methylene bridges and the polymers further degrade into smaller fragments which volatilize within a sharp temperature range. In this temperature range, chain scission occurs and no depolymerization takes place. After the second stage of degradation, a steady rate of weight loss was obtained which was attributed to the burning off of a carbonaceous residue.

The initial and final degradation temperatures are shown in Table 2. Our results indicate that the cured PC resins have higher degradation tempera-tures than those observed for uncured PC resins (with and without hexa). However, no significant change was observed when hexa was added before curing. Comparable degradation behaviour was observed in the PC resins before the curing stage with or without the use of hexa.

Similarly, degradation temperature of cured PC resins was higher than that obtained with the cured PF resin samples synthesized under similar experi-mental conditions. Thus, the temperature range for the degradation is wider for both cured PF and PC resins.

The data based on qualitative methods, such as temperature at 10 and 20% degradation are also presented in Table 2. The data reveal that the ther-mal stability of uncured resins is lower than that of cured resins and confirm that the PC resins are thermally more stable than PF resins. The thermal stability dependence of PF resin on the concentra-tion of the dihydroxydiphenylmethane moiety has already been documented.[21] The reason for higher thermal stability of cured PC resins than cured PF resins has not yet been established. This is probably because of the formation of a cyclic ring moiety with fewer alphatic groups in the polymer. Another possibility is that the cross-linking reaction with hexa leading to a strong three dimensional network with imide group bridging may play a role.

Table 2. Thermal properties of PC and PF resins

Sample	Nature of sample	Temperature (K)				
		T_i	T_f	T_f–T_i	10% DT	20% DT
PC3R	Uncured	331	847	516	421	458
PC3RH	Uncured with hexa	331	846	515	425	458
PC3C	Cured with hexa	448	1076	629	669	789
PF3C	Cured without hexa	327	1009	682	510	606
PC4R*	Uncured	331	832	501	493	544

*The aldehyde/phenol mole ratio was 2.5 and for all other samples, the ratio was 2.0.

3.3 Kinetics of thermal degradation

The activation energies in the final degradation stage were evaluated using the Anderson method.[22] The energy of activation of the resins was calculated from their DTG curves. A number of methods have been developed to compute the kinetic parameters from DTG thermograms and the methods developed by Coats–Redfern and Horowitz–Metzger are used in this study for investigating degradation kinetics of polymers. The mathematical treatment of kinetic equations makes use of differential, integral or approximation methods of evaluation. In the present study, the integral methodologies were used to deduce the activation energies. The final equations used are.[23,24]

(a) Coats–Redfern equation (CRI)[23]

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \log\left(\frac{AR}{aE}\right)\left(1-\frac{2RT}{E}\right) - \frac{E}{2.303R}$$

Fig. 3. Coats–Redfern plots for phenol–formaldehyde and phenol–crotonaldehyde resins of various compositions (last stage degration). Cured phenol–formaldehyde resin—PF3C (●); cured phenol–crotonaldehyde resin—PC3C (X); uncured phenol–crotonaldehyde resin—PC3R (△), PC3RH(○) and PC4R (■).
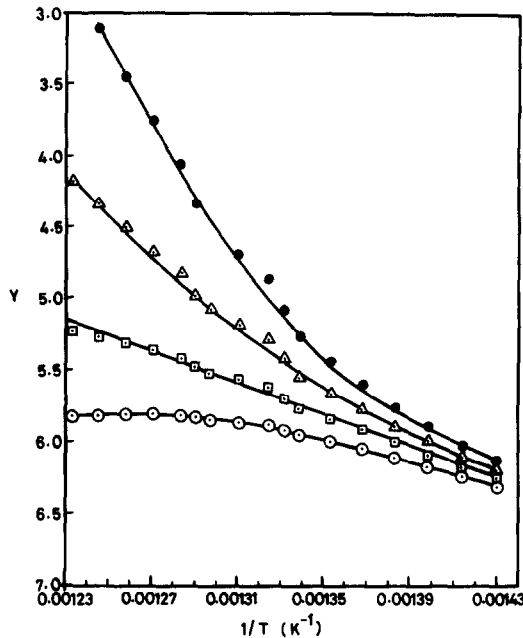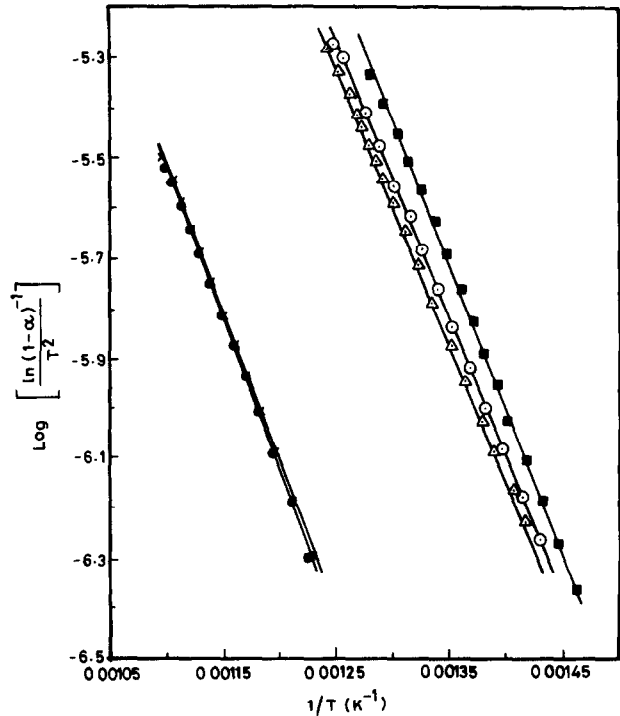
Fig. 2. Coats–Redfern plots for phenol–crotonaldehyde resin at $n = 0, 1, 2$ and 3. For order 0, 2 and 3.

$$Y = \log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]$$

For order 1,

$$Y = \log\left[\frac{\ln(1-\alpha)^{-1}}{T^2}\right]$$

Order 3 (●), 2 (△), 1 (□) and zero (○).

Fig. 4. Horowitz–Metzger plots for phenol–formaldehyde and phenol-crotonaldehyde resins of various compositions (last stage degration). Cured phenol–formaldehyde resin—PF3C (●); cured phenol–crotonaldehyde resin—PC3C (X); uncured phenol–crotonaldehyde resin—PC3R (△), PC3RH(○) and PC4R (■).
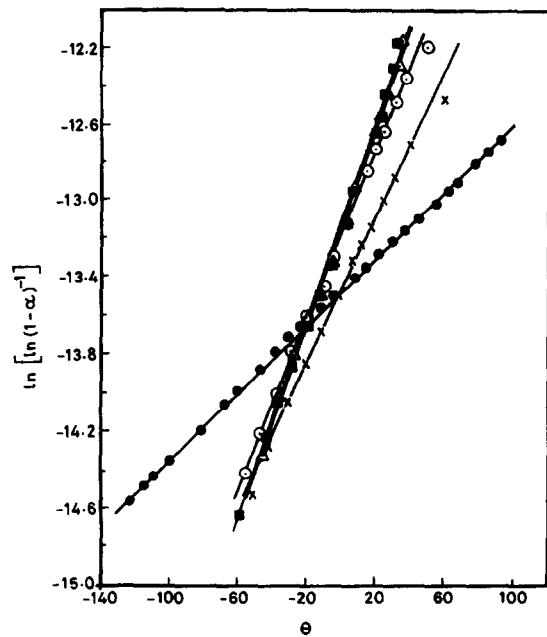
Table 3. Decomposition and activation energies in the final stage for PC and PF resins

| Sample code | Nature of sample | Aldehyde–phenol mole ratio | Analysis range | | | | Energy of activation kJ mol⁻¹ | |
| | | | Temperature (°C) | | Decomposition (%) | | | |
			Start	End	Start	End	HM	CR
PC3R	Uncured	2.0	707.0	803.0	26.3	96.7	107.9	108.7
PC3RH	Uncured with hexa	2.0	699.0	811.0	23.6	97.8	102.5	103.3
PC4R	Uncured	2.5	683.0	783.0	18.5	94.2	111.7	109.6
PC3C	Cured with hexa	2.0	823.0	915.0	29.2	92.0	114.6	115.5
PF3C	Cured without hexa	2.0	763.0	995.0	20.5	96.4	57.3	55.2

(b) Coats–Redfern equation (CRII)[23]

$$\log\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \log(\frac{AR}{aE})(1 - \frac{2RT}{E}) - \frac{E}{2.303R}$$

(c) Horowitz–Metzger method (HM)[24]

$$\log[-\ln(1-\alpha)] = \frac{E\Theta}{2.303RT_s^2}$$

where $(\alpha = (w - w_f)/(w_o - w_f)$ where w_o, w_f and w are initial, final and masses remaining at temperature T (equivalent to the final degradation stage), a and n are heating rate and order of reaction and $(\theta = T - T_s$ where T_s is the temperature at $(w/w_o) + (1/e))$. The order parameter n was evaluated using the equations CRI, CRII and the equation CRI is applicable for reaction order parameters other than unity.

Equation CRI was used for values of n in the range 0–3, excepting $n = 1$. CRII was used for $n = 1$. The superimposed plots of these equations are presented in Fig. 2. A linear relationship was observed, when CRII was used unlike for CRI. This indicates that degradation in the last stage followed first-order kinetics. This was confirmed by the HM equation. The plots based on CRII and HM are shown in Figs 3 and 4. The energy of activation was evaluated for the five resin samples. The correlation coeffcients were found to be near unity for the 10 plots, reflecting a good fit of the curves.

The temperature ranges and extent of degradation obtained from the analysis are represented in Table 3. The extent of degradation pertains only to that observed in the second degradation stage. Kinetic parameters for five resins were analysed in the 23–98% degradation range. The initial 20% degradation zone was not considered to avoid errors due to an overlap from the previous degradation zone.[25] It is also known that in the intial

stages of decomposition in solids first order kinetics are not obeyed.

The activation energies were computed from the slope of the CR and HM plots and are tabulated in Table 3. As can be seen identical activation energy values are obtained by both the methods. First order reactions have an activation energy of about 172.8 for cured and 100–109 kJ mol⁻¹ for uncured PC resins.However the value is lower (57.3 kJ mol⁻¹) for cured PF. Our activation energy of PF resin is comparable with the values reported[26] in literature (57 kJmol⁻¹).

4 CONCLUSION

Our studies show that PC resins exhibit thermoplastic characteristics and an additional cross-linking agent is required to convert them into thermoset materials. However, PC resins react with cross-linking agent, only at higher temperatures, and transform into infusible thermosets. The thermal properties of cured and uncured PC resins seem to be capable of being significantly improved through the introduction of an imide group as a bridging medium for cross-linking to achieve a three dimensional network. The cured PC resins show higher initial 10 and 20% DT as well as higher activation energy than those found for uncured PC resins. The observed activation energy of cured resins indicates that PC resins are more thermally stable over a high temperature range than PF resins. Our studies further demonstrate that the PC resins can be exploited for potential application in the area of heat resistant composite materials.

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