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STUDIES ON THE THERMAL DECOMPOSITION OF THERMOSETTING ANILINE–FORMALDEHYDE RESINS

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ABSTRACT

The thermal decomposition of different aniline–formaldehyde (A–F) resins (1:1, 1:2, 1:3, 1:4 and 1:5) is studied in nitrogen and oxygen atmospheres. Values for the apparent reaction order, activation energy, pre-exponential factor are evaluated for different stages of decomposition. The validity of the linear kinetic compensation law is observed. The apparent activation energy values are higher in a nitrogen atmosphere than in an oxygen atmosphere and the higher value of the activation energy for the 1:5 A–F resin compared with the other A–F resins may be attributed to its larger cross-link density.

INTRODUCTION

Aniline–formaldehyde (A–F) resins find wide industrial applications since the introduction of phenol–formaldehyde and melamine–formaldehyde resins [1–3]. However, since A–F resinic products are highly infusible, insoluble, hard and quickly thermosetting in nature, the conventional investigations to characterize the resins are rendered futile. Differently structured high polymeric resins are obtained when aniline and various excess concentrations of formaldehyde are reacted in the presence of acid catalysts. Kishore and Santhanalnkshmi [4,5] have attempted a thermochemical rationalization of various A–F resins. In the present investigation thermal characterizations of different A–F resins obtained from the stoichiometric reactions of 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5 A–F have been undertaken.

EXPERIMENTAL

Various A–F resins are prepared by condensing aniline with formaldehyde in the mole ratios 1 : 1, 1 : 2, 1 : 3, 1 : 4 and 1 : 5 respectively using HCl as a catalyst at 25 °C. After completion of the reaction, the gelled product is filtered and incubated at 60 °C in an air oven with occasional stirring for 5

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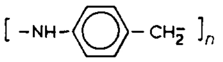
days. The dry, brittle, translucent red-coloured high polymeric materials obtained from each stoichiometric reaction are subjected to elemental analyses, IR spectral studies and thermogravimetric analyses. Carl-Zeiss UR-10 and Stanton-Red-Croft TGA instruments for IR and TG studies respectively are employed.

RESULTS AND DISCUSSION

Elemental analysis data and IR spectra of A–F resins are given in Table 1 and Fig. 1 respectively. It may be seen that each of the A–F resin products obtained from different A–F reactions differ from each other in chemical and molecular composition. From the IR group vibrational frequencies [6–7] the presence of the group skeleton in all the A–F resins may be inferred while changes in the skeletal vibrational frequencies from 1 : 1 to 1 : 5 A–F resins may be attributed to the additional methylene crosslinks to the



network. Typical TG curves of the resins are presented in Fig. 2. When the black residues left after the thermal degradation are subjected to elemental and IR spectral analyses, the presence of only a carbon and hydrogen network was observed. Thermal degradation in a nitrogen atmosphere exhibited a single-step degradation while in an oxygen atmosphere a double-step degradation was shown. From the evolved gas analysis technique, the single-step degradation in a nitrogen atmosphere was found to be due to the release of aniline and *N*-methylaniline while in the oxidative degradations, the first step was due to formaldehyde release and the second step was due to oxidized forms of anilines. A general increase in the release of *N*-methylaniline in a nitrogen atmosphere and of formaldehyde in an oxygen atmosphere was found when 1 : 1 to 1 : 5 A–F resin products are analysed. This may be inferred as due to an increasing methylene cross-link

TABLE 1

Elemental analysis and cross-link density data of A–F resins

A–F resin	C (%)	H (%)	N (%)	Cross-link density
1:1	80.00	6.67	13.33	–
1:2	81.36	6.78	11.86	0.56
1:3	82.44	6.87	10.69	0.72
1:4	75.61	7.72	16.67	0.83
1:5	70.01	8.01	12.98	0.95

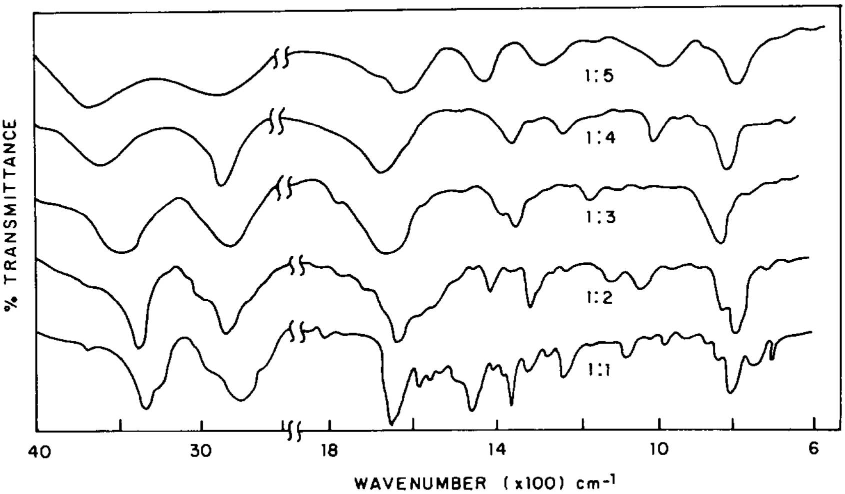


Fig. 1. IR spectra of A–F resins in KBr pellet.

density from 1 : 1 to 1 : 5 A–F resin products. The general thermal stability of the resins also varies in an analogous manner from the 1 : 1 to 1 : 5 A–F composition.

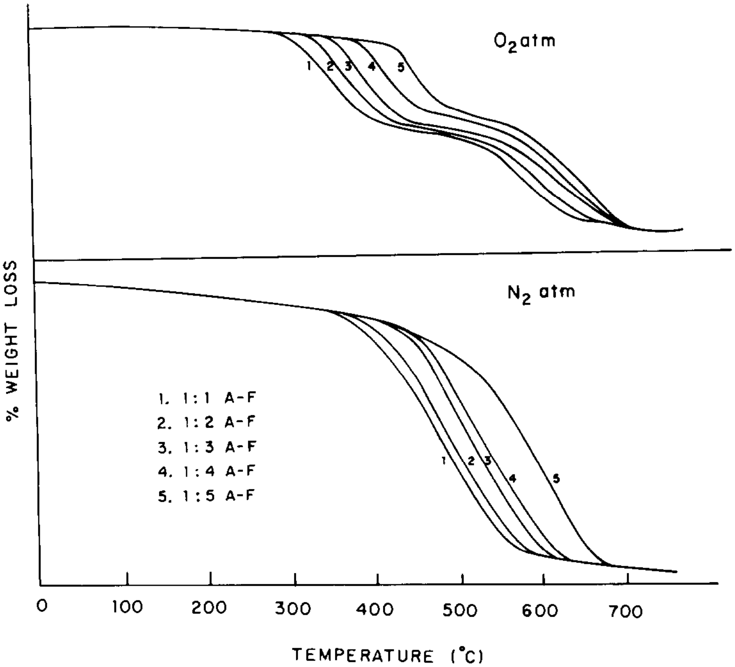


Fig. 2. Typical TG curves of A–F resins.

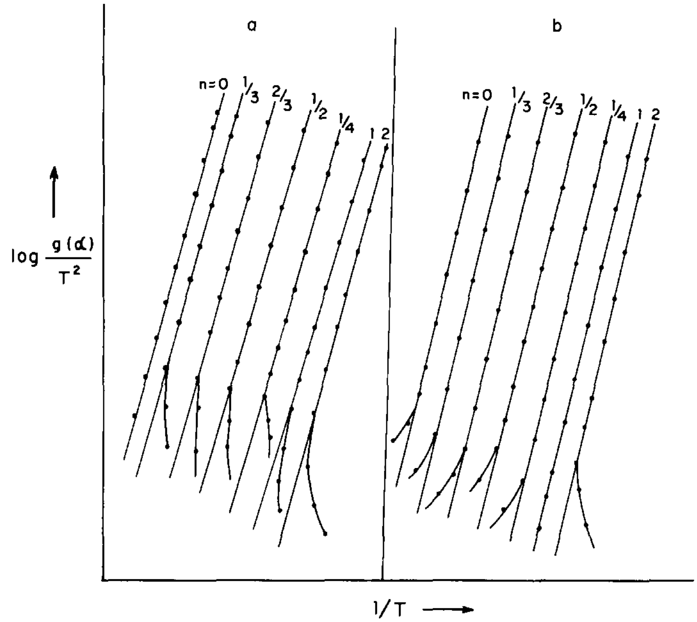


Fig. 3. Typical linearization plots: (a) 1 : 1 A–F resin, step I, N_2 atmosphere; (b) 1 : 3 A–F resin, step I, N_2 atmosphere.

In order to perform a kinetic analysis of the TG curves, the degree of transformation α has been calculated for each experimental point as the ratio of the actual weight loss to the total weight loss corresponding to the thermal decomposition stage concerned. Kinetic parameters have then been derived by means of the Coats and Redfern method [8]. Conversion integrals $g(\alpha)$ have been calculated for the formal reaction orders $n = 0$, $1/3$, $1/2$, $2/3$, 1 and 2 using the expression given elsewhere [9]. Examples of graphical plots of $\log(g(\alpha)/T^2]$ vs. $1/T$ are given in Fig. 3. It is apparent that good linearizations are obtained for the formal reaction order values $n = 0$ and $n = 1$ in Figs. 3(a) and 3(b) respectively. Adopting similar procedures, the values of n for the remaining systems are listed in Table 2. Apparent activation energy (E_a) values have been derived from the slopes of the linearized plots. Pre-exponential factors of the Arrhenius equation have been calculated using the following expression [9]

$$\log Z = \log g(\alpha) - \log p(x) + \log Rq - \log E_a \qquad (1)$$

where $g(\alpha)$ represents the conversion integral, $p(x)$ the exponential integral x for E_a/RT, E_a the apparent activation energy and q the heating rate in degrees per second. Derived kinetic parameters are presented in Table 2. Generally owing to a kinetic compensation effect, log Z values increase with E_a values. This kinetic compensation effect can be expressed as $\log Z = aE_a$

TABLE 2

Kinetic parameters of A–F resin thermal degradations

A–F resin	N_2 atmosphere			O_2 atmosphere					
				Stage I			Stage II		
	E_a (kcal mol^{-1})	n	log Z	E_a (kcal mol^{-1})	n	log Z	E_a (kcal mol^{-1})	n	log Z
1:1	13.9	0	3.90	10.6	0	1.01	11.1	1/3	0.64
1:2	12.0	0	2.85	11.2	0	1.25	12.0	1/3	0.96
1:3	11.5	1	2.56	10.2	1	0.84	13.4	2/3	1.46
1:4	11.1	1/3	2.41	9.5	1/3	0.54	11.6	2/3	0.82
1:5	10.8	1/2	2.19	8.7	1/3	0.21	10.6	2/3	0.46

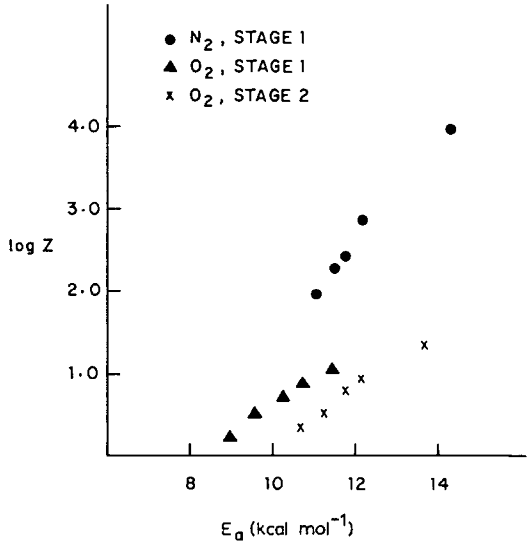


Fig. 4. Kinetic compensation effect of A–F resin thermal degradations.

TABLE 3

Kinetic compensation parameters for different stages of the thermal degradation of A–F resins

Step I	Step II	*a*	*b*
N_2 atmosphere	–	0.55 ± 0.02	−3.75 ± 0.05
O_2 atmosphere	–	0.42 ± 0.03	−3.45 ± 0.03
–	O_2 atmosphere	0.36 ± 0.01	−3.36 ± 0.02

$+ b$. The *a* and *b* parameter values derived by means of the least-squares method for the different stages of thermal decomposition are given in Table 3. These parametric values could be utilized for correlation studies of analogous condensation products of higher homologues of aniline and formaldehyde.

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