Curing and decomposition behaviour of vinyl ester resins

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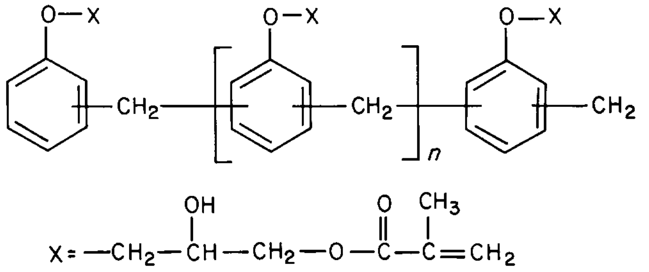
Vinyl ester resins with varied acid values (11, 22, 32, 38 and 48 mg KOH g^{-1} solid) were prepared by reacting an epoxy novolac resin with methacrylic acid. The curing and decomposition behaviour of these resins containing styrene as reactive diluent (40% w/w) and benzoyl peroxide (2 phr) as initiator were studied by d.s.c. and t.g.a. The activation energy and frequency factor for the curing reactions calculated by the Ozawa method were found to increase from 17 to 24 kcal mol^{-1} and 1.2×10^{10} to 6.6×10^{13} min^{-1}, respectively, with increase in the acid value of the samples. An isothermal temperature for the curing of all the resins was selected from the d.s.c. scans and at that temperature the cure time was found to increase with the acid value of the resins. The cured product with the lowest acid value was found to be the most thermally stable and a lifetime of 16.58 years at 400°C was estimated. The activation energy and frequency factor for the decomposition reactions, calculated by the Coats and Redfern method, decreased from 24 to 17.8 kcal mol^{-1} and 1.05×10^6 to 1.5×10^4 min^{-1}, respectively, with increase in the acid value from 11 to 48 mg KOH g^{-1} solid.

(Keywords: curing; decomposition; vinyl ester resins; d.s.c.; t.g.a.)

INTRODUCTION

Vinyl ester resins (VERs) are addition products of various epoxide resins and unsaturated carboxylic acids such as acrylic or methacrylic acid having ester groups and carbon-to-carbon double bond linkages at the end of the polymer chain. The typical structural formula for VER based on epoxy novolacs and methacrylic acid is:



$$X = -CH_2-\overset{\overset{OH}{|}}{C}H-CH_2-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}=CH_2$$

The crosslinking reaction of these resins is highly exothermic and proceeds by free-radical polymerization. VER can be used in neat form or in the presence of a vinyl-type reactive diluent[1,2]. The rate of the polymerization reaction is dependent on the temperature and concentration of the monomers and initiators. Since the monomer and initiator concentrations are established prior to curing, the curing reaction may be more readily controlled by means of adjusting the curing environment and cure time[3]. The curing environment can be controlled with a knowledge of the heat transfer during the process and the kinetics of the polymerization reaction.

The cure kinetics of VER and its thermal stability have been studied by several investigators[4–6]. Most of these studies have primarily been aimed at characterizing the kinetics of the curing reactions of VER based on bisphenol-A epoxies, in the presence of various reactive diluents and low profile additives. There are few studies related to the cure and decomposition kinetics of VER based on epoxy novolacs as the backbone. This report describes the curing and decomposition behaviour of VER with varied acid value, in the presence of styrene (40% w/w) as the reactive diluent. The scanning during curing was carried out by d.s.c. and the decomposition of the cured products was followed using t.g.a.

EXPERIMENTAL

Epoxy novolac resin (EPN-1138, Ciba-Geigy), methacrylic acid (E. Merck), triphenylphosphene (Fluka AG), benzoyl peroxide (SD's) recrystallized from chloroform, and styrene (Ranbaxy), purified according to the method of Overberger and Yammato[7], were used.

VERs were prepared using a 1:0.9 mol ratio of EPN-1138 (epoxide equivalent weight: 200, determined by the pyridinium chloride method[8]) and methacrylic acid in the presence of triphenylphosphene (1 phr by weight of the epoxy resin) at 85 ± 1°C. The esterification reaction was carried out for a definite time to obtain a product with the desired acid value. (The acid value is defined as the number of milligrams of KOH required to neutralize 1 g of substance.) The VERs were stored in a refrigerator at 10°C, after determining their acid values by the method of Ogg *et al.*[9].

The samples for curing studies were prepared using 10/4/0.2 (w/w) of resin, styrene and benzoyl peroxide, respectively. Half of the styrene was mixed with the resin and the other half with the benzoyl peroxide in separate flasks. The flasks were then sealed and kept under refrigeration to avoid premature polymerization prior to use. Then equal amounts of the solutions were placed in a small glass vial and stirred vigorously with a glass rod at room temperature.

A Dupont 99XR thermal analyser with a 910 DSC cell was used in calibrated mode. Scans were obtained under dynamic conditions with programme rates of 2, 5, 10, 15

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and 20°C min^{-1} from 40°C to the temperatures at which the exothermic reactions were complete. From the d.s.c. scans the activation energy E (within $\pm 3\%$ accuracy) was calculated by the Ozawa method[10], which assumes that the extent of reaction at the peak exotherm temperature is constant and independent of the programme rate:

$$E \cong 2.19R \frac{\mathrm{d}\log\beta}{\mathrm{d}(1/T)} \quad (1)$$

where R is the gas constant, β is the programme rate and T is the peak temperature.

Further refinements to the E values were carried out by iteration until two successive values were almost identical.

The frequency factor Z was calculated using:

$$Z = \frac{\beta E \, \mathrm{e}^{E/RT}}{RT^2} \quad (2)$$

The specific rate constant K_T was calculated using the Arrhenius equation:

$$K_T = Z\,\mathrm{e}^{-E/RT} \quad (3)$$

From the dynamic d.s.c. scans, a temperature was selected at which an appreciable rate of curing could be observed. D.s.c. runs under isothermal conditions at the selected temperatures were then carried out to determine the apparent time required for the completion of each of the curing reactions. The curing conditions (temperature and time) thus determined were used to cure the resin samples for subsequent studies on thermal stability and kinetics of decomposition using a TG-750 thermogravimetric analyser (Stanton-Redcroft). Dynamic thermograms for the cured samples were obtained using a rate of 10°C min^{-1} from ambient to 800°C under a static atmosphere. The relative thermal stability of the resins was quantitatively estimated by comparing the temperatures for a particular degree of weight loss. The lifetime at various temperatures for the most stable sample was calculated using the Flynn and Wall[11] method:

$$E = -\frac{R}{0.457}\left[\frac{\mathrm{d}\log\beta}{\mathrm{d}(1/T)}\right] \quad (4)$$

and the Toop[12] method:

$$\ln t_f = \frac{E}{RT_f} + \ln\left[\frac{E}{\beta R} P\left(\frac{E}{RT_c}\right)\right] \quad (5)$$

where t_f is the estimated time to failure, T_f is the failure temperature, $P(E/RT_c)$ is a value from the numerical integration table in reference 12 and T_c is the temperature for 5% loss at β, from the dynamic thermograms obtained at 2, 5, 10, 15 and 20°C min^{-1}, from ambient to 600°C, under a static atmosphere. The E, order of reaction n and Z for the decomposition reaction of all the cured resins were determined by the Coats and Redfern method[13] from the thermograms obtained at 10°C min^{-1}. According to which, for $n=1$:

$$\log\left[-\log\frac{(1-\alpha)}{T^2}\right] = \log\frac{ZR}{\beta E}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.3RT} \quad (6)$$

where α is the fraction of material decomposed at temperature T.

RESULTS AND DISCUSSION

Five samples of VER (S_1, S_2, S_3, S_4 and S_5) with acid values of 11, 22, 32, 38 and 48 mg KOH g^{-1} solid, respectively, were prepared and used. *Figure 1* shows the results of the esterification reaction of epoxy novolac with methacrylic acid catalysed by triphenylphosphene. The results are typical of the behaviour generally observed for polyesterification reactions. It is apparent from the plot that the decrease in acid value in the initial stages of the reaction is not linear. This is because of the high concentration of the reactive sites and the greater possibility of association of acid and epoxide groups. The linearity of the plot in the higher conversion region, $\geqslant 70\%$ (taking the decrease in acid value from the initial value as a measure of conversion), reveals that the functional group reactivity is independent of molecular size, which is a characteristic of the esterification reaction[14].

Curing studies

The typical (dynamic) d.s.c. scans for the curing of VER samples with varied acid values diluted with 40% styrene, when heated at 10°C min^{-1} are given in *Figure 2*. The peak exothermic temperatures were 85.5, 94, 100, 102 and 105.5°C and the onset temperatures were 64, 75, 83, 87 and 92°C for samples S_1–S_5, respectively. This indicates an increase in the onset and peak temperatures with increase in acid value. D.s.c. scans of S_1–S_5 at programme rates of 2, 5, 15 and 20°C min^{-1} also showed a similar trend. It is apparent from *Figure 2* that the VERs with lower acid values were more reactive during the crosslinking reactions than the resins with higher acid values. The thermograms show that the rate of curing becomes sluggish in the latter stages of the reaction, whereas it is predominant in the early stages because of

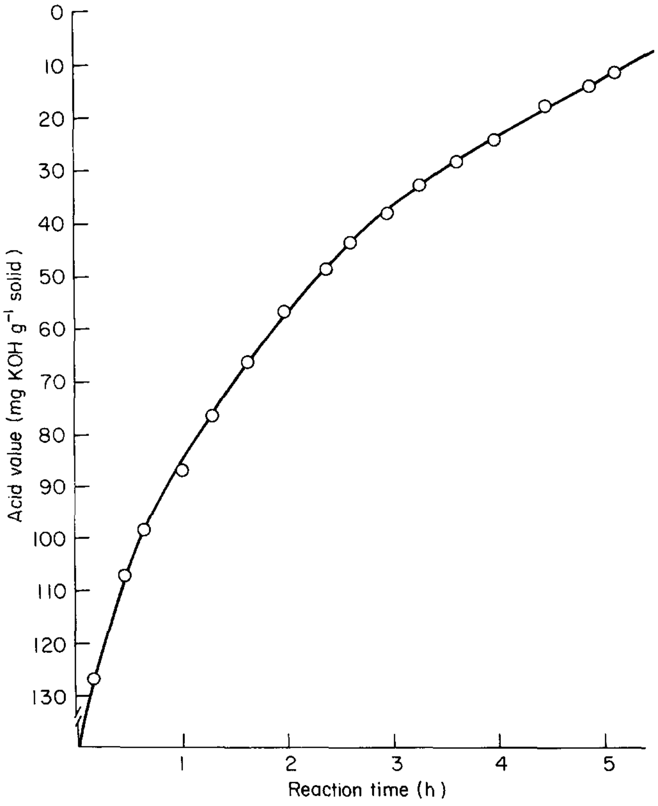

Figure 1 Acid value *versus* reaction time

the specific heat changes. Due to this fall in the reaction rate in the latter part of the reaction, it becomes difficult to draw an exact baseline for the determination of the total heat of reaction and the parameters related to it.

Using the Ozawa method[10], $\log \beta$ was plotted against the reciprocal of the peak temperature (*Figure 3*) and from the slope obtained by regression analysis the value of E for the curing reactions was calculated. The values of E and Z at different β values for S_1–S_5 are given in *Table 1*. It is apparent from *Table 1* that E and Z decrease with increase in the extent of reaction or decrease in the acid value of the resins. The increase in E with increase in acid value could be attributed to the presence of acid groups. The value of Z for a particular VER at different β values varies over a narrow range, which suggests that the curing reactions are first order.

The specific rate constants of the curing reactions of S_1–S_5 were plotted against temperature, and it is apparent from *Figure 4* that they obey Arrhenius' law.

The isothermal d.s.c. scans of S_1–S_5 were recorded at 75, 80, 85, 90 and 95°C and the apparent time for completion of the curing reaction was found to be 50,

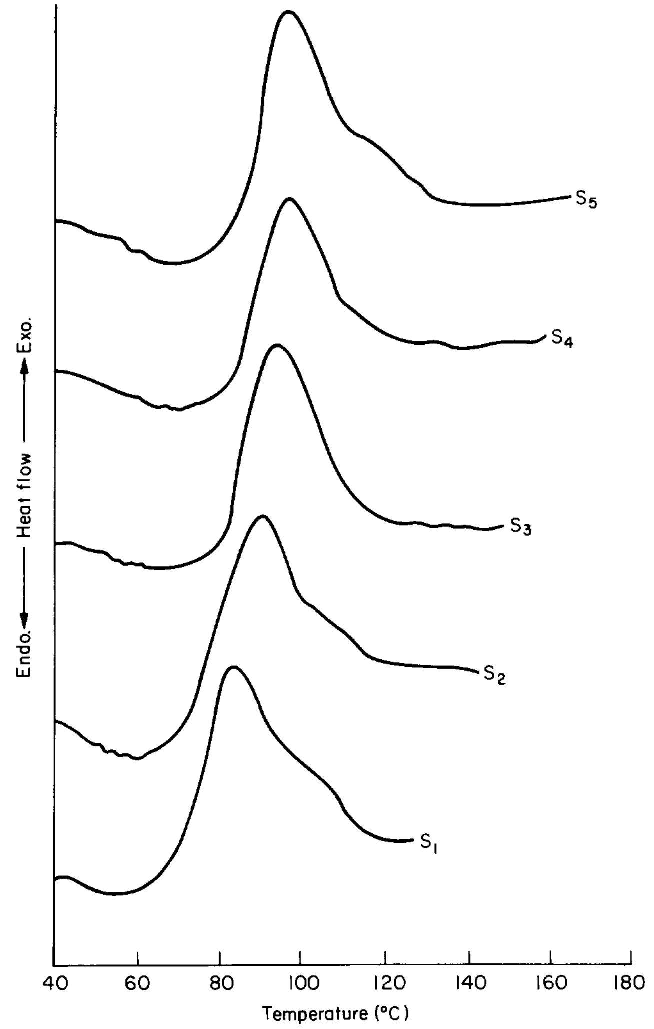

Figure 2 Dynamic d.s.c. scans for the curing of VER samples diluted with 40% styrene at 10°C min^{-1}. Acid values (mg KOH g^{-1} solid) of S_1–S_5 are 11, 22, 32, 38 and 48, respectively

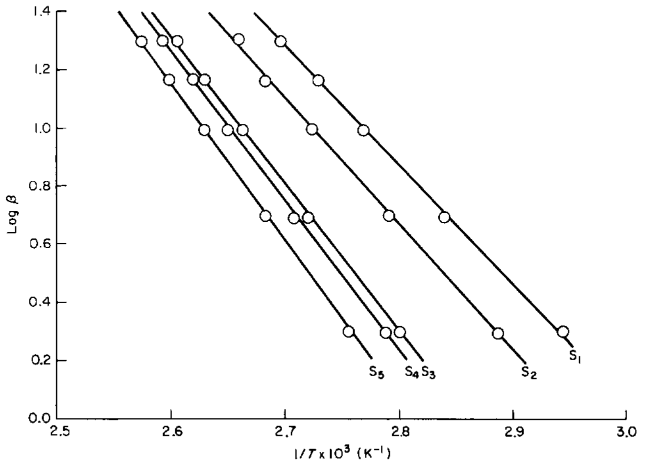

Figure 3 Plots of $\log \beta$ *versus* the reciprocal of the peak temperature to calculate the activation energy: S_1, $y = 12.1312 - 4.0130x$, ($r = 0.9638$); S_2, $y = 13.4021 - 4.5502x$, ($r = 0.9941$); S_3, $y = 14.4757 - 5.0551x$, ($r = 0.9992$); S_4, $y = 14.5738 - 5.1137x$, ($r = 0.9955$); S_5, $y = 15.7642 - 5.6127x$, ($r = 0.9982$)

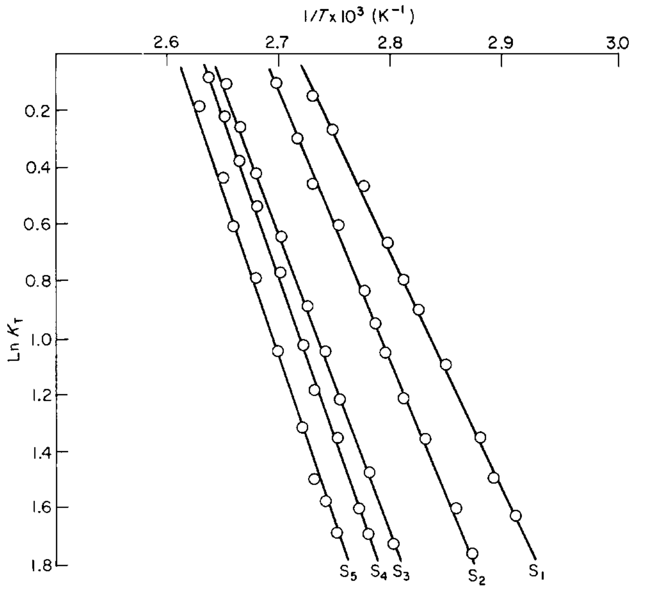

Figure 4 Plots of $\ln K_T$ *versus* the reciprocal of temperature for all the VER samples

Table 1 Activation energies and frequency factors of the curing reactions of VERs with varied acid values diluted with 40% styrene

Sample	Acid value (mgKOH g^{-1} solid)	Activation energy (kcal mol^{-1})	Frequency factor (min^{-1}) at different programme rates (°C min^{-1})				
			2	5	10	15	20
S_1	11	17.46	0.82×10^{10}	1.52×10^{10}	1.41×10^{10}	1.17×10^{10}	1.03×10^{10}
S_2	22	19.36	2.34×10^{11}	2.44×10^{11}	2.86×10^{11}	2.32×10^{11}	2.48×10^{11}
S_3	32	21.64	3.04×10^{12}	2.91×10^{12}	3.76×10^{12}	3.45×10^{12}	2.76×10^{12}
S_4	38	21.90	3.68×10^{12}	3.80×10^{12}	4.55×10^{12}	4.30×10^{12}	3.42×10^{12}
S_5	48	24.17	6.24×10^{13}	6.38×10^{13}	7.72×10^{13}	6.79×10^{13}	6.13×10^{13}

Table 2 Temperature of 1–10% weight loss in thermogravimetric analysis (programme rate 10°C min^{-1}) of cured VER samples

Weight loss (%)	Temperature (K) for				
	S_1	S_2	S_3	S_4	S_5
1	593	583	563	543	526
2	606	598	588	573	551
3	615	608	603	599	563
4	625	615	611	609	593
5	634	628	628	618	603
6	638	632	625	621	610
7	642	636	629	626	616
8	648	638	630	628	617
9	652	643	633	631	618
10	657	645	638	633	621

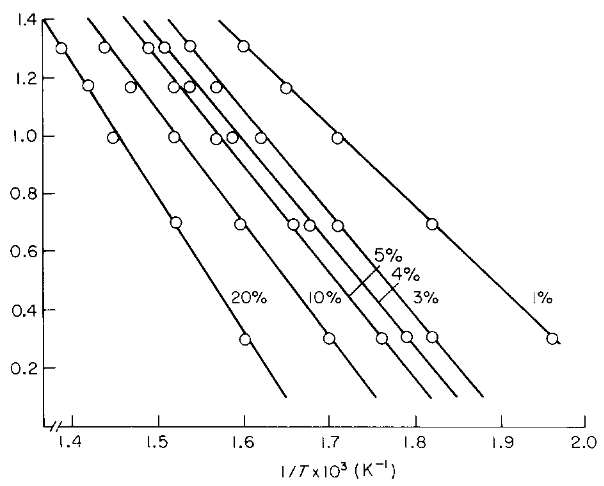

Figure 5 Plots of log β *versus* the reciprocal of temperature of constant conversion from t.g.a. data: 1%, $y=5.7300-2.7586x$, $(r=0.9925)$; 3%, $y=5.7223-3.5195x$, $(r=0.9907)$; 4%, $y=6.7034-3.5686x$, $(r=0.9763)$; 5%, $y=6.7179-3.6258x$, $(r=0.9924)$; 10%, $y=6.7665-3.7941x$, $(r=0.9787)$; 20%, $y=7.8245-4.6821x$, $(r=0.9796)$

Table 3 T.g.a. data for sample S_1 at different programme rates

Conversion (%)	Temperature (K) at different programme rates (°C min^{-1})					Activation energy (kcal mol^{-1})
	2	5	10	15	20	
1	508	548	583	605	600	11.99
2	548	584	615	634	649	15.30
3	557	594	625	645	660	15.51
5	565	602	634	654	669	15.76
10	586	625	657	678	694	16.50
20	622	657	686	704	717	17.69

60, 70, 76 and 85 min, respectively. It was also observed from these scans that the reaction rate was initially a maximum without exhibiting an induction time, which indicated that the curing reactions follow *n*th order kinetics, i.e. the rate of conversion is proportional to the concentration of the material which is yet to react[15].

Thermogravimetric studies

The temperatures for 1–10% weight loss in t.g.a. at a rate of 10°C min^{-1} for curved VER samples are given in *Table 2*. From the temperature for a particular degree of weight loss it is apparent that the thermal stability of S_1, which has the lowest acid value, was the greatest. The E values for the various levels of conversion were calculated from the slope of the plot of the logarithm of the programme rate *versus* the reciprocal of the temperature of conversion (*Figure 5*) according to the method of Flynn and Wall[11]. *Table 3* gives values for the decomposition temperature and E for different degrees of conversion α (where α is the fraction of active material decomposed). It is apparent from *Table 3* that for a particular α the decomposition temperature increases with the programme rate, and E for the decomposition reaction increases with conversion. It is apparent from *Figure 5* that the slopes of the lines for 3–10% decomposition are similar. The value for E (15.76 kcal mol^{-1}) at 5% decomposition, which is also the average value obtained by neglecting the values at lower and higher levels of decomposition, was taken to calculate the lifetime of the most stable sample S_1 at various temperatures by the Toop[12] method.

Figure 6 shows the plot of estimated lifetime *versus* the reciprocal of failure temperature. From the plot it is evident that the lifetime of the resin at 400°C is 16.58 years. A decrease in failure temperature by 5°C increases the lifetime from 16.58 years to 18.12 years.

The Flynn and Wall method only takes into consideration the earlier stages of the decomposition profile and thermograms at different programme rates are required. However, in the Coats and Redfern method[13] a major portion of the thermogram obtained at a constant programme rate is used to determine the kinetic parameters of the decomposition reaction. *Figure 7* show a plot of $-\log_{10}[-\log_{10}(1-\alpha)/T^2]$ *versus* the reciprocal of the decomposition temperature, where α is the fraction of the sample decomposed at the decomposition temperature for samples S_1–S_5. The slope of the plot obtained by regression analysis was used to calculate E and the

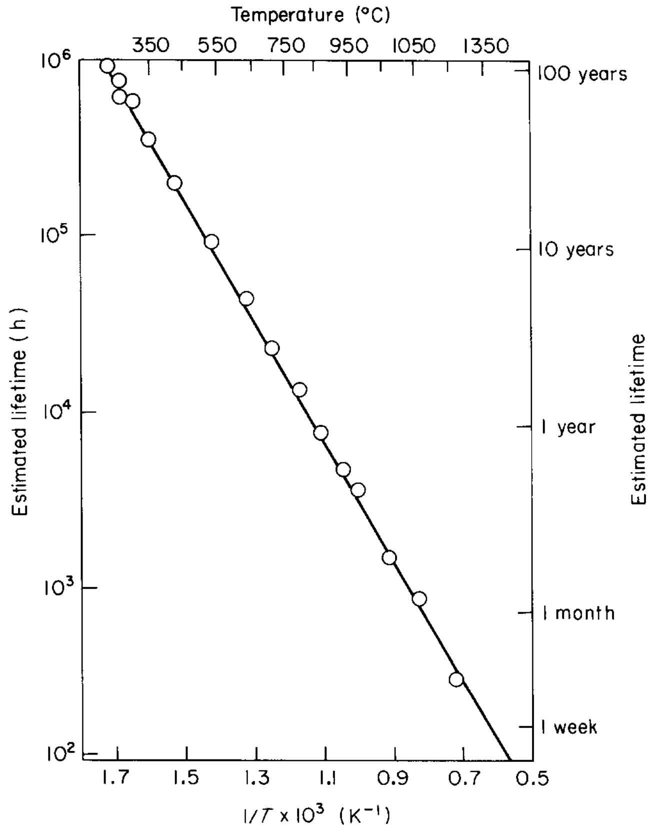

Figure 6 Estimated lifetime (temperature dependence) of sample S_1

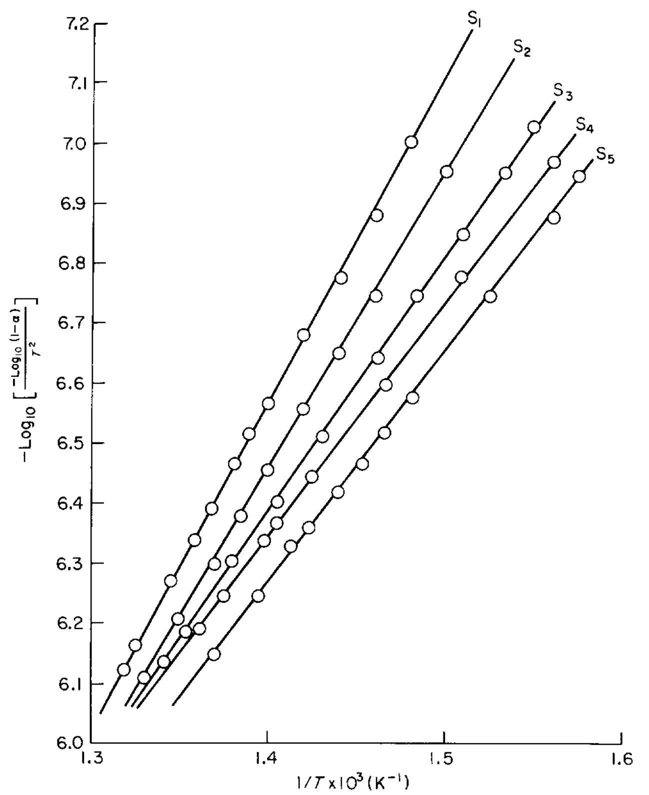

Figure 7 Plots of $-\log_{10}[-\log_{10}(1-\alpha)/T^2]$ *versus* the reciprocal of the decomposition temperature from t.g.a. data: S_1, $y=-0.8775+5.3017x$, ($r=0.9978$); S_2, $y=-0.3481+4.8475x$, ($r=0.9992$); S_3, $y=-0.1720+4.5170x$, ($r=0.9920$); S_4, $y=7.4140+4.0043x$, ($r=0.9963$); S_5, $y=0.8371+3.8746x$, ($r=0.9947$)

intercept gave the Z value. The correlation coefficient r varied between 0.9920 and 0.9998, which indicated that the Coats and Redfern function was sufficient to explain the decomposition behaviour of VER. *Table 4* gives the E and Z values for the decomposition reactions of S_1–S_5.

Table 4 Activation energies and frequency factors of the decomposition reactions of S_1–S_5 determined by Coats and Redfern[13]

Sample	Activation energy (kcal mol^{-1})	Frequency factor (average value) (min^{-1})
S_1	24.42	1.05×10^6
S_2	22.30	2.85×10^5
S_3	20.80	1.79×10^5
S_4	18.44	1.98×10^4
S_5	17.84	1.54×10^4

From the values of E it can be seen that S_1 is thermally more stable than the other samples.

REFERENCES

1 Launikitis, M. B. in 'Handbook of Composites' (Ed G. Luben), Van Nostrand Reinhold Co., New York, 1982, p. 38
2 Kay, R. in 'Fibre Composite Hybrid Materials' (Ed. N. L. Hancox), Applied Science, London, 1981, p. 42
3 Stonecypher, T. E., Allen, E. L., Mastin, D. E. and Willionghby, D. A. *Chem. Eng. Symp. Ser.* 1966, **62**, 7
4 Han, C. D. and Lem, K. W. *Polym. Eng. Sci.* 1984, **24**, 175
5 Han, C. D. and Lem, K. W. *J. Appl. Polym. Sci.* 1984, **29**, 1879
6 Bhatnager, R. and Varma, I. K. *J. Thermal Anal.* 1989, **35**, 1241
7 Overberger, C. G. and Yammato, N. *J. Polym. Sci.* 1966, **4**, 3101
8 Knoll, D. W., Nelson, D. H. and Kehres, P. W. *Am. Chem. Soc. Symp.* 134th Meeting, 1958
9 Ogg, C. L., Porter, W. L. and Willitis C. O. *Ind. Eng. Chem. Anal. Edn* 1945, **17**, 394
10 Ozawa, T. *J. Therm. Anal.* 1976, **9**, 217, 369
11 Flynn, J. H. and Wall, L. A. *J. Polym. Sci. B* 1966, **4**, 323
12 Toop. D. J. *IEEE Trans. Elec. Ins.* 1971, **E1-6**, 2
13 Coats, A. W. and Redfern, J. P. *Nature* 1964, **68**, 201
14 Odian, G. 'Principles of Polymerization', 2nd Edn, Wiley Interscience, New York, 1970, pp. 46–49
15 Prime, R. B. in 'Thermal Characterization of Polymeric Materials' (Ed. E. A. Turi), Academic Press, New York, 1981, Ch. 5, pp. 441–445