RHEOLOGICAL AND THERMAL BEHAVIOUR OF VINYL ESTER RESIN

BHARTI GAUR and J. S. P. RAI*

Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur 208002, India

Abstract—The rheological behaviour of synthesized vinyl ester resin (VER) based on epoxy novolaks containing methyl, ethyl and butyl acrylates as reactive diluent (40% w/w) was studied using a Haake Rotovisco RV 20 viscometer. The zero-shear viscosity of VER containing acrylates decreases linearly with temperature and increases with the size of the alkyl substituent in the acrylate. The average values of activation energy for flow at constant shear stress (25–100 Pa) were 11.79, 13.29 and 14.75 kcal/mol for VER containing methyl, ethyl and butyl acrylates, respectively. The activation energy at constant shear rate decreases with increase in the shear rate (50–400 sec^{-1}). The curing and decomposition behaviour of the resin containing acrylates as reactive diluent (40% w/w) and benzoyl peroxide (2 phr) as initiator were studied by DSC and TGA. The activation energy for the curing reaction calculated by the Ozawa method, was found to be minimum whereas the thermal stability and the activation energy for the decomposition reaction calculated by the Coats and Redfern method were found to be maximum, for the resin with ethyl acrylate as reactive diluent.

INTRODUCTION

Vinyl ester resins (VER) are the addition products of an epoxy resin and an unsaturated carboxylic acid [1, 2]. The esterification produces a multifunctional VER depending upon the number of available epoxy groups in the main chain. Therefore, VER yield highly crosslinked rigid structures having high strength and good chemical resistance. These resins may be used in the neat form or may contain reactive diluents [3, 4]. The investigation of rheological behaviour of these resins, especially the dependence on the reactive diluent, concentration, temperature, shear rate and shear stress becomes a pre-requisite for gaining an insight of the structure–property relationship. The exothermic curing reaction of such resins may occur between the vinylic double bonds of the resin or with that of a reactive diluent in the presence of free-radical initiators, or by irradiation with u.v., electron beams etc. It becomes essential to understand the cure kinetics for controlling the rate of heat generation and temperature variation during processing of these materials. The cure kinetics of VER based on bis-phenol-A epoxy in the presence of styrene [5, 6], α-methylstyrene [7] and acrylates [8] have been investigated. The cure and the decomposition kinetics of VER based on epoxy-novolaks as backbone in the presence of styrene as reactive diluent was reported in our earlier communication [9]. In this paper we report the rheological behaviour as well as the cure and decomposition kinetics of VER based on epoxy-novolaks, in the presence of acrylates as reactive diluent.

EXPERIMENTAL PROCEDURES

Epoxy-novolak resin (EPN-1138; Ciba-Geigy), methacrylic acid (Merck), triphenyl phosphine (Fluka), benzoyl

peroxide (SD's) recrystallized from chloroform and re-agent grade monomers purified by the method given by Overberger and Yammato [10] were used in the present study.

Vinyl ester resins were prepared using 1:0.9 mole ratio of EPN-1138 (epoxide equivalent weight: 200, determined by pyridinium chloride method [11]) and methacrylic acid in the presence of triphenyl phosphine (1 phr by weight of the epoxy resin) and hydroquinone (200 ppm) at 85 $\pm$ 1°. The esterification was carried out for ~5 hr till the acid value was 10. The VER was stored at ~10°.

The samples for rheological and thermal studies were prepared by mixing the resin with 40% w/w of reactive diluents viz. methyl, ethyl and butyl acrylates. The solution was stirred at 40° $\pm$ 1° for 30 min, in a flask fitted with a condenser; it was then kept in a sealed bottle in a refrigerator to avoid evaporation of the reactive diluent. The solution was stirred for 10 min before being used for rheological studies. Thermal studies were carried out by mixing 2% of benzoyl peroxide with the solution, by stirring vigorously with a glass rod in a small glass vial at room temperature.

Rheological measurements

A Haake Rotovisco RV20 coaxial cylinder viscometer with HS-1 sensor was used to measure the solution viscoities of the samples at shear rates ranging from 0.1 to 1500 sec^{-1} at 25, 30, 35 and 40°. After a sample was loaded, the sensor was accelerated to the maximum shear rate in 5 min and then maintained at that shear rate for 4 min before the shear stress values were recorded.

The zero shear viscosity (η_0) of all samples at 25, 30, 35 and 40° was determined by direct extrapolation of low-shear data from the plot of viscosity-shear rate. The energy of activation for viscous flow at constant shear stress (E_τ) and shear rate (E_D) was calculated using the Arrhenius equation:

$$\eta = A_{\exp}(E/RT)$$

where A is a constant characteristic of the polymer at a shear stress or shear rate, E is the activation energy for the flow, R is the gas constant, η is the viscosity at constant shear stress or shear rate and T is the temperature in degrees Kelvin.

*To whom all correspondence should be addressed.

Curing studies

A DuPont 99XR thermal analyser with a 910 DSC cell was used in calibrated mode and the scans were obtained under dynamic conditions with program rates of 2, 5, 10, 15 and 20° min⁻¹ from 40° to the temperature at which the exothermic reactions were complete. From the DSC scans, the activation energy (E) with $\pm 3\%$ accuracy was calculated by the Ozawa method [12]. Further refinements of E values were carried out using a series of iterations until two successive values of E were almost identical. The frequency factor (Z) was calculated using Kissinger's equation [13]:

$$Z(\text{min}^{-1}) = \frac{\beta E\, e^{E/RT}}{RT^2}$$

where E is the activation energy (cal/mol), T is the peak temperature (K), R is the gas constant (1.987 cal/mol K), β is the program rate (deg min⁻¹).

The specific rate constant (k_T) has been calculated using the Arrhenius equation:

$$k_T = Z\, e^{-E/RT}.$$

The experimental resin samples in aluminum pans were cured in an air circulating oven at 85° ± 1° for 90 min. After cooling, the cured samples from the pans were taken for subsequent studies on thermal stability and kinetics of decomposition using a TG-750 thermogravimetric analyser (Stanton-Redcroft). Thermograms for the cured samples were obtained using a program rate of 10° min⁻¹ from ambient to 800° under N_2. The relative thermal stability of a resin sample was quantitatively estimated by comparing the temperature for a particular degree of weight loss. The activation energy and order of reaction for decomposition of all cured samples were determined by the Coats and Redfern [14] method, according to which, for $n = 1$

$$\log_{10}\left[\frac{-\log_{10}(1-\alpha)}{T^2}\right] = \log_{10}\frac{ZR}{\beta E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{2.3RT}$$

where α is the fraction of material decomposed at temperature T (K), E is the activation energy (cal/mol), R is the gas constant (1.987 cal/mol K) and Z is the frequency factor (min⁻¹).

RESULT AND DISCUSSION

Typical logarithmic plots between viscosity and shear rate for VER samples having methyl, ethyl and butyl acrylates at 25°, are given in Fig. 1. The figure shows that the viscosity of VER at any shear rate increases with the bulkier monomer as reactive diluent. Similar behaviour was observed at 30, 35 and 40°. It is also apparent from the figure that the apparent viscosity of the samples decreases under the action of shear rate. However, at very low shear rates, the viscosity seems to be independent of shear rate as the molecular orientation does not occur below a threshold shear rate. A significant decrease in the viscosity of VER with methyl, ethyl and butyl acrylates was observed from the initial shear rate to 200, 300 and 400 sec⁻¹, respectively at 25°. With further increase in shear rate, there is little decrease in viscosity.

The shear stress–shear rate data of the sample were analysed for their flow behaviour, using Bingham and Casson [15] models. The Bingham model fitted the data best in all cases and therefore, the flow behaviour of samples could be considered as plastic.
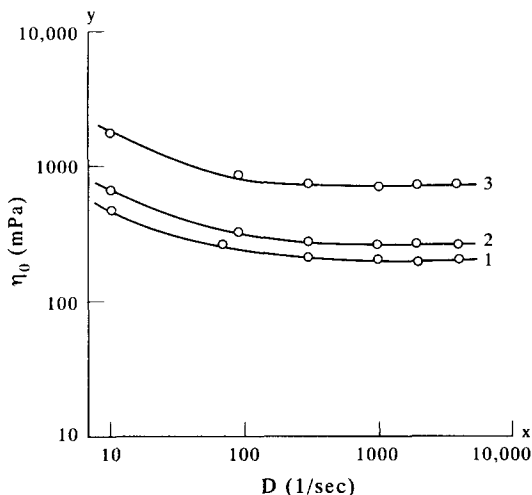

Fig. 1. Plot between viscosity and shear rate for VER containing: 1, methyl acrylate; 2, ethyl acrylate; 3, butyl acrylate.

The Bingham equation for VER samples at 25° were; $\tau = -1.653 + 0.2136D$ $(r = 1.00)$ for methyl acrylate; $\tau = 1.116 + 0.284D$ $(r = 1.00)$, for ethyl acrylate; $\tau = 3.614 + 0.7615D$ $(r = 1.00)$ for butyl acrylate, where τ is shear stress, D is the shear rate and r is the correlation coefficient.

The zero-shear viscosity of VER containing methyl, ethyl and butyl acrylates at 25, 30, 35 and 40° are shown in Fig. 2. It is apparent that the zero shear viscosity decreases linearly with the temperature and at any temperature the VER sample containing methyl acrylate shows a lower value than other acrylates.

The activation energies for flow at constant shear rate (E_D) and at constant shear stress (E_τ), were calculated from the slope of the plots between log η
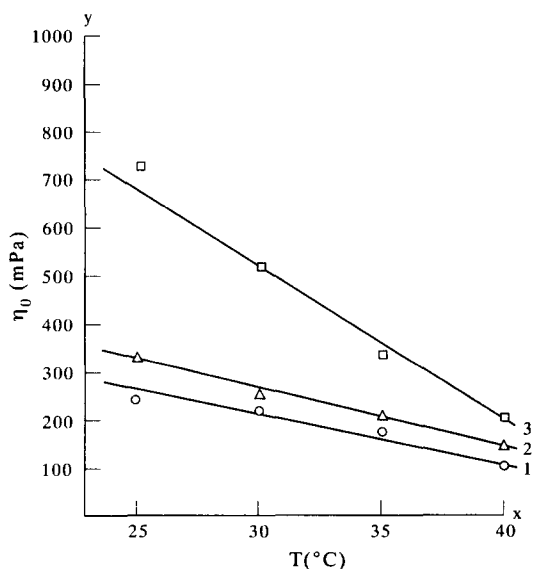

Fig. 2. Plot between zero shear viscosity and temperature for VER containing: 1, methyl acrylate; 2, ethyl acrylate; 3, butyl acrylate.
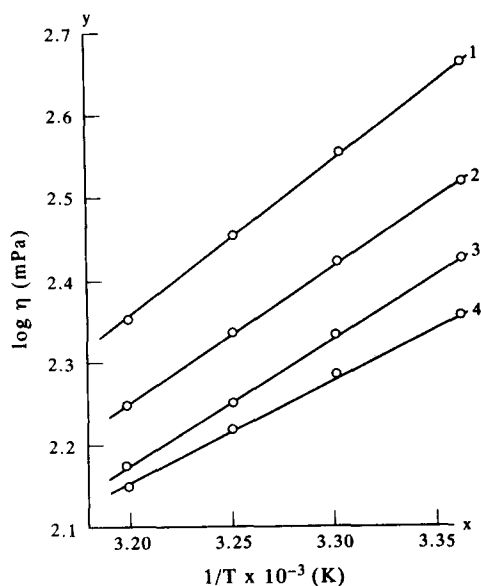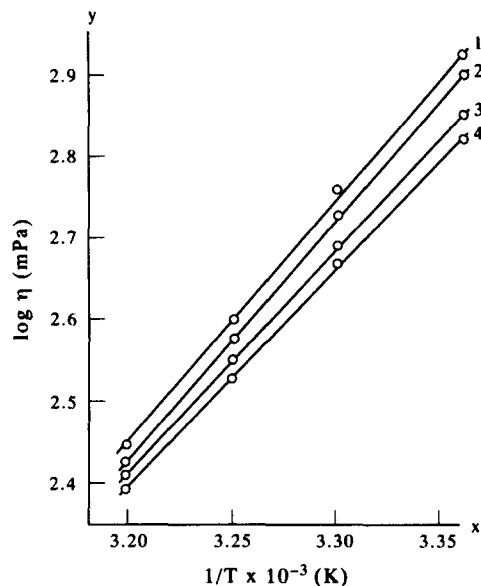
Fig. 3. Plot between $\log\eta$ (apparent viscosity) and reciprocal of temperature for VER containing methyl acrylate at shear rates. 1, $50\,\text{sec}^{-1}$, $y = -3.5770 + 1.8571x$ ($r = 0.9999$); 2, $100\,\text{sec}^{-1}$, $Y = -3.1169 + 1.6782x$ ($r = 0.9992$); 3, $200\,\text{sec}^{-1}$, $y = -2.6826 + 1.5207x$ ($r = 0.9961$); 4, $400\,\text{sec}^{-1}$, $y = -2.1386 + 1.3414x$ ($r = 0.9931$).

Fig. 5. Plot between $\log\eta$ (apparent viscosity) and reciprocal of temperature for VER containing butyl acrylate at shear rates. 1, $50\,\text{sec}^{-1}$, $y = -7.2739 + 3.0402x$ ($r = 0.9998$); 2, $100\,\text{sec}^{-1}$, $y = -7.0485 + 2.8644x$ ($r = 0.9999$); 3, $200\,\text{sec}^{-1}$, $y = -6.3068 + 2.7275x$ ($r = 0.9999$); 4, $400\,\text{sec}^{-1}$, $y = -6.2683 + 2.7103x$ ($r = 0.9982$).

(apparent viscosity) and reciprocal of temperature using the Arrhenius equation. Figures 3, 4 and 5 show the E_D values of VER samples containing the acrylates at shear rates 50, 100, 200 and $400\,\text{sec}^{-1}$. It is apparent that, in all the samples, E_D values decrease with increase in the shear rate. The E_t values for all

the samples at a typical shear stress of 100 Pa are shown in Fig. 6. The E_t values were calculated at 25, 50, 75 and 100 Pa and were almost constant, with the average values 11.79 kcal/mol for methyl acrylate, 13.29 kcal/mol for ethyl acrylate and 14.75 kcal/mol for butyl acrylate.
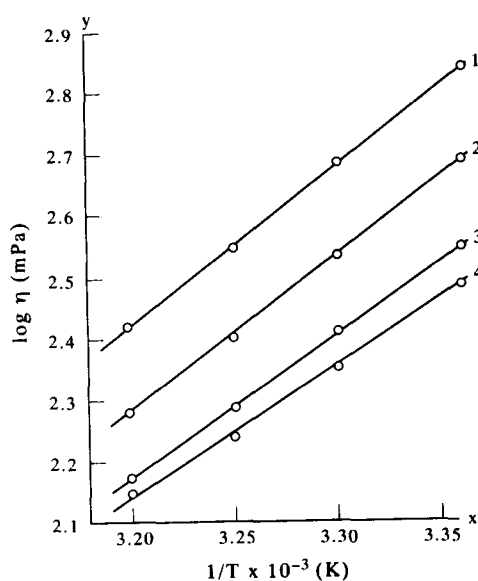

Fig. 4. Plot between $\log\eta$ (apparent viscosity) and reciprocal of temperature for VER containing ethyl acrylate at shear rates. 1, $50\,\text{sec}^{-1}$, $y = -6.3682 + 2.7431x$ ($r = 0.9651$); 2, $100\,\text{sec}^{-1}$, $y = -6.2502 + 2.6582x$ ($r = 0.9907$); 3, $200\,\text{sec}^{-1}$, $y = -6.1705 + 2.6003x$ ($r = 0.9980$); 4, $400\,\text{sec}^{-1}$, $y = -5.9402 + 2.5114x$ ($r = 0.9605$).
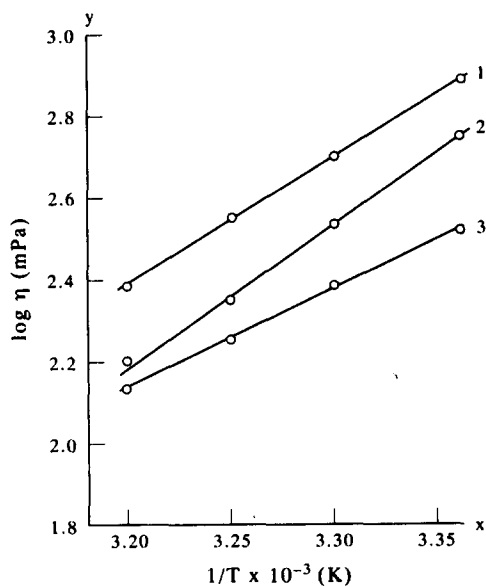

Fig. 6. Plot between $\log\eta$ (apparent viscosity) and reciprocal of temperature at shear stress 100 (Pa) for VER containing; 1, methyl acrylate, $y = -6.0815 + 2.5625x$ ($r = 0.9999$); 2, ethyl acrylate, $y = -6.9402 + 2.8824x$ ($r = 0.9846$); 3, butyl acrylate, $y = -7.7474 + 3.1689x$ ($r = 0.9995$).
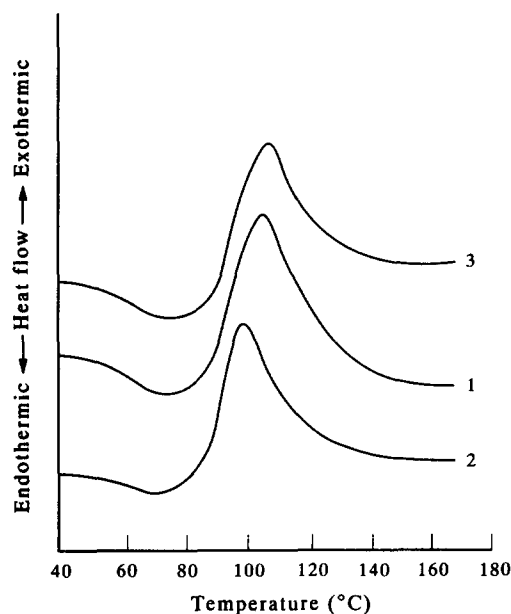
Fig. 7. DSC scans for the curing reaction at $10°\,min^{-1}$ of VER containing: 1, methyl acrylate; 2, ethyl acrylate; 3, butyl acrylate.

Table 1. Activation energy and frequency factor of curing reaction of VER containing acrylates (40% w/w)

Reactive diluent (40% w/w)	Activation energy (kcal/mol)	Frequency factor (average value) (min $^{-1}$)
Methyl acrylate	20.49	3.03×10^{11}
Ethyl acrylate	16.49	2.55×10^{9}
Butyl acrylate	20.77	6.38×10^{11}

Curing studies

The curing behaviour of VER varies with the structure of the reactive diluent. A typical DSC scans for the curing of VER samples containing methyl, ethyl and butyl acrylates (40% w/w) at a program rate of $10°\,min^{-1}$ are given in Fig. 7. The onset temperatures were 83.5, 79 and 85.5° and the peak exothermic temperatures were 104.5, 99 and 106.5°, for samples containing methyl, ethyl and butyl acrylates, respectively. It is apparent that the onset and peak exothermic temperatures of VER containing
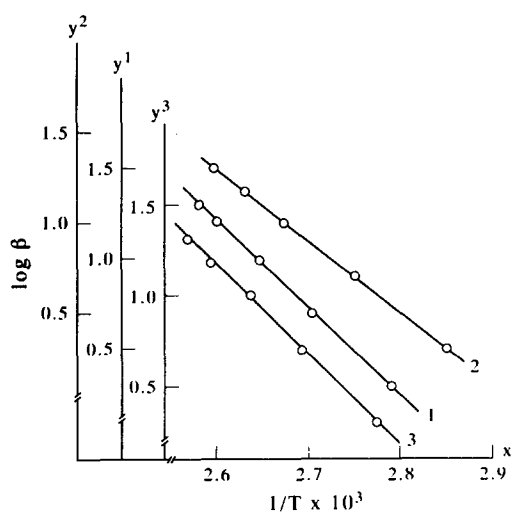
ethyl acrylate are lower than those for samples containing methyl and butyl acrylates. DSC scans of these samples obtained at 2, 5, 15 and $20°\,min^{-1}$ also show a similar trend. This result indicates that ethyl acrylate is comparatively more reactive to VER than methyl and butyl acrylates during curing in the presence of the free-radical initiator, benzoyl peroxide.

Using the Ozawa [12] method, $\log \beta$ (programme rate) was plotted against reciprocal of peak temperature (Fig. 8); from the slope obtained by regression analysis, the activation energy for the curing reaction was determined for the VER with each of the three acrylates. The values of activation energy and frequency factor are given in Table 1. It is apparent from this table that the activation energy of the VER containing ethyl acrylate was low in comparison to those for butyl and methyl acrylates. This behaviour is probably due to large differences in the polarity of the acrylates. Ethyl acrylate being less polar reacts more readily with VER during the curing.

The specific rate constants, calculated using the equation $k_T = Z\,e^{-E/RT}$, of the curing reactions of VER were plotted agains temperature and it is apparent from Fig. 9, that the Arrhenius Law is obeyed.

Thermogravimetric studies

The plots of weight loss against the temperature obtained from the thermograms at a programme

Fig. 8. Plot between $\log \beta$ (program rate) and reciprocal of peak temperature. 1, Methyl acrylate; $y = 13.7124 - 4.8065x$ ($r = 0.9996$); 2, ethyl acrylate, $y = 11.4576 - 3.9141x$ ($r = 0.9951$); 3, butyl acrylate, $y = 13.8054 - 4.8673x$ ($r = 0.9999$).
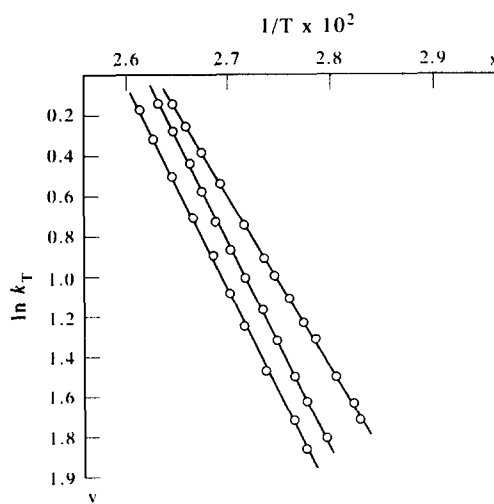

Fig. 9. Plot between k_T and reciprocal of temperature for VER sample containing: 1, methyl acrylate; 2, ethyl acrylate; 3, butyl acrylate.
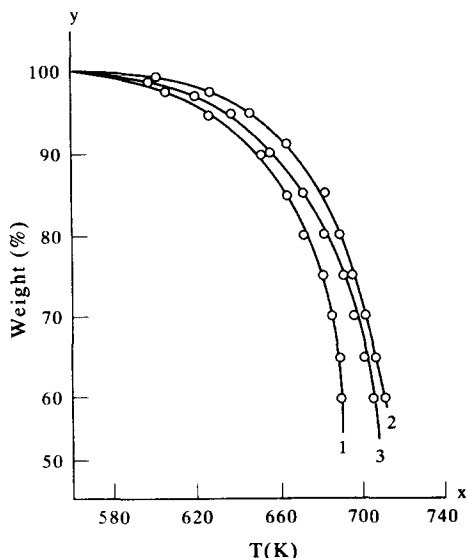
Fig. 10. Plot between weight (%) and temperature for VER containing: 1, methyl acrylate, 2, ethyl acrylate; 3, butyl acrylate.
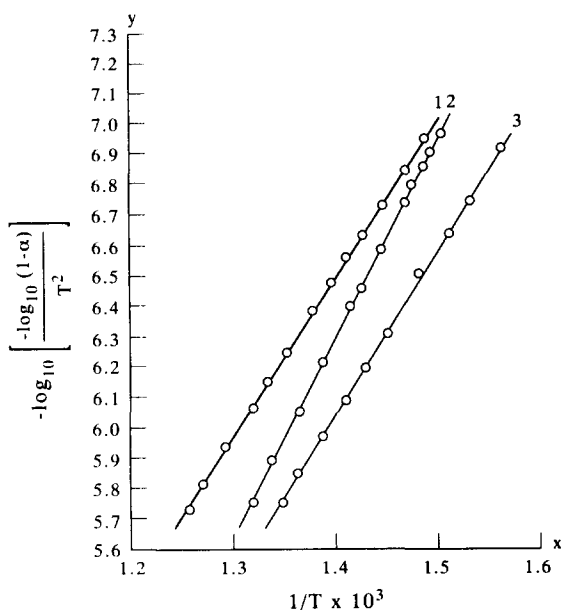
rate of $10°$ min^{-1}, of cured VER samples are given in Fig. 10. From the temperatures for a particular degree of weight loss it is apparent that the thermal stability of the VER sample containing ethyl acrylate was highest. The kinetic parameters of the decomposition reaction of the samples were calculated using the method of Coats and Redfern [14]. Figure 11 shows the plot between

$$-\log_{10}\left|\frac{-\log_{10}(1-\alpha)}{T^2}\right|$$

and reciprocal of decomposition temperature T, where α is the fraction of the sample decomposed at T. The slope of the plot obtained by regression analysis was used to calculate the activation energy. The values of activation energy for the decomposition reaction of VER samples containing methyl-, ethyl- and butyl acrylates are 24.18, 32.27 and 25.07 kcal/mol, respectively. This indicates that VER containing ethyl acrylate as reactive diluent gave a more thermally stable product than other acrylates probably due to its more reactivity towards VER during cure.

Fig. 11. Plot between $-\log_{10}|(-\log_{10}(1-\alpha))/T^2|$ and reciprocal of decomposition temperature from TGA data. 1, methyl acrylate, $y = -0.8585 + 5.2517x$ ($r = 0.9971$); 2, ethyl acrylate, $y = -3.5521 \pm 7.0061x$ ($r = 0.9930$); 3, butyl acrylate, $y = -1.5821 + 5.4448x$ ($r = 0.9870$).

REFERENCES

1. A. M. Clayton and H. A. Howey. 20th ANTEC, SPI, February (1965).
2. E. Takeyama and S. Hokamura 26th ANTEC, SPI, Sect. 29-B (1971).
3. M. B. Launkitis. In Handbook of Composites, (edited by G. Luben), p. 38. Van Nostrand, Reinhold Co., New York (1982).
4. R. Kay. In Fibre Composite Hybrid Materials (edited by N. L. Hancox), p. 142. Applied Science Publishers Ltd, London (1981).
5. C. D. Han and K. W. Lem. J. Appl. Polym. Sci. 29, 1879 (1984).
6. C. D. Han and K. W. Lem. Polym. Engng Sci. 24, 175 (1984).
7. R. Bhatnagar and I. K. Varma. J. Therm. Anal. 35, 1241 (1989).
8. Krishna Kant, A. Mishra and J. S. P. Rai. Polym. Int. 28, 189 (1992).
9. B. Gaur and J. S. P. Rai. Polymer 33, 4210 (1992).
10. C. G. Overberger and N. Yammato. J. Polym. Sci. 4, 3101 (1966).
11. D. W. Knoll, D. H. Nelson and P. W. Kehres. Am. Chem. Soc. Symp. 134th meeting (1958).
12. T. Ozawa. J. Therm. Anal. 9, 217, 369 (1976).
13. H. E. Kissinger. Anal. Chem. 29, 1702 (1957).
14. A. W. Coats and J. P. Redfern. Nature 68, 201 (1964).
15. N. Casson. In Rheology of Disperse Systems (edited by C. C. Mill), p. 84. Pergamon Press, Oxford (1959).