



CURING AND DECOMPOSITION BEHAVIOUR OF VINYL ESTER RESINS IN PRESENCE OF METHYL METHACRYLATE

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Abstract

Vinyl ester resins V₁, V₂ and V₃ of acid value (5 mg KOH/g solid) were synthesized using bisphenol-A epoxy and acrylic acid in presence of triethyl-, tripropyl- and tributyl-, amines, respectively. The synthesized resins were characterized by FTIR spectroscopy and amines were found to be attached to the resin structure by a hydrogen bond. The curing behaviour of synthesized resin containing 40 % methyl methacrylate (w/w) and 2 % benzoyl peroxide was studied using DSC and found to be affected by the presence of amines. Amines played dual role during the curing, it acted as an accelerator as well as chain transfer agent. The kinetic parameters for the curing reactions were determined using Ozawa's method. The energy of activation and frequency factor for V₁ to V₃ increases from 16 - 21 kcal mol⁻¹ and 2.16 x 10⁹- 5.01 x 10¹¹ min⁻¹, respectively. The curing reactions followed first order kinetics and obeyed the Arrhenius rate expression. The decomposition behaviour of all the samples were studied using TGA at 10°C min⁻¹. The TG and DTG thermograms show single step degradation. The energy of activation and frequency factor for the degradation were determined using Coats and Redfern method.

Keywords: Methyl methacrylate, TGA.

INTRODUCTION

Acrylate terminated vinyl ester resin (VER) contains terminal unsaturation which makes them highly reactive [1-2] and preferred in various industrial applications where rapid curing is a necessity viz surface coatings, varnishes, printed circuit board coatings, radiation curable inks, laminates, electrical insulation, flame retardant and optical discs, etc. [3-10]. Although vinyl esters are capable of homopolymerization, yet they are more commonly diluted with vinyl monomers to provide a fully reactive system with appropriate reactivity and viscosity along with the reduction in cost [11,12]. Curing of vinyl esters is a process of free radical copolymerisation between the unsaturation of monomer and vinyl ester molecule. The reactivity of monomers to vinyl esters affect the rate of curing and therefore the curing behaviour is expected to vary with the nature of monomers. An understanding of cure is needed to establish relationship between processing and properties of these resins. The cure kinetics of VERs and its thermal stability and mechanical properties have been studied by several investigators [13-16]. Most of these studies have primarily been aimed at characterising the kinetics of the curing reactions in presence of styrene [17-18], substituted styrene and acrylates [19-20], yet the effect of catalyst used during the synthesis has rarely been discussed. In our earlier communication the esterification of epoxy with acrylic acid using tertiary amines as catalyst and its effect on the cure kinetics in presence of styrene as reactive diluent has been reported [21]. The present paper deals with the role of amines on the cure and decomposition behaviour of vinyl ester resins in presence of methyl methacrylate.

EXPERIMENTAL

Bisphenol-A epoxy resin (EPG-180; SIP Resins, Madras), acrylic acid (Fluka, Switzerland), triethyl amine and tributyl amine (SD's, Bomby), tripropyl amine (J.T. Baker, England), benzoyl peroxide (SD's, Bombay) and reagent grade methyl methacrylate [MMA] (SD's, Bombay) after purifying by standard procedure were used in the present study [22]. Vinyl ester resins were prepared using 1 : 0.9 mole ratio of bisphenol-A epoxy (epoxide equivalent weight : 185) determined by pyridinium chloride method [23] and acrylic acid in presence of triethyl-, tripropyl- and tributyl-, amines as catalyst (1 phr by weight of the epoxy resin). The reaction was carried out at 85° ± 2°C till the VER of desired acid value (5 mg KOH g⁻¹ solid) determined by the method of Ogg et al. [24] is obtained. The progress of the reaction was monitored by determining the acid number of the reaction mass at every 30 minutes. The extent of reaction and number average degree of polymerisation was calculated by using Carother's equation. The light coloured transparent VERs thus prepared were cooled and stored in refrigerator operating at 10°C to prevent further reactions. A Nicolet 400D Spectrophotometer was used to obtain the Fourier Transform Infrared Spectra of resins. The samples for curing studies were prepared using 10 : 4 : 0.2 (w/w) of resin, MMA and benzoyl peroxide, respectively. Half of the amount of MMA was mixed with the resin and other half with the benzoyl peroxide in separate flasks at room temperature. The flasks were then sealed and kept under refrigeration to avoid premature polymerisation and evaporation of monomer prior to use. The equal amounts of the solution were taken in a small glass vial and stirred properly with a glass rod at 35 ± 1°C. A Thermal Analyst 2000 (TA Instrument) equipped with 2910 Differential Scanning Calorimeter was used to study the curing behavior of

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resins. Scans were obtained under dynamic conditions with programme rates of 2⁰, 5⁰, 10⁰, 15⁰, and 20⁰Cmin⁻¹ from 40⁰C to the temperature at which the exothermic reactions were complete. From the DSC scans the activation energy E (within ± 3% accuracy) was calculated by the Ozawa method [25], which assumes that the extent of reaction at the peak exotherm temperature is constant and independent of the programme rate:

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

where, R is the constant, β is the programme rate and T is the peak temperature. Further refinements of the values were carried out by iteration until two successive values were almost identical.

The frequency factor Z was calculated using Kissinger's equation [26]

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

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

$$K_T = Z e^{-E/RT}$$

From the dynamic DSC scan obtained at 5⁰C min⁻¹ a temperature was selected at which an appreciable rate of curing could be observed. The curing temperature (90⁰ ± 2⁰C) thus determined was used to cure the resin samples in an air circulating oven for 1 hour. After cooling, the cured samples were taken for subsequent studies on thermal stability. Thermal Analyst 2000(TA Instruments) equipped with 2950 thermal gravimetric analyser was used to study the decomposition behaviour of cured vinyl ester resins. TG analysis were performed under nitrogen atmosphere from 50⁰-700⁰C at the heating rate of 10⁰C min⁻¹. The relative thermal stability of a resin sample was quantitatively estimated by comparing the temperature for a particular degree of weight loss. The values of activation energy (E) and pre-exponential factor (Z) were determined by Coats and Redfern equation [27] as given below:

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

Where,

$$g(\alpha) = \begin{cases} \frac{1 - (1 - \alpha)^{1-n}}{1-n} & \text{for } n \neq 1 \\ -\log_{10} \{-\log_{10} (1 - \alpha)\} & \text{for } n = 1 \end{cases}$$

$$\alpha = \frac{W_T - W_f}{W_0 - W_f}$$

Where

- α = Fractional weight loss
 W_T = Weight at temperature T
 W_f = Final weight

W₀ = Initial weight

R = Gas constant

Equation (1) can be reduced to

$$Y = A + \frac{B}{100} X$$

Where,

$$Y = \log_{10} \left(\frac{g(\alpha)}{T^2} \right) \text{ for different values of } n \text{ lying between } 0 \text{ and } 2.0$$

$$X = \frac{1000}{T}$$

$$A = \log_{10} \left\{ \frac{ZR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right\}$$

$$B = \frac{-E}{2.3R}$$

Best fit techniques was used to calculate the value of order of reaction (n) which is further confirmed by regression analysis. The validity of the data was checked by t- test analysis [28]. If the calculated value of 't' ≥ Table value of 't' the data are significant.

RESULTS AND DISCUSSION

Vinyl ester resins V₁, V₂ and V₃ of ~ 5 acid value were synthesized in presence of triethyl-, tripropyl- and tributyl-, amines, respectively. The resins were characterized by FTIR spectroscopy and their spectra has been discussed in our earlier communication [23]. FTIR spectra of VERs (V₁, V₂ and V₃) mixed with MMA and benzoyl peroxide were recorded and are shown in Fig 1.

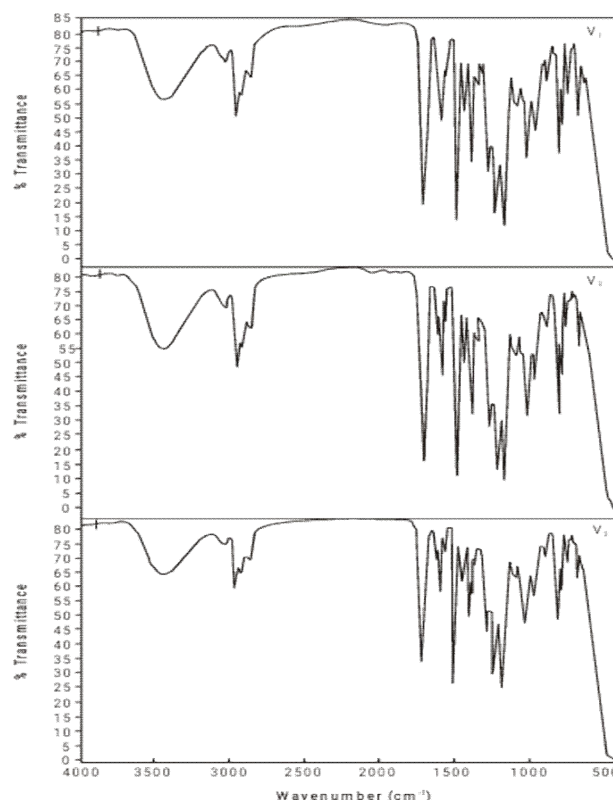
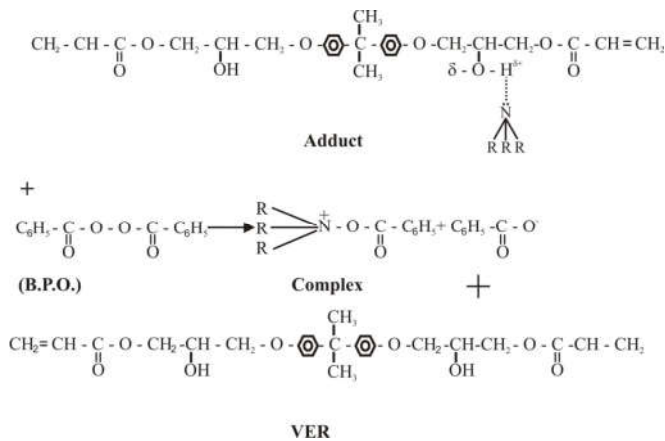


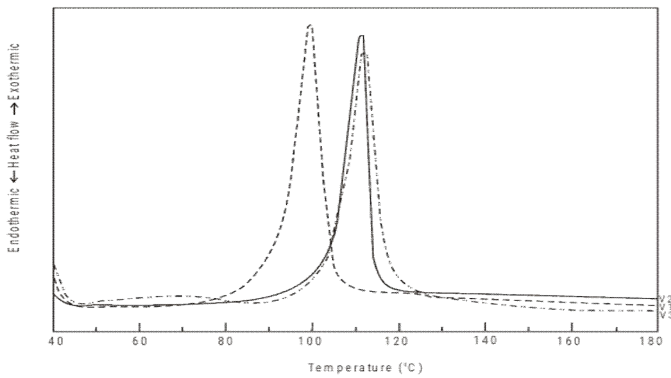
Fig. 1

It is clear from the figure that the peak at 2360 cm^{-1} found in V_1 , V_2 and V_3 dues to formation of adduct between hydroxyl group of vinyl ester and tertiary amine has disappeared which indicates the dissociation of the adduct, as given below.



Curing behaviour

Typical dynamic DSC scans for the curing of V_1 , V_2 and V_3 resins mixed with 40% methyl methacrylate and 2% benzoyl peroxide as initiator at 10°Cmin^{-1} are given in Figure 2.



The figure shows that the exothermic curves are in the range 70° to 150°C with peaks at 99.62° , 109.50° and 113.60°C for V_1 , V_2 and V_3 respectively. The thermograms show that the rate of curing reaction is sluggish in the early stages of the reaction where it is comparatively faster in the later stages. From these DSC scans the onset temperature of curing (T_0), the exothermic peak position (T_p) and final temperature of curing (T_f) were noted down and are summarized in Table 1.

Table 1. Curing behavior of vinyl ester resins containing 40% MMA and 2% benzoyl peroxide at heating rate $10^\circ\text{C}/\text{min}$

Sample Name	T_0 ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	Activation Energy Kcal mol^{-1}	Frequency Factor min^{-1}
V_1	72.91	99.62	147.2	16.33	2.16×10^9
V_2	84.62	109.5	150.52	20.47	3.39×10^{11}
V_3	88.41	113.6	150.2	21	5.01×10^{11}

T_0 : Temperature of onset of exotherm

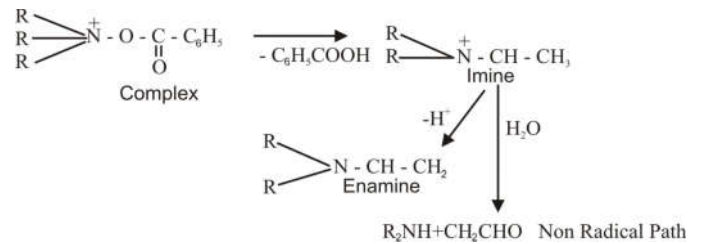
T_p : Temperature of peak

T_f : Temperature of completion of exotherm

It was observed that T_0 and T_p is increasing from V_1 to V_2 whereas T_f remained almost same for all the sample. The DSC scans at 2° , 5° , 15° and $20^\circ\text{C min}^{-1}$ also showed a similar trend. It indicates that the resins prepared in presence of different amines show variation in their curing behaviour. The amines form a complex with benzoyl peroxide which lower its

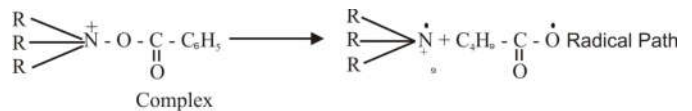
decomposition temperature during the cure and accelerates the reaction [29]. It can be observed from Table 1 that T_0 and T_p for V_1 is lower than V_2 and V_3 , while T_f is almost same which shows that V_1 requires more time for the completion of cure. This may be attributed to higher reactivity of triethylamine towards benzoyl peroxide than tripropyl and tributyl amines. The result reveals that the rate of reaction of amines with peroxide decreases with the increase in the size of alkyl substituent. The higher time required for the completion of cure of V_1 can be explained on the basis of dissociation of complex formed during the curing reactions. The complex can be dissociate by two different routes as shown below.

Possible complex dissociation in presence of triethyl amine:



Where $R - C_2H_5$,

Possible complex dissociation in presence of tributyl amine:



Where $R - C_4H_9$

It is apparent from the above scheme that complex dissociation by radical path is favoured in presence of higher amines in comparison to simpler amines [30]. This is because of +I effect of alkyl groups which increases in order $C_2H_5 < C_3H_7 < C_4H_9$. Higher +I effect decreases the reactivity of methylene group so the abstraction of hydrogen as cation is difficult. This can be inferred that radical path with tributylamine is preferred over non radical path with triethylamine. It is clear from the Figure 2 that curing of VER in presence of MMA is sluggish in the initial stages which is different than that reported with styrene [23]. The difference in the nature of exotherms containing styrene and MMA may be due to their polar characteristics. The growing methyl methacrylate chains, being electron acceptor in nature, abstract hydrogen as free radicals from the tertiary amines and get terminated. This chain transfer reaction gives tertiary amine free radical which can further terminate the another chain [31-32]. It is observed that the reactions of amines in presence of MMA may be the reason for its delayed curing with vinyl ester in the initial stages whereas the effect of similar reactions are difficult in the later stages of reaction. Using the Ozawa method, $\log \beta$ (programme rate) was plotted against the reciprocal of the peak temperature (Figure 3) and from the slope obtained by regression analysis, the activation energy of curing reactions was calculated for samples V_1 , V_2 and V_3 . The values of E and Z are given in Table 1. It is apparent from the table that E and Z values are increasing from V_1 to V_3 which again confirms that the resin prepared in presence of triethyl amine as catalyst is more reactive than others during the curing reactions. The value of Z for a particular VER at different programme rates varies over a narrow range which suggests that the curing reactions are of

first order. The specific rate constant (K_T) was calculated for the curing reactions of V_1 , V_2 and V_3 and were plotted against the reciprocal of temperature (Figure 4). It is apparent from the figure that the Arrhenius's law is obeyed.

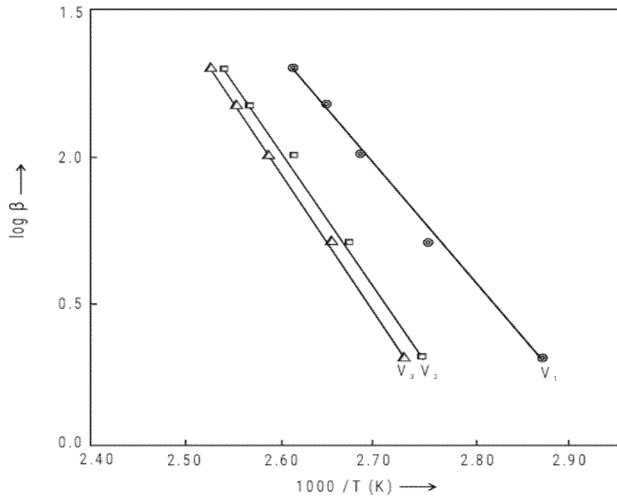


Fig. 3.

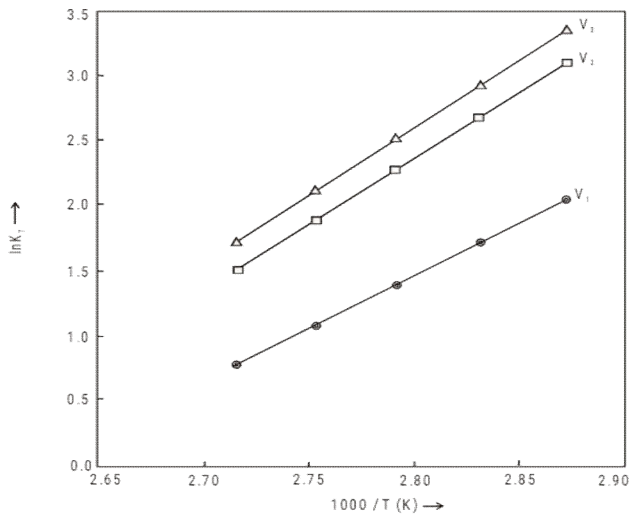


Fig. 4

Decomposition behaviour

The thermograms at $10^\circ\text{C min}^{-1}$ from 50°C to 700°C of cured vinyl ester resins V_1 , V_2 and V_3 containing methyl methacrylate (40% w/w) are shown in Figures 5-7.

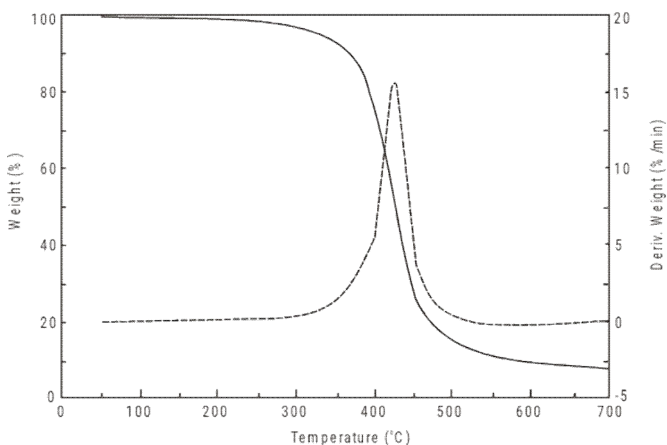


Fig. 5.

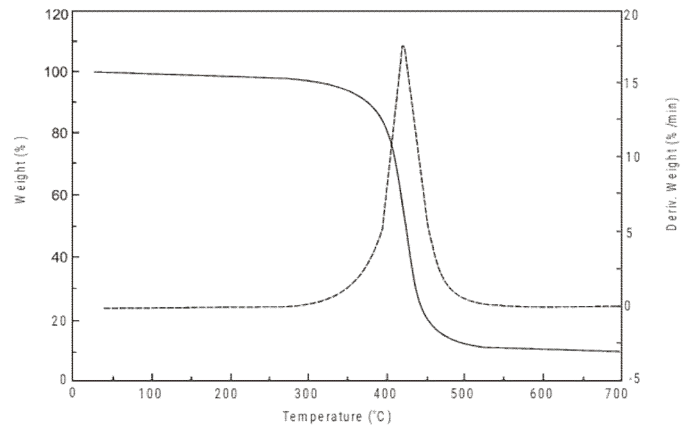


Fig. 6.

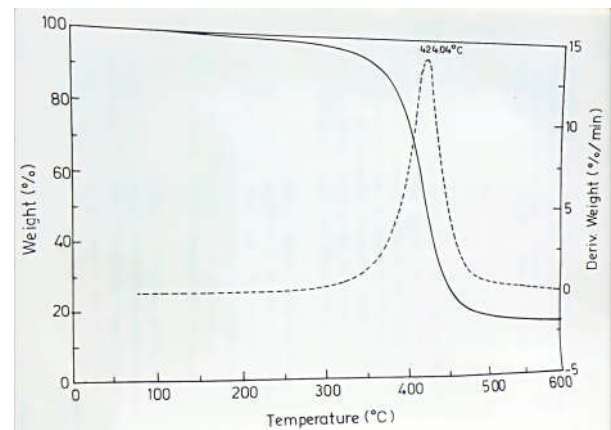


Fig. 7.

It is apparent from the thermograms that the degradation of all the samples consists of single step and were stable upto $\sim 300^\circ\text{C}$. The decomposition was rapid and almost 93-88% volatilization of the samples occurred between 350°C - 500°C . However, initial loss of mass about 2-5% was observed above 90°C , which may be due to volatilisation of residual methylmethacrylate and other by-products produced during cure. DTG curves are also showing only one sharp maxima at 427.02°C , 422.80°C and 424.04°C for the cured V_1 , V_2 and V_3 . The thermal stability of the cured samples was determined by comparing the onset (T_i), peak (T_{max}), final temperature of peak (T_f) and char yield at 700°C . The results of these thermal studies are summarized in Table 2. It is clear from the table that there is no significant difference in these temperatures for V_1 , V_2 and V_3 . The char yield at 700°C was found to be the maximum in case of V_3 indicating that it is thermally more stable than V_1 and V_2 . The area under the DTG curve which is proportional to the total change in weight was found to be 74.80%, 72.18 %, 69.66% for V_1 , V_2 and V_3 respectively. The relative thermal stability of vinyl ester resins were also studied by comparing the temperatures of 1 to 10% weight loss and the data are given in Table 3. The difference in the decomposition temperature up to 5% degradation is significant, which descends and after 10% degradation, it becomes almost same for all the resins. From the temperature for a particular degree of weight loss, it is apparent that the thermal stability of V_3 , prepared using tributylamine as catalyst, was higher than V_1 and V_2 . Higher thermal stability of V_3 can be attributed to the steric hindrance and high + I effect of butyl group. The large size of butyl group causes the formation of TBA and BPO complex comparatively difficult and High + I effect of butyl group promotes dissociation of the complex by radical path explained earlier in the curing studies.

Table 2. Thermal behavior of vinyl ester resins V1, V2 and V3 containing MMA 40% w/w at 10⁰C/min (Cured at 90⁰C for 1 hr)

Sample	T _i (°C)	T _{max} (°C)	T _f (°C)	Area (%)	Char Yield 700°C (%)	Activation Energy(kcalmol ⁻¹)	Frequency Factor (min ⁻¹)
V ₁	303.01	427.02	504.32	74.8	7.13	26.68	31.43 x10 ¹³
V ₂	305.17	422.8	507.56	72.18	9.74	26.9	38.43 x 10 ¹³
V ₃	306.2	424.04	506.84	69.66	12.6	28.27	12.52 x 10 ¹⁴

T_i : Initial temperature of decomposition
 T_{max} : Peak temperature of decomposition
 T_f : final temperature of decomposition

Table 2. Temperature of 1-10% weight loss in thermo gravimetric analysis of V1, V2 and V3 containing MMA 10% w/w at 10⁰C/min (Cured at 90⁰C for 1 hr)

Weight Loss	Temperature (K)		
	V ₁	V ₂	V ₃
1	411	430	437
2	431	470	501
3	474	541	553
4	537	575	584
5	576	598	607
6	593	611	617
7	610	618	624
8	618	623	630
9	627	631	635
10	630	638	645

Table - 4 : Statistical Data for Vinyl Ester Resins in presence of MMA

Sample Name	Reaction Order (n)	Correlation Coefficient (r)	Degree of Freedom	Standard Error of Y Coefficient	Standard Error of X Coefficient	Regression Equation	t _{calculated}	t _{table}
V ₁	0	0.9726	16	0.0834	0.2342	Y = -3.9172x + 5.2724	4.15	2.12
	1/2	0.9854	16	0.0721	0.2022	Y = -4.6826x + 6.4682	4.87	2.12
	2/3	0.9882	16	0.0691	0.1939	Y = -5.0120x + 6.9790	5.1	2.12
	1	0.9874	16	0.0831	0.2331	Y = -5.8246x + 7.8692	4.24	2.12
	2	0.2894	16	0.4807	1.3483	Y = 1.6312x - 3.2532	0.21	2.12
V ₂	0	0.969	16	0.0884	0.25	Y = -3.9253x + 5.2982	3.88	2.12
	1/2	0.9841	16	0.0752	0.2126	Y = -4.7191x + 6.5389	4.63	2.12
	2/3	0.9879	16	0.0701	0.1983	Y = -5.0561x + 7.0618	4.98	2.12
	1	0.9906	16	0.0716	0.2026	Y = -5.8684x + 7.9539	4.89	2.12
	2	0.3152	16	0.4101	1.1592	Y = 1.5401x - 3.1183	0.27	2.12
V ₃	0	0.9625	15	0.0966	0.2946	Y = -4.0489x + 5.5107	3.26	2.12
	1/2	0.9792	15	0.0857	0.2613	Y = -4.8981x + 6.8389	3.75	2.12
	2/3	0.9841	15	0.0804	0.2454	Y = -5.2663x + 7.4104	4.01	2.12
	1	0.989	15	0.078	0.2379	Y = -6.1730x + 8.4479	4.15	2.12
	2	0.378	15	0.4415	1.3463	Y = 2.1296x - 3.9997	0.28	2.12

This reduces the possibilities of formation of byproducts during cure, which volatilises as the temperature is raised in the decomposition. Tertiary amines as a chain transfer reagent also affect the decomposition of resins. As a chain transfer reagent tributyl amine is more reactive, again due to + I effect (high + I effect facilitates the abstraction of hydrogen as a free radical). This reduces crosslink density of V₃ resin the most. Similar reactions are not possible in the later stages of curing so V₃ is most stable.

Conclusion

The kinetic parameters viz order of reaction (n), energy of activation (E) and frequency factor (Z) of degradation reactions were obtained using Coats and Redfern equation. For different values of n (0, 1/2, 2/3, 1 and 2), graphs were plotted between X and Y. The value of n = 1 gave the best fit with highly significant correlation coefficients 0.987, 0.991, and 0.989 for V₁, V₂, and V₃, respectively. The data (Table 4) are

significant up to 95% level of significance as the calculated value of 't' is more than that of table value of 't' for all values of n. The values of E and Z were calculated from the slope and intercept of the plot and given in Table 2. It is apparent from the table that the activation energy is highest for V₃.

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