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CURING AND RHEOLOGICAL BEHAVIOR OF VINYL ESTER RESINS PREPARED IN THE PRESENCE OF TERTIARY AMINES

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Key Words: Vinyl Ester Resin, Styrene, Tertiary Amine, Cure Kinetics, Rheological Behavior

ABSTRACT

Vinyl ester resins V_1, V_2 & V_3 of acid value (~6 mg KOH g^{-1} solid) were synthesized using bisphenol-A epoxy and acrylic acid in the presence of triethyl-, tripropyl- and tributyl-, amines in 210, 270 and 340 minutes, respectively. The synthesized resins were characterized by FTIR spectroscopy and a new peak at 2360 cm^{-1} was observed which is due to attachment of amines to resin structure by hydrogen bond. The curing behavior of synthesized resin containing 40% styrene (w/w) and 2% benzoyl peroxide was studied using DSC technique and found to be affected by presence of amines. Activation energy and frequency factor for the curing reaction increases from 14 Kcal mol^{-1} to 23 Kcal mol^{-1}. Rheological behavior of resins containing 40% styrene was studied using a Haake Rotovisco RV20 viscometer, and viscosity was found to increase with shear rate up to 200 sec^{-1}. The average values of activation energy at constant shear stress (6-15 Pa) were 12.94, 13.20, 13.70 Kcal mol^{-1} for V_1, V_2 and V_3, respectively. The activation energy at constant shear rate decreases with an increase in the shear rate.

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INTRODUCTION

Acrylate terminated vinyl ester resin (VER) has become increasingly important in various industrial applications such as surface coatings, varnishes, printed circuit board coatings, radiation curable inks, laminates, electrical insulation materials and optical discs, etc. These resins are prepared by endcapping the acrylic acid to epoxy resin backbone in the presence of a basic catalyst. The esterification of epoxy with acrylic acid in the presence of triethylamine, dimethyl benzylamine, quaternary ammonium salts, diethanol amine, etc. has been studied [1-3].

Esterification produces a multifunctional VER depending upon the number of available epoxy groups in the main chain. Therefore, VER yield highly crosslinked structures having high strength and good chemical resistance. These resins may be used in the neat form or may contain reactive diluents [4]. The investigation of rheological behavior of these resins, especially the dependence on the reactive diluent, temperature, shear rate, and shear stress becomes a prerequisite for understanding 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. The processing of these resins require the understanding of its cure kinetics for better control on the rate of heat generation and temperature variation. The cure kinetics of VER based on bisphenol-A epoxy synthesized using triphenyl phosphine, imidazole and quaternary ammonium salts in the presence of styrene [5], α-methyl styrene [6] and acrylates [7] have been investigated.

In this paper, we report the cure and rheological behavior of VERs based on bisphenol-A epoxy as backbone and synthesized in the presence of triethyl-, tripropyl- and tributyl-, amines as catalyst. In most of the situations reported [8] so far, the catalyst is usually washed after synthesis of the resin, which is comparatively a difficult and costly process.

EXPERIMENTAL

Bisphenol-A epoxy resin (EPG-180; SIP Resins), acrylic acid (Fluka), triethyl amine and tributyl amine (SD's), tripropyl amine (J. T. Baker), Benzoyl Peroxide (SD's) and reagent grade monomers styrene and methyl methacrylate (SD's) were used in the present study.

Vinyl ester resins were prepared using 1:0.9 mole ratio of bisphenol-A epoxy (epoxide equivalent weight:190) determined by pyridinium chloride method [9] 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 90° ± 2°C till the VER of desired acid value (~6 mg KOH g^{-1} solid) determined by the method of Ogg *et al.* [10] 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 the reaction and number average degree of polymerization was calculated by using Carother's equation [11]. The light colored 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, styrene and benzoyl peroxide, respectively. Half the amount of styrene was mixed with the resin and the other half with the benzoyl peroxide in separate flasks at room temperature. The flasks were then sealed and kept under refrigeration to avoid premature polymerization and evaporation of monomer prior to use. Equal amounts of the solution were placed in a small glass vial and stirred properly with a glass rod at 35 ± 1°C. The samples for rheological measurements were prepared in one flask without benzoyl peroxide and were used for the rheological studies only after stirring for 30 minutes at 35 ± 1°C.

A Thermal Analyst 2000 (TA Instruments), equipped with 2910 Differential Scanning Calorimeter, was used to study the curing behavior of resins. Scans were obtained under dynamic conditions with program rates of 2°, 5°, 10°, 15° and 20°C min^{-1} from 40°C 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 [12] , which assumes that the extent of reaction at the peak exotherm temperature is constant and independent of the program rate:

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

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

The frequency factor Z was calculated using Kissinger's Equation [13]

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

The specific rate constant K^T was calculated using the Arrhenius equation:

$$K^T = Z\, e^{-E/RT}$$

A Haake Rotovisco RV20 coaxial cylinder viscometer with MV-2 sensor was selected to measure the solution viscosities of vinyl ester resins containing 40% styrene at 25°, 30°, 35° and 40°C. Viscosity data were obtained at shear rate ranging from 0.1 S^{-1} to 400 S^{-1}. A test sample was loaded and the sensor was accelerated to the maximum shear rate in 5 minutes and it was kept there constant for 5 minutes before the shear stress values were recorded.

The energy of activation for viscous flow at constant shear stress (E_τ) and constant shear rate (E_D) was calculated using the Arrhenius equation.

$$\eta = Ae^{(E/RT)}$$

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

RESULTS AND DISCUSSION

Vinyl ester resins V_1, V_2 and V_3 of ~ 6 acid value were synthesized in the presence of triethyl-, tripropyl- and tributyl -, amines, respectively. Figure 1 shows the results of the esterification of bisphenol-A epoxy with acrylic acid catalyzed by amines. The results are typical of the behavior generally observed for polyesterification reactions. It is apparent from the plot that acid value decreases up to desired level in 210, 270 and 340 minutes for V_1, V_2 and V_3, respectively. The increase in reaction time for a particular acid value of the resin increases with an increase in the size of the substituent in amine which decreased their reactivity towards the esterification reaction. It is also clear from the plots that the decrease in acid value in the initial stages of the reaction is not linear. This is due to a 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 (>75%), reveals that the functional group reactivity is independent of molecular size, which is a characteristic of the esterification reaction.

The number average degree of polymerization (X_n) of samples V_1, V_2 and V_3 calculated using Carother's equation was found to increase with time and the values are given in Table 1. At a particular time X_n of V_1 was found to be more than that of V_2 and V_3. In all samples, the plot between X_n versus t showed non linearity in the initial stages (<50% conversion) and in higher con-version region (>83%), which is again a characteristic of the catalyzed esterification reactions.

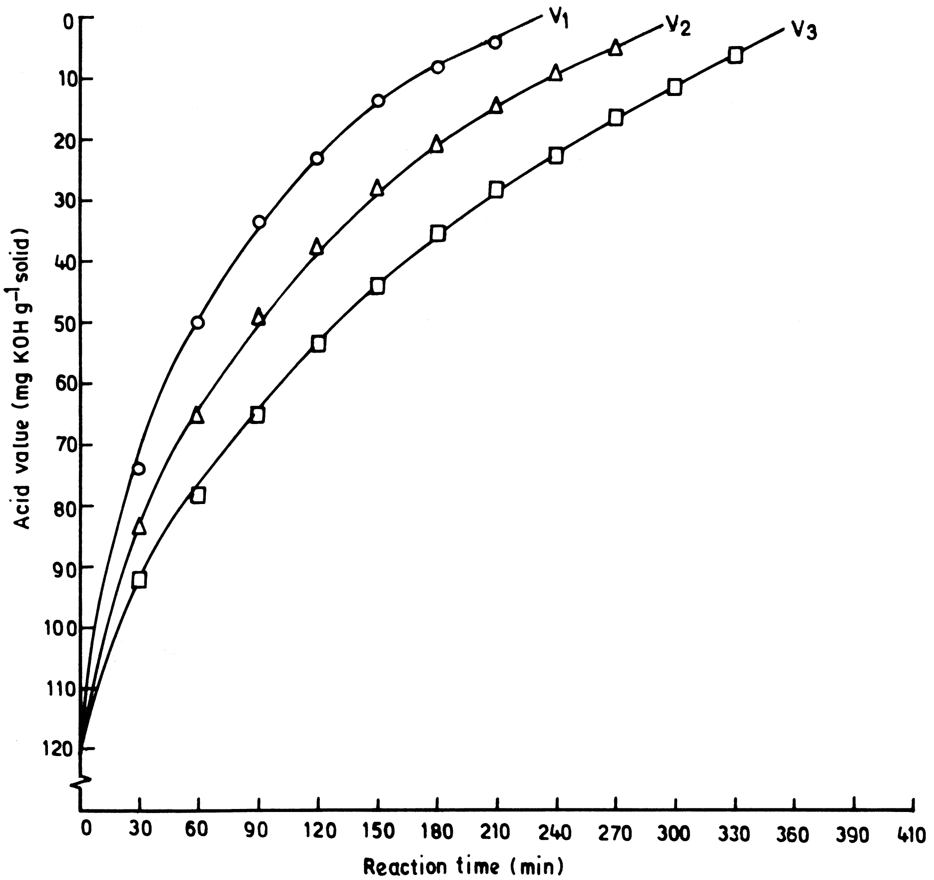


Figure 1. Acid value versus reaction time for vinyl ester resins prepared in the presence of triethyl amine-V_1, tripropyl amine-V_2, tributyl amine-V_3.

TABLE 1. Extent of Reaction and Degree of Polymerization with Time for Vinyl Ester Resins

Reaction time (min.)	V_1		V_2		V_3	
	Extent of reaction (p)	Degree of polymerization (x_n)	Extent of reaction (p)	Degree of polymerization (x_n)	Extent of reaction (p)	Degree of polymerization (x_n)
30	0.38	1.56	0.30	1.39	0.23	1.27
60	0.59	2.26	0.45	1.74	0.35	1.49
90	0.72	3.14	0.58	2.20	0.46	1.77
120	0.82	4.48	0.68	2.80	0.56	2.13
150	0.88	6.00	0.77	3.50	0.63	2.48
180	0.92	7.78	0.82	4.48	0.71	3.05
210	0.95	10.00	0.88	6.00	0.77	3.69
240	–	–	0.92	7.78	0.82	4.48
270	–	–	0.95	10.00	0.87	5.39
300	–	–	–	–	0.91	6.78
330	–	–	–	–	0.94	8.40
340	–	–	–	–	0.95	10.00

The samples V_1, V_2 and V_3 prepared in the presence of amines were found to be colorless and transparent, whereas an amber color of the resin was reported when prepared in the presence of triphenyl phosphine and imidazole [5, 6] as the catalyst of esterification reaction.

FTIR spectra of the prepared resin, V_1, V_2 and V_3 are shown in Figure 2. The band at 910 cm^{-1} associated with the oxirane ring of epoxy resin [14] is replaced by a band at 1729 cm^{-1}, 1740 cm^{-1}, 1736 cm^{-1} for V_1, V_2 and V_3, respectively which is due to the carboxyl group of the ester formed. In spectra of V_1, V_2 and V_3 another band was observed at 1608 cm^{-1}, 1610 cm^{-1}, and 1615 cm^{-1}, respectively which is attributed to the acryloyl double bond. These spectra were also matched with the standard I.R. spectra of epoxy acrylate [15] and found to be in close agreement up to 93%, which confirms to the formation of vinyl ester.

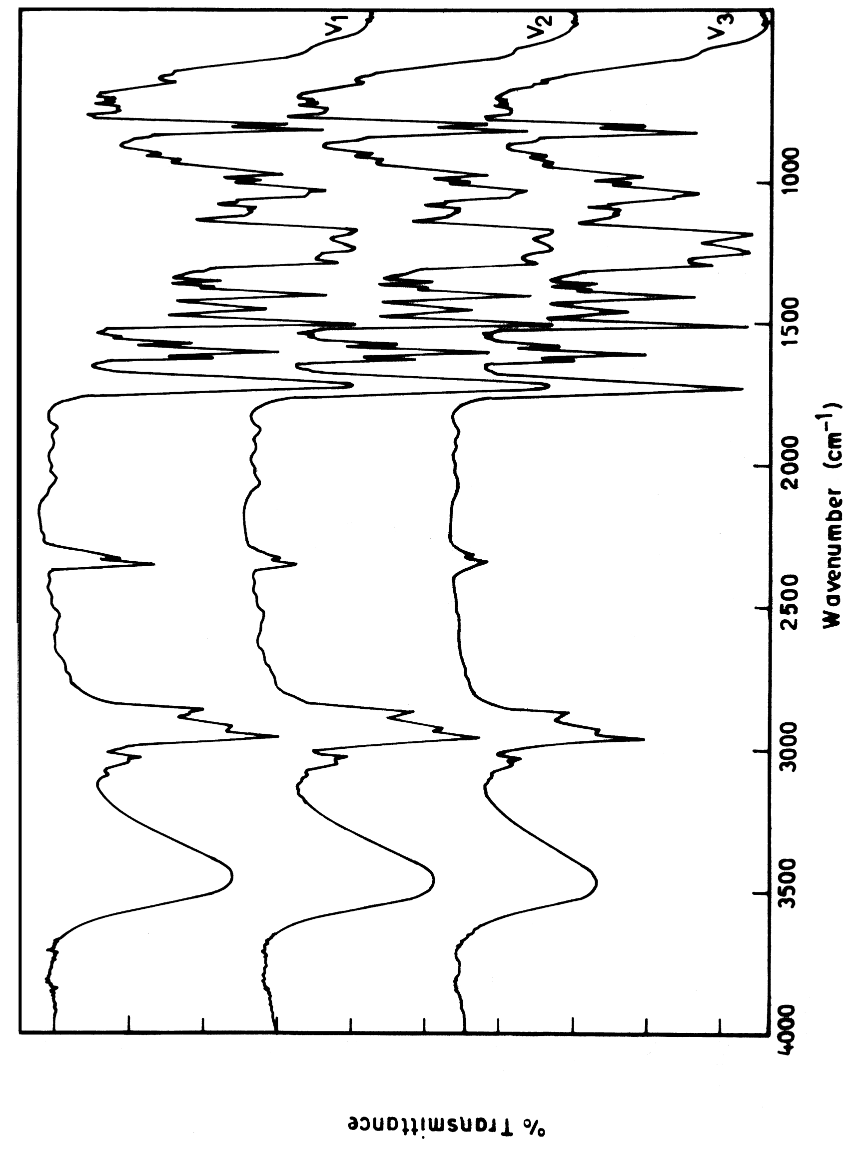
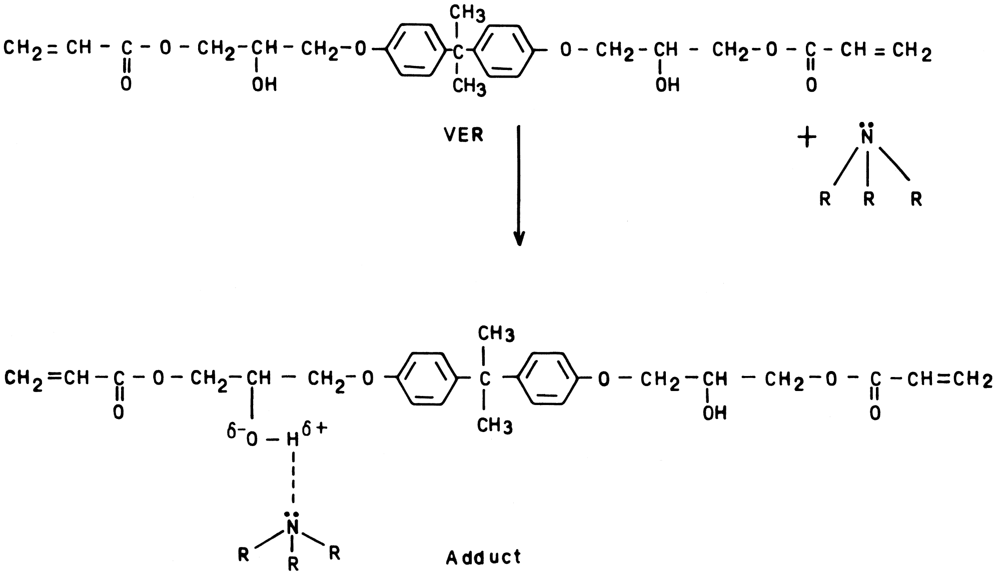


Figure 2. FTIR spectrum of vinyl ester resins.

Figure 2 also shows a new band at 2360 cm^{-1} in the spectra of all samples and does not match with the standard spectra [15]. This band could be attributed to the formation of adduct between nitrogen of amine containing a lone pair of electrons with the hydrogen of hydroxyl group present in VER [16, 17, 18]. The possible structure is given below:



The transmittance intensity of band at 2360 cm^{-1} is higher in spectra of V_1 than V_2 and V_3. This is probably due to steric effects caused by higher amine in V_2 and V_3.

Curing Studies

Typical dynamic DSC scans for the curing of V_1, V_2, and V_3 resins mixed with 40% styrene and 2% benxoyl peroxide as initiator when heated at 10°C min^{-1} are given in Figure 3. From these DSC scans, the onset temperature of curing (T_o), the exothermic peak position (T_p) and final temperature of curing (T_f) were noted, and are summarized in Table 2. It was observed that T_o and T_p is increasing from V_1 to V_3, whereas T_f remained almost the same for all samples. DSC scans at 2°, 5°, 15° and 20°C min^{-1} also showed a similar trend. This indicates that resins prepared in the presence of different amines show variation in their curing behavior. This is due to the nucleophilic nature of amines, which in the presence of benzoyl peroxide, forms a complex with it and acts as an accelerator

TABLE 2. Curing Behavior of Vinyl Ester Resins Containing 10% Styrene and 2% Benzoyl Peroxide at Heating Rate 10°C/Min.

Sample Name	T_o °C	T_p °C	T_f °C	ΔH Jg^{-1}	E Kcal mol^{-1}	Z min^{-1}
V_1	88.6	103.0	144.0	245.8	14.04	7.13×10^{7}
V_2	101.1	108.7	145.3	233.1	21.95	2.33×10^{12}
V_3	107.7	116.0	142.8	267.9	22.90	5.03×10^{12}

T_o : Temperature of onset of exotherm
T_p : Temperature of peak
T_f : Temperature of completion of exotherm
ΔH : Heat of reaction
E : Activation energy
Z : Frequency factor

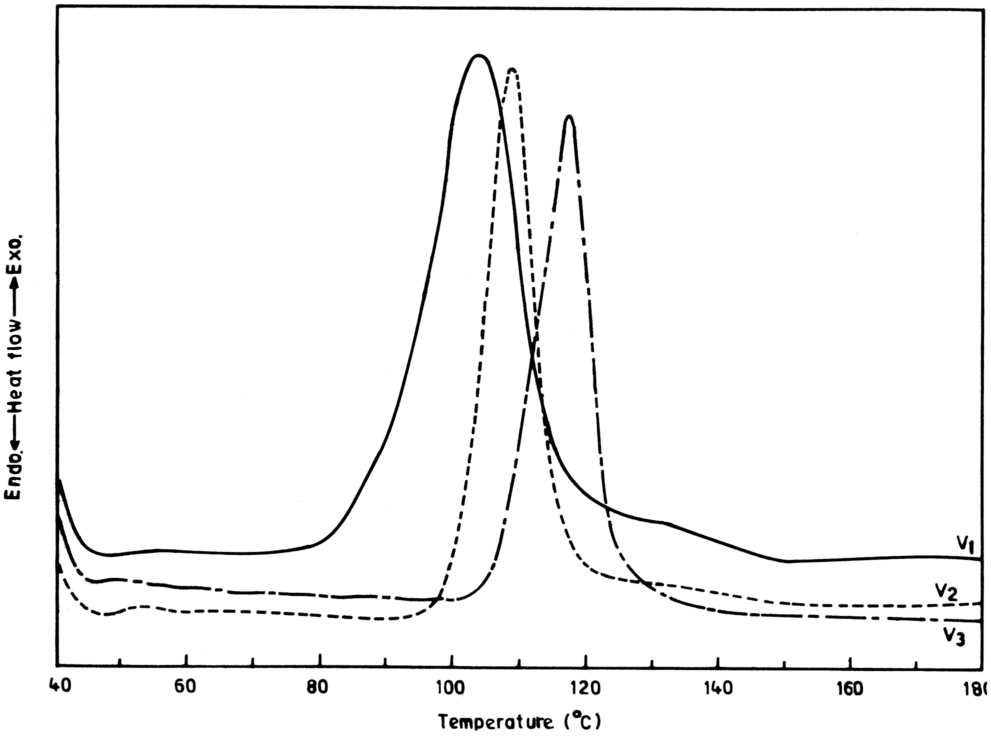
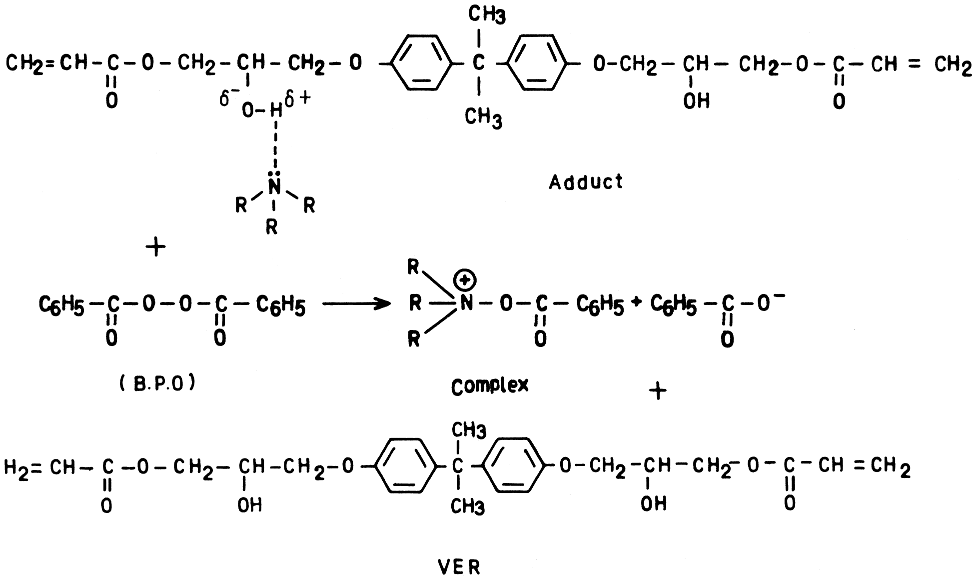


Figure 3. Dynamic D.S.C. scans for the curing of VER samples diluted with 40% styrene at 10°C min^{-1}.

for the curing reactions by lowering the decomposition temperature of benzoyl peroxide according to the mechanism proposed by [19, 20]. It is also clear from Figure 3 that T_o and T_p for V_1 is lower than V_2 and V_3, thus, V_1 requires more time for the completion of cure. This may be attributed to a higher reactivity of triethylamine towards benzoyl peroxide present in resin V_1 than tripropyl and tributyl amines in the resin V_2 and V_3. The result reveals that the rate of reaction of amines with peroxide depends on the steric accessibility of nitrogen atom present in the resin.

The higher time required for the completion of the cure of V_1 can be explained on the basis of dissociation of complex by non radical path formed during the curing reactions which is favored in the presence of simpler amines in comparison to higher amines [19, 20], where the loss of hydrogen as cation takes place without any difficulty. Heat of curing reactions for all samples was also calculated and reliable data was not obtained probably due to side reactions.

FTIR spectra of VERs (V_1, V_2, and V_3) freshly mixed with styrene and benzoyl peroxide and fully cured samples, were recorded and are shown in Figure 4. It was observed that the peak at 2360 cm^{-1} in neat VER (Figure 2) has disappeared. This is due to the dissociation of adduct formed between amine and resin in presence of benzoyl peroxide in the following manner:



Using the Ozawa method [12], log β (program rate) was plotted against the reciprocal of the peak temperature (Figure 5) and from the slope obtained by

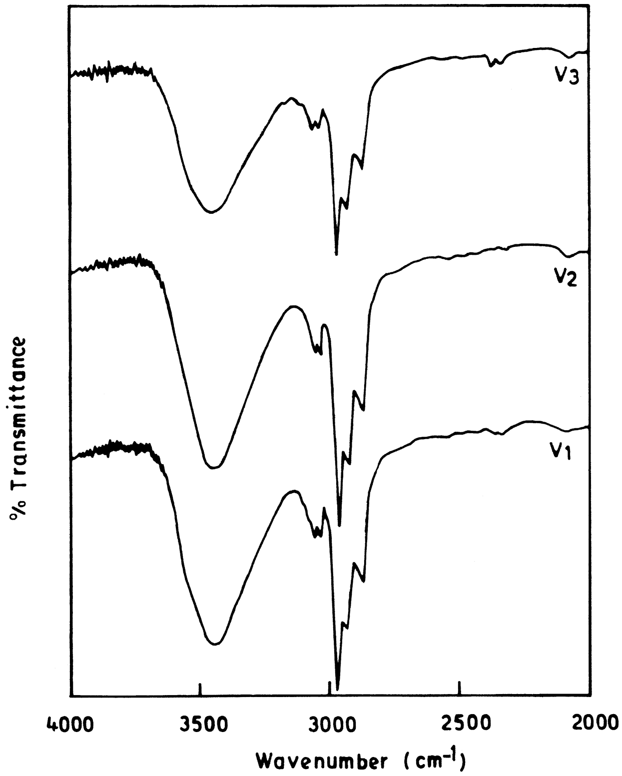


Figure 4. FTIR spectrum of vinyl ester resins mixed with 40% styrene and 2% benzoyl peroxide.

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 2. It is apparent from the table that E and Z values are increasing from V to V_3, which again confirms that the resin prepared in presence of triethyl amine as catalyst is more reactive than others during curing reactions. The value of Z for a particular VER at different program 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 curing reactions of V_1, V_2, and V_3 and were plotted against the reciprocal of temperature, shown in Figure 6. It is apparent from the figure that they obey the Arrhenius's law.

Rheological Studies

A plot between viscosity and shear rate for VER samples prepared in the presence of triethyl-, tripropyl- and tributyl-, amines at 25°C are given in Figure

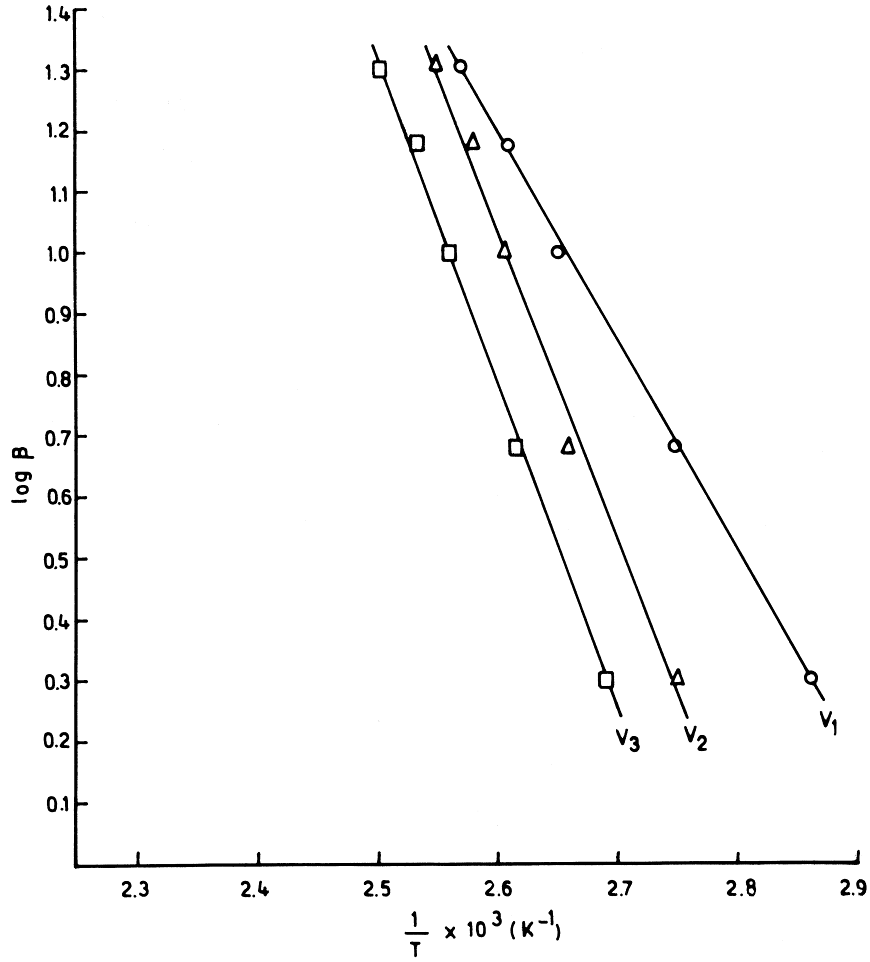


Figure 5. Plots of log β versus the reciprocal of the peak temperature to calculate the activation energy V_1, y = 9.9966 -3.3766 x, (r = 0.9992); V_2, y = 14.3437 -5.1134 x, (r = 0.9929); V_3, y = 14.6715 - 5.3416 x (r = 0.9989).

7. The figure shows that the viscosity of VER at any shear rate increases with the bulkier amine used as esterification catalyst in its synthesis. Similar behavior was observed at 30°, 35°, and 40°C. It is also apparent from the figure that the apparent viscosity of the samples increases up to the shear rate 200 sec^{-1} beyond which the viscosity remains almost constant. The increase in viscosity of all the samples is contrary to that reported by earlier workers in the field including the work reported by this laboratory [21]. In the present study, the VER was also prepared in the presence of triphenyl phosphine as catalyst under similar condi-

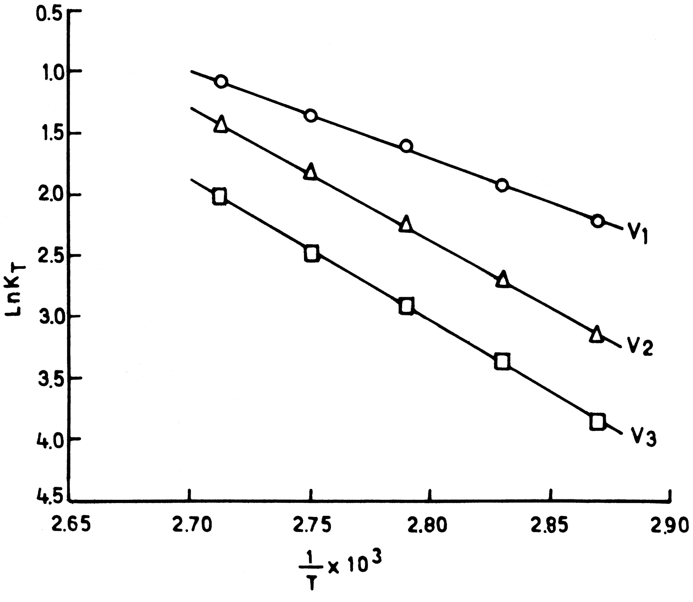


Figure 6. Plots of ln K_T versus the reciprocal of temperature.

tions as used for V_1, V_2, and V_3. The plot between viscosity and shear rate of the resin prepared in the presence of triphenyl phosphine is shown in Figure 8. It is apparent from the figure that viscosity decreases with the increase in shear rate. Thus, observed shear thickening behavior of V_1, V_2, and V_3 could be attributed to

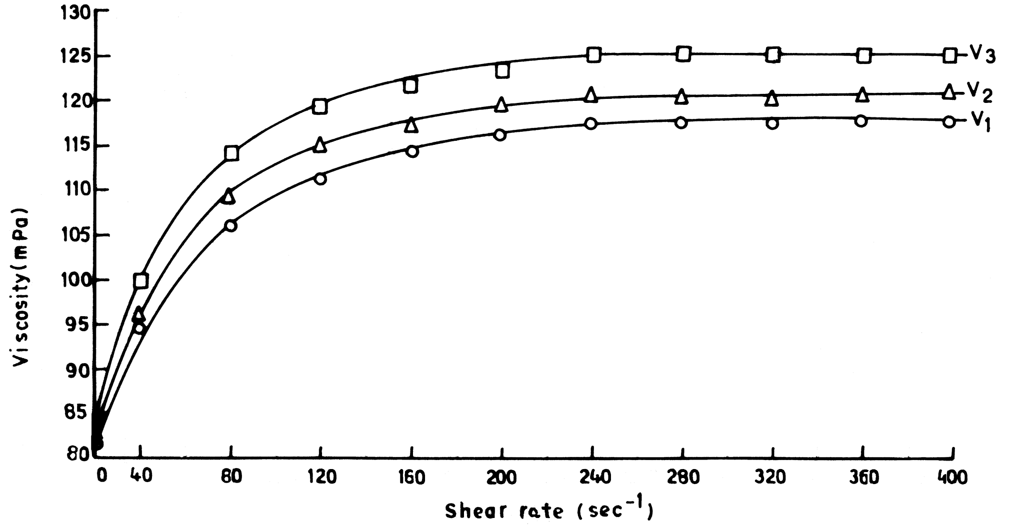
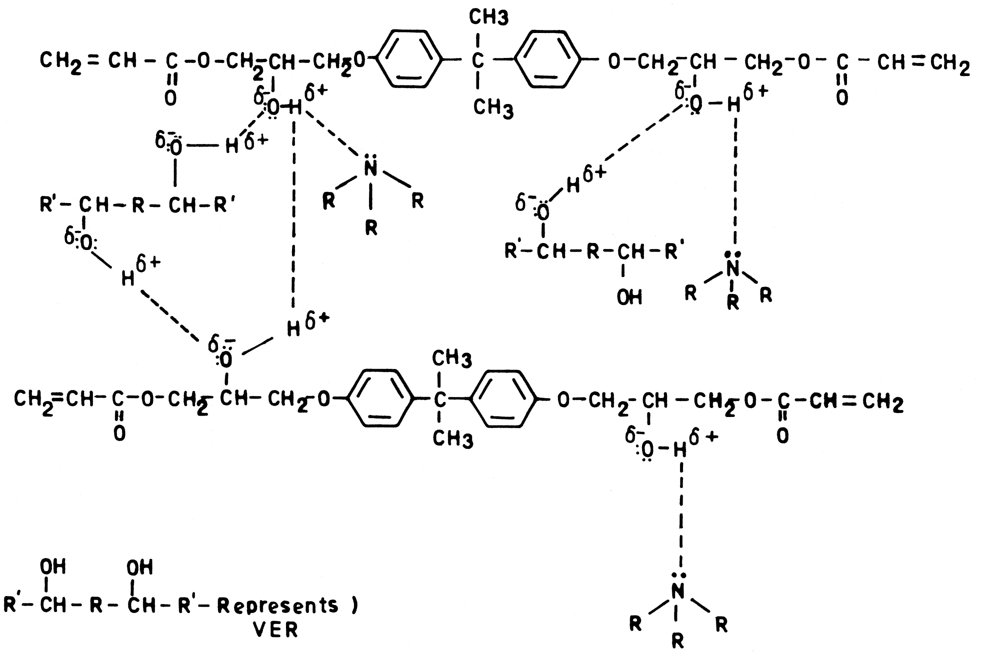


Figure 7. Plots between viscosity and shear rate for vinyl ester resins.

the adduct formed between the amines and hydrogen of hydroxyl group present in the resin which helps in the formation of molecular aggregates [22, 23]. The possible structure of aggregate is given below:



Aggregate

The aggregate formation predominates during shearing because shear stretches and orients the molecules and therefore, enhances the chances of interaction that are effectively screened in the unsheared state [24].

The shear stress and shear rate data of the samples were analyzed for their flow behavior, using Bingham and Casson [25] models. The Bingham model fitted the data best in all cases and therefore, the flow behavior of samples could be considered as plastic. The Bingham equation for VER samples at 30°C were:

$$\pi = -1.122 + 0.07624D \ (r = 1.0) \text{ for } V_1,$$
$$\pi = -1.119 + 0.07896D \ (r = 1.0) \text{ for } V_2, \text{ and}$$
$$\pi = -1.078 + 0.08370D \ (r = 1.0) \text{ for } V_3$$

where, π is shear stress, D is the shear rate and r is the correlation coefficient.

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

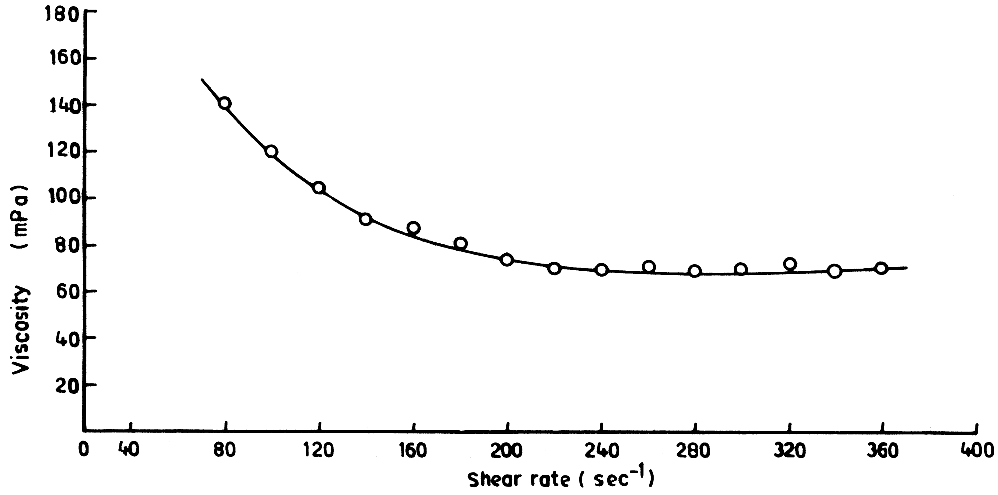


Figure 8. Plot between viscosity and shear rate for VER prepared in the presence of triphenyl phosphine.

TABLE 3. Activation Energy and Pre-exponential Factor for VERs at Constant Sheat Rate and Constant Shear Stress

Sample Name	Const. Shear Rate (Sec $^{-1}$)	Activation Energy (Kcal mol^{-1})	-log (pre-exponential factor (min^{-1})	Const. Shear Stress (Pa)	Activation Energy (Kcal mol^{-1})	-log (pre-exponential factor (min^{-1})
V_1	100	16.95	10.337	6	13.36	7.876
	150	16.12	9.710	9	12.98	7.448
	200	15.47	9.418	12	12.89	7.360
	250	14.37	8.733	15	12.62	7.146
V_2	100	17.04	10.380	6	13.54	7.866
	150	16.12	9.685	9	13.26	7.632
	200	15.30	9.063	12	13.17	7.544
	250	14.85	8.383	15	12.98	7.330
V_3	100	17.40	10.627	6	13.80	8.123
	150	16.39	9.859	9	13.72	7.967
	200	15.54	9.237	12	13.72	7.947
	250	14.92	8.571	15	13.63	7.927

(apparent viscosity) and reciprocal of the temperature using the Arrhenius equation. The values of E_D, E_τ and negative of the logarithm of the pre-exponential factor, for V_1, V_2 and V_3 containing 40% styrene are given in Table 3. It is apparent that in all the samples, E_D values decreases with an increase in shear rate. E_τ values calculated at shear stresses 6, 9, 12 and 15 Pa were found to be almost constant.

REFERENCES

[1] Jungang Gao, Qing Jin, and Biao Yang, *Huaxae Yu Zhanhe, 91* (1991).

[2] B. A. Patel, R. R. Pachha, J. R. Thakkar, and R. D. Patel*,* *Macromolecular Reports*, *A31 Suppls. (1 & 2), 145-151* (1994).

[3] N. G. Videnia and S. A. Bratslavakaya, *Zh. Priki. Khim*., Leningrad, Russia, *64*, 5, 1065-70 (1991).

[4] M. B. Launikitis, in *Handbook of Composites*, G. Luben, Ed, Van Nostrand, Reinhold Co., New York, 1982, p. 38.

[5] Bharti Gaur and J. S. P. Rai, *Polymer, 33*, 19, 4210 (1992).

[6] R. Bhatnagar and I. K. Verma, *J. Therm. Anal., 35*, 1241 (1989).

[7] Kant Krishna, A. Mishra, and J. S. P. Rai, *Polym. Int., 28*, 189 (1992).

[8] Der Jang Liaw and Wen-Chang Shen, *Polymer Engineering Science, 34*, 16 (1994).

[9] D. W. Knoll, D. H. Nelson, and P. W. Kehres, *Am. Chem. Soc. Symp*., 134th Meeting, 1958.

[10] C. L. Ogg, W. L. Porter, and C. O. Willitis, *Ind. Eng. Chem. Anal. Edn., 17*, 394 (1945).

[11] G. Odian, *Principles of Polymerization*, 2nd Edn., Wiley Interscience, New York, 1970.

[12] T. J. Ozawa, *Thermal Anal., 9*, 217, 369 (1976).

[13] H. E. Kissinger, *Anal. Chem., 29*, 1702 (1957).

[14] H. Lee and K. Neville, in *Handbook of Epoxy Resins*, McGraw-Hill Book Co., New York, 1967.

[15] Henkel Corporation, Vol. 1, Page 363B.

[16] C. Brisette and C. Sandorfy, *Can. J. Chem., 38*, 34 (1960).

[17] P. J. Stone, J. C. Craig, and H. W. Thompson, *J. Chem. Soc*., London, 1958, p. 52.

[18] Mansingh and Sunita, *Asian Journal of Chem., 9*, 2, 159-161 (1997).

[19] D. Buckley, Sonia Dunstan, and H. B. Henbest, *J. Chem. Soc*., 1957, p. 4901.

[20] Cheves Walling and Norman Indictor, *J. Am. Chem. Soc*., London, 80, 1958, p. 5814.

[21] B. Gaur and J. S. P. Rai, *Eur. Polym. J. , 29*, 8, 1149-1153 (1993).

[22] C. A. Parker and Thelma A. Joyce, *J. of Appl. Polym. Sci., 18*, 155-165 (1974).

[23] J. A. Odell, A. J. Muller, and A. Keller, *Polymer, 29*, 1179 (1987).

[24] James D. Katsaros, Michael F. Malone, and H. Winter Henning, *Polym. Bulletin, 16*, 83-88 (1986).

[25] N. Casson, in *Rheology of Disperse Systems,* C. C. Mill, Ed., Pergamon Press, Oxford, 1959, p. 84.

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