Effect Of Diluents on the Decomposition Behavior of Vinyl Ester Resin

S. Agrawal,[1] A. Mishra,[2] J.S.P. Rai[1]

[1]*Department of Plastic Technology, Harcourt Butler Technological Institute, Kanpur-208 002, India*
[2]*Department of Chemistry, Institute of Engineering and Technology, C.S.J.M.University, Kanpur-208 024, India*

ABSTRACT: An acidic vinyl ester resin (~6 mg KOH per gram of solid) was prepared by reacting a bisphenol-A-based epoxy resin with acrylic acid in the presence of tributylamine. The acrylated epoxy resin thus obtained was characterized by Fourier transform infrared spectroscopy. Five samples of vinyl ester resin containing styrene and methyl methacrylate (MMA) in the weight ratios 40:0, 30:10, 20:20, 10:30, and 0:40 were prepared at 30°C. These samples were cured, using 2 phr benzoyl peroxide, at 90 ± 2 °C for 1 h. The decomposition behavior of all the samples was studied by thermogravimetric analysis (TGA) at 10°C min^{-1}. The TG and dynamic thermogravimetry (DTG) thermograms showed single-step degradation in the individual cases of styrene and MMA, whereas a two-step degradation process was observed when styrene was mixed with MMA in any proportion. For all the samples, the order of the reaction was one for the first step. This value was calculated with the Coats and Redfern equation in accordance with the best-fit analysis and further confirmed by linear regression analysis. From this value of reaction order (n), the activation energy (E) and pre-exponential factor (Z) were calculated, and the validity of the data was checked by statistical analysis. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1952–1956, 2003

Key words: resins; thermogravimetric analysis; kinetics; activation energy; degradation

INTRODUCTION

Vinyl ester resins (VERs), a class of thermosets, are the unsaturated esters of epoxy resins. The combination of excellent mechanical and chemical resistance properties of epoxies with handling properties comparable to those of unsaturated polyesters[1,2] have made VERs a viable product for industrial applications such as coatings, printing inks, adhesives, printed circuit boards, metal foil laminates, building materials, automotive parts, rigid foams, and fiber-reinforced composites.[4–7] These resins are widely accepted because of their high reactivity (rapid curing) and easy processing. Kinetic modeling of thermosetting systems has provided valuable information regarding optimal processing and thermal stability predictions. Thermal stability is primarily dependent on chemical structure and the cross-link density of the system. Several investigators have studied the decomposition behavior of VERs, usually with styrene as the reactive diluent.[9–14] However, the effect of other diluents and their mixtures have not been emphasized much. In the present communication, we report on the decomposition behavior of VER in the presence of mixtures of styrene and methyl methacrylate (40%w/w) as the reactive diluents.

EXPERIMENTAL

Bisphenol-A-based epoxy resin (EPG-280; SIP Resins, Madras, India; epoxide equivalent weight of 190 as determined by the pyridinium chloride method[15]) acrylic acid (Fluka Chemie, Germany), tributyl amine (SD, India); benzoyl peroxide (SD's); styrene (Ranbaxy, India), and methyl methacrylate (MMA; Robert Johnson) were used in this study. Styrene and MMA were used after they were purifyied by standard procedures.[16,17]

VER was prepared with a 1:0.9 mole ratio of bisphenol-A epoxy and acrylic acid in the presence of tributylamine as catalyst (1 phr by weight of the epoxy resin). The reaction was carried out at 90 ± 2°C until the VER of the desired acid value (~6 mg of KOH per gram of solid), determined by the method of Ogg et al.,[18] was obtained. The progress of the reaction was monitored by determining the acid number of the reaction mass every 30 min. The extent of reaction and number average degree of polymerization were calculated using Carother's equation. The light-colored transparent VER thus prepared was cooled and stored in a refrigerator at ~10°C to prevent further reactions.

Five samples were prepared by mixing the VER, diluent(s), and benzoyl peroxide (2 phr) at 30°C until the mixtures became homogeneous. The samples were

TABLE I
Samples and their Corresponding Weight Fractions

Diluent	Percent weight fraction				
	V_A	V_B	V_C	V_D	V_E
Styrene	40	30	20	10	0
MMA	0	10	20	30	40

prepared just before the thermal studies were to be performed, and the details are given in Table I.

A thermal analyzer (Thermal Analyzer 2000; TA Instruments), equipped with a differential scanning calorimeter (DSC; 2910 Differential Scanning Calorimeter) and thermogravimetric analyzer (TGA; 2950 ThermoGravimetricAnalyser), was used to select and study the curing conditions and decomposition behavior of VERs. From dynamic DSC scans obtained at $5°C$ min^{-1}, a curing temperature of $90°C$ was selected to obtain an appreciable rate of curing in all the samples This temperature was used to cure the resin samples in an air-circulating oven ($\pm2°C$) for subsequent studies on thermal stability and the kinetics of decomposition. Dynamic thermograms for the cured samples were obtained at the rate of $10°C$ min^{-1} from 50 to $700°C$ under a nitrogen atmosphere. The relative thermal stability of the resin was quantitatively estimated by comparing the temperatures for a particular degree of weight loss. The values of activation energy (E) and pre-exponential factor (Z) were determined by the Coats and Redfern equation[19] 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 $g(\alpha)$ is defined as follows:

$$g(\alpha) = \begin{cases} \left[\dfrac{1 - (1-\alpha)^{1-n}}{1-n}\right] & \text{for } n \neq 1 \\ -\log_{10}\{-\log_{10}(1-\alpha)\} & \text{for } n = 1 \end{cases} \quad (2)$$
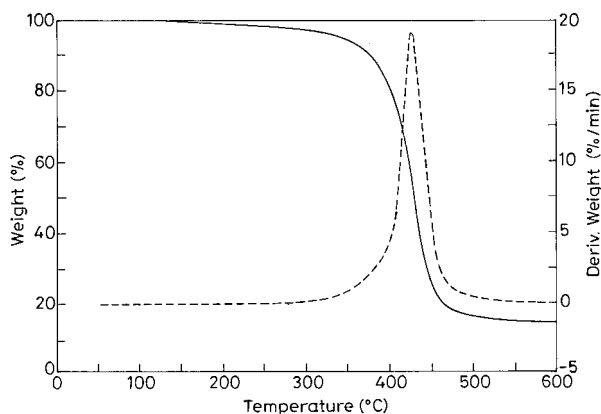

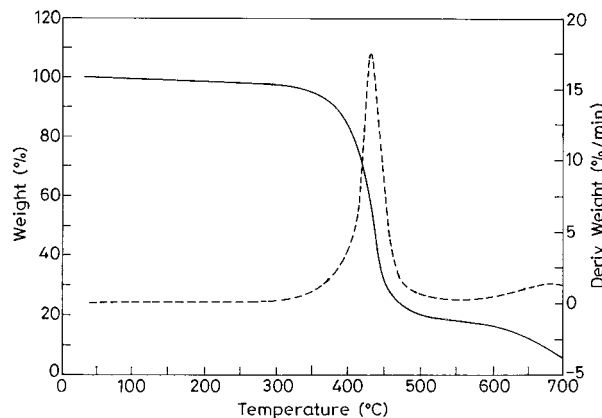**Figure 1** Dynamic TG scan of V_A containing 40% styrene at $10°C$ min^{-1}.

Figure 2 Dynamic TG scan of V_B containing 30% styrene and 10% MMA at $10°C$ min^{-1}.

Equation 1 can be reduced to eq. 3:

$$Y = A + \frac{B}{1000}X \quad (3)$$

The parameters in eq. 3 are defined as follows for different values of n between 0 and 2.0:

$$Y = \log\left[\frac{g(\alpha)}{T^2}\right] \quad (4)$$

$$X = \frac{1000}{T} \quad (5)$$

$$A = \log_{10}\left\{\frac{ZR}{\beta E}\left[1 - \frac{2RT}{E}\right]\right\} \quad (6)$$
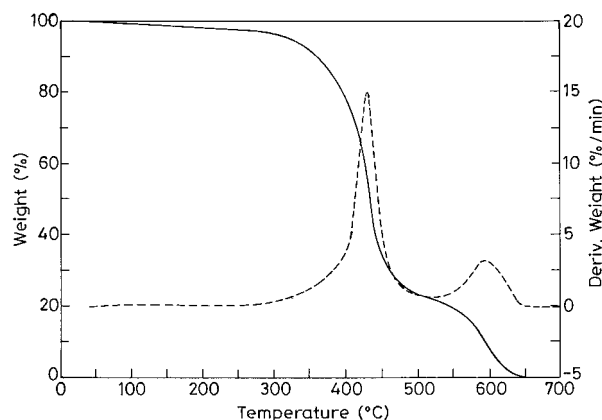
$$B = \frac{-E}{2.3R} \quad (7)$$

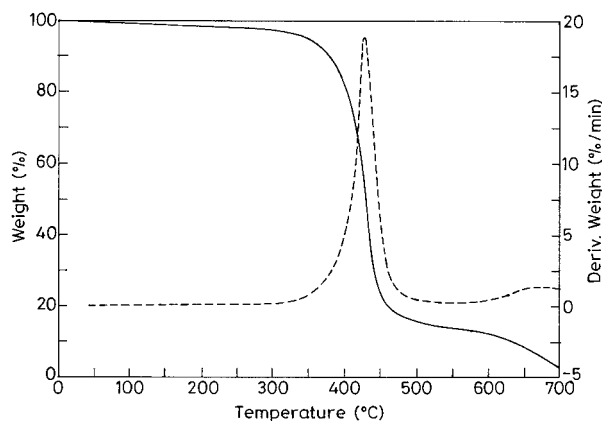**Figure 3** Dynamic TG scan of V_C containing 20% styrene and 20% MMA at $10°C$ min^{-1}.

Figure 4 Dynamic TG scan of V_D containing 10% styrene and 30% MMA 10°C min^{-1}.

$$\alpha = \frac{W_T - W_f}{W_o - W_f} \qquad (8)$$

where α is the fractional weight loss, W_T is the weight at temperature T, W_f is the final weight, W_o is the initial weight, and R is the gas constant.

The best-fit technique was used to calculate the value of order of reaction (n), which was further confirmed by regression analysis. The validity of the data was checked by t test analysis.[20] If the calculated value of 't' was greater than or equal to the Table value of 't', the data being compared were considered significantly different.

RESULTS AND DISCUSSION

The prepared resin was characterized by Fourier transform infrared spectroscopy (FTIR).[21] The thermogravimetric (TG) and dynamic thermal gravimetric (DTG) scans for the decomposition of samples V_A–V_E at a rate of 10°C min^{-1} from 50 to 700°C are shown in Figures 1–5. It is clear from the thermograms of V_A and V_E that the degradation of these samples consisted of a single step, whereas thermograms of V_B, V_C, and V_D show two-step degradation. These results clearly indicate that the nature of crosslinks formed
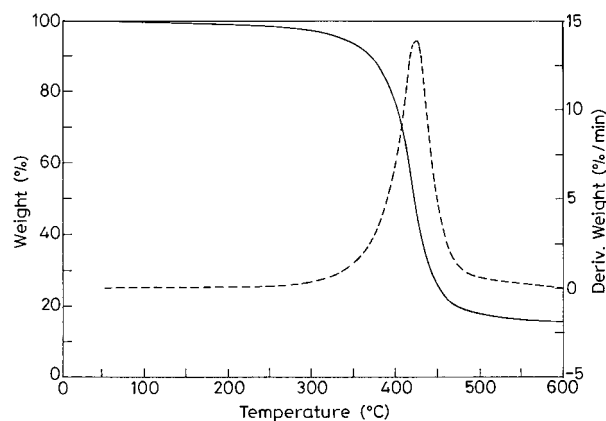

Figure 5 Dynamic TG scan of vinyl ester resin V_E containing 40% MMA 10°C min^{-1}.

during the cure was different in the presence of a mixture of diluents, which might have resulted in changes in the decomposition behavior. Rapid decomposition was observed between 300 and 500°C, and ~85–76% of the sample was lost in this decomposition step. However, in all the samples, initial weight loss of ~1–3% was observed between 100 and 300°C, which was probably due to residual diluents and byproducts of the curing reactions, etc.[22]

The results of thermal studies of all the samples are summarized in Table II. It is apparent from the data that the initial decomposition temperatures (T_i) of V_B, V_C, and V_D are higher than those of V_A and V_E. However, significant variations in peak (T_{max}) and final temperature (T_f) of decomposition of these samples were not observed. The area under the DTG curve, which is proportional to total change in weight, was lowest for V_C, indicating that the sample cured using equivalent proportions of the reactive diluents was more stable than V_B and V_D. The char yield at 500°C was also highest for V_C, indicating the better stability of this sample. However, sample V_C was completely degraded at ~700°C without yield. These observations could be due to variation in the copolymerization behavior of VER in the presence of the two monomers or their copolymers, which might have formed prior to entering the crosslinking network.

TABLE II
Decomposition Behavior of Cured Vinyl Ester Resins Containing Styrene and MMA at 10°C min^{-1a}

Sample	T_i (°C)	T_{max} (°C)	T_f (°C)	DTG Area (%)	Char yield % 500°C	Char yield % 700°C	E (kcal mol^{-1})	Z (min^{-1})
V_A	327.01	428.74	488.78	66.15	15.44	15.10	30.72	67.45×10^{14}
V_B	332.10	432.30	496.03	64.60	20.56	3.21	32.67	27.86×10^{15}
V_C	338.05	430.17	490.97	54.80	23.80	0.71	32.86	28.06×10^{15}
V_D	329.07	428.80	501.07	65.68	16.15	2.49	31.70	11.63×10^{15}
V_E	306.20	424.04	506.84	69.66	14.60	14.14	28.27	12.52×10^{14}

[a] T_i, Initial temperature of decomposition; T_{max}, peak temperature of decomposition; T_f, final temperature of decomposition; E, activation energy; Z, frequency factor.

TABLE III
Temperature of 1–10% Weight Loss in
Thermogravimetric Analysis of Cured Vinyl Ester Resins

Weight loss (%)	Temperature (K)				
	V_A	V_B	V_C	V_D	V_E
1	436	445	462	439	427
2	512	543	561	532	501
3	566	591	600	579	553
4	597	613	615	606	584
5	615	627	630	619	607
6	626	632	636	630	617
7	634	641	643	638	624
8	640	647	648	644	630
9	645	651	651	649	635
10	649	654	654	651	645

The relative thermal stabilities of all the samples were studied by comparing the temperatures of 1–10% weight loss, and the data are given in Table III. From the temperature for a particular degree of weight loss, it is apparent that the thermal stability was highest for V_C, which has equal proportion of the diluents. The thermal stabilities of samples V_B and V_D, containing mixture of diluents in different proportions, were also better than those of samples V_A and V_E, which contained only one diluent. The kinetic parameters [viz. order of reaction (n), energy of activation (E), and frequency factor (Z)] of the degradation reaction up to

500°C were obtained with the Coats and Redfern equation. For different values of n (0, $\frac{1}{2}$, 2/3, 1, and 2), the graphs were plotted between $1000/T$ and $\log_{10}\{-\log_{10}(1-\alpha)/T^2)\}$ for $n = 1$, and $\log_{10}\{1 - (1-\alpha)^{1-n}/T^2(1-n)$ for $n \neq 1$. The statistical data for the decomposition reaction of VERs for the different values of (n) are given in Table IV, which shows that the value of $n = 1$ gave the best fit, with highly significant correlation coefficients. The data are significant up to the 95% level of significance because 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 are given in Table II. It is clear from the data in Table II that the activation energy for degradation is highest for V_C and lowest for V_E, which indicates that the mixture of diluents has improved the thermal stability of the cured product.

CONCLUSIONS

The decomposition behavior of VER containing styrene, MMA, and their mixtures showed single and two steps, respectively. The mixture of diluents gave a cured product of better thermal stability than the cured product containing individual diluents. Degradation reactions followed first-order kinetics for the first step.

TABLE IV
Statistical Data for Decomposition of Vinyl Ester Resins

Sample	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_A	0	0.9514	15	0.1096	0.3719	$Y = -4.4546x + 6.0497$	2.56	2.13
	1/2	0.9639	15	0.1125	0.3818	$Y = -5.3595x + 7.4482$	2.52	2.13
	2/3	0.9575	15	0.1142	0.3875	$Y = -5.7502x + 8.0476$	2.49	2.13
	1	0.9711	15	0.1251	0.4245	$Y = -6.7066x + 9.1455$	2.29	2.13
	2	0.3456	15	0.4206	1.4273	$Y = +2.0375x - 3.8345$	0.82	2.13
V_B	0	0.9557	15	0.1049	0.3683	$Y = -4.6331x + 6.2886$	2.59	2.13
	1/2	0.9713	15	0.1008	0.3539	$Y = -5.5949x + 7.7654$	2.74	2.13
	2/3	0.9762	15	0.0982	0.3449	$Y = -6.0258x + 8.4218$	2.83	2.13
	1	0.9812	15	0.1030	0.3615	$Y = -7.1341x + 9.7373$	2.71	2.13
	2	0.3974	15	0.5309	1.8636	$Y = +3.1263x - 5.4215$	0.21	2.13
V_C	0	0.9645	14	0.0933	0.3241	$Y = -4.4269x + 5.9440$	2.97	2.14
	1/2	0.9850	14	0.0736	0.2557	$Y = -5.4673x + 7.5261$	3.86	2.14
	2/3	0.9903	14	0.0639	0.2221	$Y = -5.9409x + 8.2408$	4.46	2.14
	1	0.9924	14	0.0683	0.2373	$Y = -7.1743x + 9.7291$	4.18	2.14
	2	0.4828	14	0.5955	2.0687	$Y = +4.2678x - 7.0645$	0.23	2.14
V_D	0	0.9478	14	0.1129	0.4097	$Y = -4.5603x + 6.1472$	2.31	2.14
	1/2	0.9657	14	0.1092	0.3962	$Y = -5.5104x + 7.5986$	2.44	2.14
	2/3	0.9713	14	0.1067	0.3872	$Y = -5.9202x + 8.2200$	2.51	2.14
	1	0.9795	14	0.1049	0.3807	$Y = -6.9213x + 9.3687$	2.57	2.14
	2	0.3771	14	0.4028	1.4616	$Y = +2.2267x - 4.0698$	0.26	2.14
V_E	0	0.9625	15	0.0966	0.2946	$Y = -4.0489x + 5.5107$	3.26	2.13
	1/2	0.9792	15	0.0857	0.2613	$Y = -4.8981x + 6.8389$	3.75	2.13
	2/3	0.9841	15	0.0804	0.2454	$Y = -5.2663x + 7.4104$	4.01	2.13
	1	0.9890	15	0.0780	0.2379	$Y = -6.1730x + 8.4479$	4.15	2.13
	2	0.3780	15	0.4415	1.3463	$Y = +2.1296x - 3.9997$	0.28	2.13

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