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A Kinetic Approach On Thermal Properties of Vinyl Ester Resin Synthesized by Different Molecular Weight Epoxy Resin with Phenyl Glycidal Ether

Neelam Pal[1], Anuradha Tiwari[2], Nand Lal[3*], Tamanna Begam[4]
[1,2,3]*Department of Chemistry, V. S. S. D. College, Kanpur, India*
[4]*Department of Chemistry, D. B. S. College, Kanpur, India*

***Abstract*: The esterification of bisphenol-A based epoxy resin having different molecular weight epoxies in presence of phenyl glycidyl ether and acrylic acid was carried out at 85°C using triphenyl phosphine as a catalyst. The structural changes were studied by FTIR. The thermal properties of the prepared vinyl ester resin (VER) samples were studied by (DSC) and (TG) analysis. The cure temperature increased with the increase of molecular weight of the parent epoxy resin. It was also found that the degradation of all the samples proceeded with two-step degradation mechanism. In the first step, it preceded with second order whereas in the second step the order of reaction increased with increasing molecular weight of parent epoxy. The energy of activation, E, was found to be maximum in the case of VER synthesized with low molecular weight epoxy, the value of pre-exponential factor (Z) and rate decomposition constant, k, for decomposition of the samples was found to be similar trend as activation energy.**

***Keywords*: Orientation, Monoepoxy diluent, Infrared, Spectroscopic analysis, Cure temperature.**

1. Introduction

Vinyl ester resins (VERs) are made by reacting unsaturated mono carboxylic acids [1] with bisphenol-A based epoxy resin [2] and these have various industrial applications such as structural part of land transportation, electrical insulator, radiation curable ink, laminates, corrosion resistance ability, optical discs and coating formulation [3]-[7] .

VERs synthesized by epoxies having high EEW possess problems in processing and affects the thermal decomposition. The addition of reactive/nonreactive diluents reduces the viscosity of the VERs. The most commonly used reactive diluents are vinyl monomers, viz., styrene, α-methyl styrene, acrylates and methacrylates [8]-[11]. In present paper this problem can be overcome by adding vinyl groups containing mono epoxy diluent during synthesis of VERs [12]. The addition of such diluents reduces the viscosity of the VERs at low concentrations [13]. The decomposition kinetics of VERs synthesized in presence of mono epoxy is yet to be explored [14]. Therefore, in the present paper, we have studied the kinetic of thermally decomposed VERs having phenyl glycidyl ether during the synthesis of VERs.

2. Experimental

A. Materials

DGEBA based epoxy resins, (M/s Parikh Resins, Kanpur), and (M/s SIP Resins, Chennai), phenyl glycidyl ether (PGE) Shell Chemical Co. USA), acrylic acid (AA) and triphenylphosphine (M/s Fulka A. G. Switzerland) were used for the preparation of VERs.

B. Synthesis of VERs

The vinyl ester resin was prepared by using 1:0.9 mole ratio of DGEBA epoxy resins with different molecular weight) and AA mixed, separately, with phenyl glycidyl ether (40% wt of epoxy resin). All the contents were charged into a three-necked R.B. flask equipped with a mechanical stirrer, nitrogen inlet tube, and thermometer at 85±2^{0}C with triphenyl phosphine as catalyst (1% wt of the resin).

C. Curing of vinyl ester resins

The curing of vinyl ester resins by using a reactive diluent, viz., styrene and free radical initiator benzoyl peroxide in the ratio 10:4:0.2 (w/w).

D. Characterization of VERs

Fourier transform infra-red (FTIR) spectroscopic analysis

Fourier transform infra-red (FTIR) spectra of all the VER samples cured with 40% styrene were performed on Perkin Elmer Paragon 1000 FTIR spectrophotometer. KBr pellets (0.3mm) of VERs (~1% samples) were formed under pressure and scanned from wave number range 500-4000 cm^{-1}.

E. Differential Scanning Calorimetric analysis (DSC)

The starting temperature, programmed rate and final temperature were taken at heating rate of 10^{0}C/min. Dynamic

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*Corresponding author: drnandlal71@rediffmail.com

scans were obtained which were used for assuming the cure temperature.

F. Thermogravimetric analysis (TGA):

The percent weight loss and thermal degradation characteristics of prepared samples were evaluated by thermogravimetric analyzer (TGA).

G. Study of kinetic parameter

The kinetic parameters viz. order of reaction (n) activation energy (E), and pre-exponential factor (Z) for thermal decomposition reaction of VERs were evaluated by the data as obtained from the dynamic thermograms from TGA [15]. The data obtained from TG curves were utilized in solving Coat-Redfern equation [16]. The graph was plotted between X and Y. The X is 1000/T and Y= log10(g(α)/T^2 as per Coat-Readfern equation for different value of n.

3. Results and Discussion

A. FTIR spectroscopic analysis of VERs

FTIR spectra of samples V1, V2, V3 (Fig. 1) while studying the chemical kinetics of the reaction. The peak related to oxirane ring functionality (i.e. at 910 cm^{-1}) disappeared and a new peak near 1725cm^{-1}, for sample V1, appeared. The intensity of this peak decreased as the molecular weight of the parent epoxy resin was increased i.e for samples V2 and V3 (Refer Fig. 1) for which the peaks related to ester group appeared near 1725 and1723 cm^{-1}, respectively. A broad band appeared in the region of 3628-3100 cm^{-1} centered at 3437cm^{-1} which might be due to stretching vibration of hydroxyl group for vinyl ester sample. This indicated that the increase of molecular weight of parent epoxy resin marginally shifted the band appeared due to hydroxyl group stretching. The position of peak related to hydroxyl group appeared to near 3462, 3436, and 3510 cm^{-1} for samples V1, V2, and V3, respectively. All the VER samples showed absorptions near 1605 and 1510 cm^{-1} which might be due to the presence of aromatic ring.

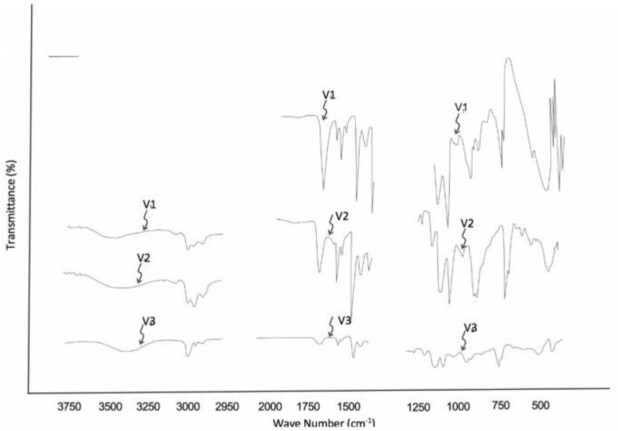

Fig. 1. FTIR spectrum of synthesized V1, V2, V3

B. Curing studies

Dynamic DSC scans for the curing of VER samples are given in fig. 2.

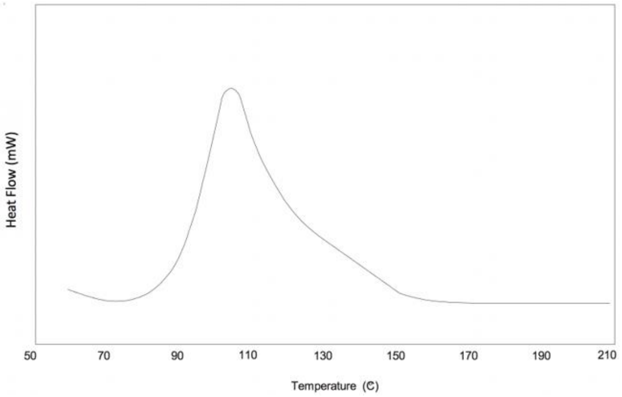

Fig. 2. Dynamic DSC scans for the curing of V1(vinyl ester resin synthesized in presence of low molecular weight epoxy with phenyl glycidyl ether) mixed with 2 % benzoyl peroxide as initiator at 10°C min^{-1}

From the above scan, the typical DSC scan for the curing of V1 (vinyl ester resin synthesized in presence of low molecular weight epoxy with phenyl glycidyl ether) mixed with 2 % benzoyl peroxide as initiator at 10°C min^{-1} have been shown in figure 2. The onset temperature of curing (T_0), the exothermic peak temperature (T_p) and final temperature of curing (T_f) were noted and are summarized in table 1. From the table it shown clear that the cure time increased with increase of EEW at fixed temperature. This might be due to the higher crosslink density produced in the cured product of V1 as compared to V2 and V3 [17], [18].

The exothermic peak temperature, as considered a measure of cure temperature, shifted marginally to higher temperature side scale as the molecular weight of the parent epoxy in VER was increased from 370g mol $^{-1}$ to 1762 g mol^{-1}.

C. Thermogravimetric Analysis

1) Thermal stability

The dynamic thermogravimetric (TG) as well as the differential thermo gravimetric (DTG) trace of VERs synthesized with presence of monoepoxy diluent i.e., phenyl glycidyl ether with pure epoxy of different epoxy molecular weight (i.e., samples V1, V2, and V3) obtained at programmed heating rate of 10°C/min are shown in fig 3.

The data on initial (IDT), peak (T_{max}) and final (FDT) decomposition temperatures as well as char residue at 600^{0}C, derived from these traces are given in table 2 for different vinyl ester resin samples. to V1 & V2. Enhancement in the thermal stability of the samples and also showed an increase in the final degradation temperatures (refer Table 2). Percent weight loss at characteristic peak temperatures as enumerated in table 2 also justified enhanced thermal stability of the vinyl ester resins

Table 1
Results of DSC and TG/DTG traces of vinyl ester resins

Sample Code	**Cure Temperature**			**First Step**				**Second Step**				**Char Yield at 600°C**
	T_0	T_p	T_f	IDT	T_{max}	FDT	%ML	IDT	T_{max}	FDT	%ML	
V1	85.09	101.25	129.01	170	359	376	46	376	400	555	33	21
V2	90.10	109.09	141.32	178	351	389	30	350	394	551	44	26
V3	94.89	122.84	144.20	172	372	419	64	382	405	544	21	15

Table 2
TGA Data

S. No.	Sample code	Plot of X and Y				Linear regression analysis		R^2		n	
		Slope		Intercept							
		Ist- step	IInd-step	Ist- step	IInd-step	Ist- step	IInd-step	Ist- step	IInd-step	Ist- step	IInd-step
1	V1	-2.96	-2.45	-10.36	-9.34	Y=-3.02x-10.96	Y=-3.02x-9.49	0.9236	0.9989	2	0
2	V2	-9.10	-1.35	-19.15	-7.15	Y=-10.01x-20.01	Y=-1.85x-8.10	0.9796	0.9913	2	0.5
3	V3	-1.43	-1.05	-8.35	-6.35	Y=-2.45x-9.40	Y=-1.25x-7.05	0.9621	0.9894	2	1

Table 3
Kinetic parameters

S. No.	Sample code	E(kJ/mole)				Zx10 ^{23} (s^{-1})				K x10^{23}(S^{-1})			
		$E_{calculated}$		E_{plot}		$Z_{calculated}$		Z_{plot}		$K_{calculated}$		k plot	
		Ist- step	IInd-step	Ist- step	IInd-step	Ist- step	IInd-step	Ist- step	IInd-step	Ist- step	IInd-step	Ist- step	IInd-step
1	V_1	78.80	50.50	84.92	56.60	0.974	0.706	1.55	0.845	9.76	7.00	14.21	11.98
2	V_2	69.51	30.10	74.30	25.63	0.912	0.632	1.32	0.789	8.94	5.69	13.10	10.56
3	V_3	62.30	17.96	64.50	15.49	0.805	0.594	0.988	0.699	7.61	5.00	12.26	9.84

synthesized with in presence of phenyl glycidyl ether. The higher char yield of VERs (refer Table 2) could be attributed to the presence of more cross-links present in the different molecular weight epoxy with phenyl glycidyl ether.

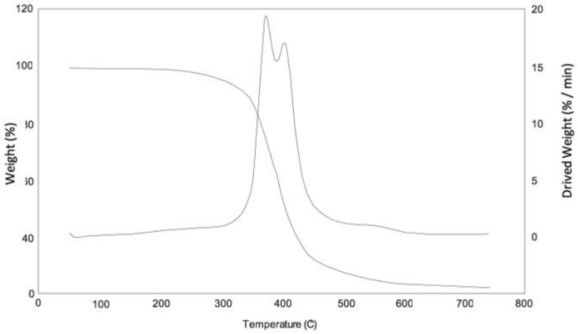

Fig. 3. Dynamic TG/DTG scans of V1 (vinyl ester resin synthesized in presence of low molecular weight epoxy with phenyl glycidyl ether)

D. *Study of kinetic parameters*

The kinetic parameters viz; order of reaction (n), energy of activation (E) and pre-exponential factor (Z) for thermal decomposition of the vinyl ester resins cured with styrene and benzoyl peroxide were evaluated by the data obtained from the dynamic thermograms from TGA shown in Table 3. The data obtained from TG curves were utilized in solving Coats – Redfern equation [16].

The fractional decomposition α for the respective temperature has been calculated from the TG curves. The graphs were plotted between X and Y for different values of n ranging between zero to two for different epoxy and its blend samples. Table 2 showed the best fit values of n for the samples of epoxies and their blends. A typical plot between X and Y with best fit values of n, for both the steps, in case of low molecular weight epoxy with phenyl glycidyl ether has been shown in Fig. 3. The figure clearly indicated that the first and second steps of both the samples followed 0.5th and 2nd (Table 2) order degradation kinetics, respectively. Similar plots can be shown for other samples.

This was further confirmed by linear regression analysis using regression equations (Table 2) along with the values of coefficient of determination, R^2, for each step. The values of R^2 indicated the suitability of the data and its value was very close to one in the both steps. This is also clear from the higher char yield of resin systems. Higher activation energy for the decomposition of resin led to better thermal stability. This fact has been evidenced by various workers in the past [19] for different systems.

4. Conclusion

It is concluded from the results that VERs prepared with higher molecular weight took higher temperature than the low molecular weight epoxy with phenyl glycidel ether. It was also observed that degradation of all the samples proceeded with two – step degradation process. The value of n were found to be second order in all the system in first step. The value of n increased with increased molecular weight in second step.

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