

Effect of structure on properties of vinyl ester resins

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Abstract. The paper describes the synthesis of vinyl ester resins based on diglycidyl ether of bisphenol-A (epoxy equivalent = 450–465 g/eq) (VR resin) and tetrabromobisphenol-A (epoxy equivalent = 380–420 g/eq) (VR-1 resin). The viscosity of styrenated VR resin was higher than VR-1 resin. The effect of styrene and α -methyl styrene on curing of VR resins was studied. An increase in styrene from 30 to 50 wt% resulted in an increase in gel time and a decrease in exothermic peak. Addition of α -methyl styrene delayed and depressed the exotherm. The mechanical properties of VR resin sheets and glass fabric reinforced laminates were better than VR-1 resins; whereas LOI of VR-1 was higher. A resin formulation containing 20–30 wt% of VR : VR-1 showed optimum mechanical properties and LOI.

Keywords. Vinyl ester resin; synthesis; mechanical properties.

1. Introduction

Methacryloxy or acryloxy derivatives of epoxy resins (vinyl ester resin) are suitable materials for corrosion resistant equipments, body and structural part for land transportation vehicles, electrical insulation, radiation curable inks and coating formulations. Vinyl ester (VE) resins combine the excellent thermal and mechanical properties of epoxy resins with the ease of processing and rapid curing of polyester resins (Kay 1981). The viscosity of neat vinyl ester resins is high, thereby making processing difficult. Hence reactive diluents such as styrene, alkyl methacrylates (Yilgor *et al* 1985), α -methyl styrene are added to the resin which not only help in processing but improve some properties (e.g. strength, % elongation, hardness, chemical and scratch resistance) and brings down the cost of the resin. The effect of reactive diluent content on properties of VE resins has already been reported (Goel *et al* 1985; Varma *et al* 1985).

In our earlier studies we have reported the synthesis and characterization of vinyl ester resins based on diglycidyl ether of bisphenol-A (DGEBA) (Bhatnagar and Varma 1989; Padma *et al* 1993b) and epoxy novolac resins (Padma *et al* 1993a). The epoxy equivalent weight of the epoxy resins used were 221 (DGEBA) and 186 g/eq (epoxy novolac resin). An epoxy backbone of higher molecular weight is expected to produce greater toughness and resiliency. Therefore it was considered of interest to study the properties of VE resins based on an epoxy resin of higher molecular weight. The flame resistance of VE resins can be improved by incorporation of bromine containing compounds. The present paper reports the synthesis,

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characterization and properties of vinyl ester resins based on diglycidyl ether of -bisphenol A/tetrabromobisphenol-A. The effect of reactive diluent content on the curing behaviour was also investigated.

2. Experimental

2.1 *Synthesis of vinyl ester resins*

The synthesis of vinyl ester resin was done in a 1 L three necked flask equipped with a condenser having a CaCl₂ guard tube. Air was bubbled through one inlet and a temperature sensor was fixed in another. 183 g of epoxy resin (Ciba Geigy) (epoxy equivalent 450–465 g/eq), 85 g of methacrylic acid (GSFC), 80 mL of methyl ethyl ketone (E. Merck), 85 mg of hydroquinone and 5 g of quaternary ammonium salt were placed in the flask, which was then heated on a heating mantle maintained at 90–100°C. The reaction was stopped when the acid number was below ten. The solvent was distilled off and the resin was cooled and stored at 10°C. This resin has been designated as VR in subsequent discussion.

The synthesis of brominated vinyl ester resin (designated as VR-1) was carried out in a similar manner using 180 g of diglycidyl ether of tetrabromobisphenol-A (Taiwan) (epoxy equivalent = 380–420 g/eq), methacrylic acid (70 g), methyl ethyl ketone (80 mL), quaternary ammonium salt (5 g) and hydroquinone (80 mg).

2.2 *Characterization*

The viscosity of vinyl ester resins containing different amounts of styrene (30–50 wt%) was determined using a Brookfield synchroelectric viscometer equipped with a LV-2 spindle at room temperature. The viscosity of VR : VR-1 resins (weight of VR-1 from 0–40) containing 50% styrene as reactive diluent were also determined.

Gel time determination of 50 g resin samples was done at 25 ± 1°C using 1 g benzoyl peroxide and 1 g N,N-dimethyl aniline (2%) at room temperature. The increase in temperature of the sample as a function of time was measured and gel time was determined by extrapolation.

2.3 *Fabrication of vinyl ester resin sheets and composites*

The sheets were fabricated using styrenated VR, and VR : VR-1 resin, methyl ethyl ketone peroxide (1%), N,N-dimethylaniline (0.1%) and cobalt octoate (0.1%). The requisite amount of reagents were placed in a 1L beaker and stirred using a mechanical stirrer for 30 min. After filtration (using a high vacuum pump) to remove suspended particles and degassing, the viscous syrup was poured into the toughened glass mould (40 × 30 cm²) having PVC gasket (3 mm). The filled glass mould was then kept in an air oven at 80–90°C for 3–4 h for curing. Density of the cured sheet was determined by displacement method according to ASTM D-792, by using a Mettler electronic balance and sample of size 2.5 × 2.5 cm².

Glass fabric reinforced vinyl ester resin composites were fabricated using hand lay up technique. Benzoyl peroxide (2%) and N,N-dimethyl aniline (0.06%) was

used as the initiator. The required quantity of vinyl ester resin, styrene and initiator were mixed in a 500 ml beaker. The total quantity of the solution was 130 g. It was then stirred using a mechanical stirrer for complete mixing and filtered. This resin solution was then brush-coated uniformly on the glass fabric of dimension $25 \times 25 \text{ cm}^2$. Ten plies were coated with the resin and stacked between steel plates covered with mylar sheets. Initial curing was done at room temperature for 24 h and then the assembly was placed between the platens of a Carver hydraulic press at $80\text{--}90^\circ\text{C}$ for 2 h (pressure 176–180 psi). Post curing of the laminates was done at 130°C for 3 h. After post curing, the laminates were machined to the required dimensions. Residual cure of resin sheets was evaluated by using a Du Pont 9900 thermal analyzer having a 910 DSC module. The resin content of the laminates was determined by heating a weighed specimen ($0.6 \times 0.6 \text{ cm}^2$) in a silica crucible in a muffle furnace at 600°C for 2 h. The glass fibre was unaffected at this temperature but the resin completely burnt off. The fibres were weighed and resin content evaluated.

Thermal stability of cured resins in nitrogen atmosphere (flow rate = $60 \text{ cm}^3/\text{min}$) was evaluated using Du Pont 1090 thermal analyzer having a 951 TG module. A heating rate of 10 K/min and sample weight of $10 \pm 1 \text{ mg}$ was used. TG traces were analyzed for (a) initial decomposition temperature (T_i) obtained by extrapolation, (b) temperature of maximum rate of weight loss (T_m) obtained from differential thermogravimetric traces and final decomposition temperature (T_f). In case decomposition proceeded in two steps, then characteristic decomposition temperature of both the steps were noted, and indicated by writing a suffix 1 or 2. The % weight loss in each step was also noted.

The limiting oxygen index (LOI) of resin sheets were determined according to ASTM D-2863. The Stanton Redcroft flammability tester was used for this purpose.

2.4 Mechanical properties of neat sheet and composites

An Instron tensile tester model 1121 was used to determine the mechanical properties. The tensile strength of specimen was determined by ASTM D-638-76. The conditions used were gauge length 7 cm, full scale load 500 kg, chart speed 200 mm/min and cross head speed 10 mm/min.

Flexural strength was measured according to ASTM D-790-71 using a three point loading system. Specimen having span-to-depth ratio of 32 : 1, width 13 mm were used. The testing conditions were: cross head speed 10 mm/min for sheets and 50 mm/min for composite, chart speed 200 mm/min, full scale load 20 kg for neat sheets and 50 kg for composite.

Inter laminar shear strength (ILSS) was determined according to ASTM-D-2344-76. The test conditions employed were: span-to-depth ratio 5 : 1, length-to-thickness ratio 7 : 1, cross head speed 1 mm/min and chart speed 100 mm/min.

3. Results and discussion

The structure of VR and VR-1 resins synthesized in the present studies can be depicted as follows:

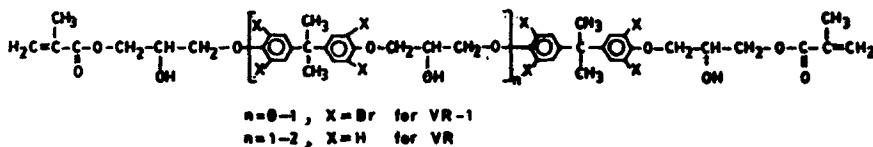


Table 1. Brookfield viscosity of styrenated VR and VR : VR-1 resins.

Resin designation	Vinyl ester resin (% w/w)		Styrene content (% w/w)	Viscosity (cps)
	VR	VR-1		
VR-A	50	0	50	15.75
VR-B	55	0	45	20.25
VR-C	60	0	40	30.50
VR-D	65	0	35	45.00
VR-E	70	0	30	78.00
VR-1A	0	50	50	5.75
VER-P	40	10	50	13.00
VER-Q	30	20	50	11.00
VER-R	25	25	50	10.25
VER-S	20	30	50	9.25
VER-T	10	40	50	7.25

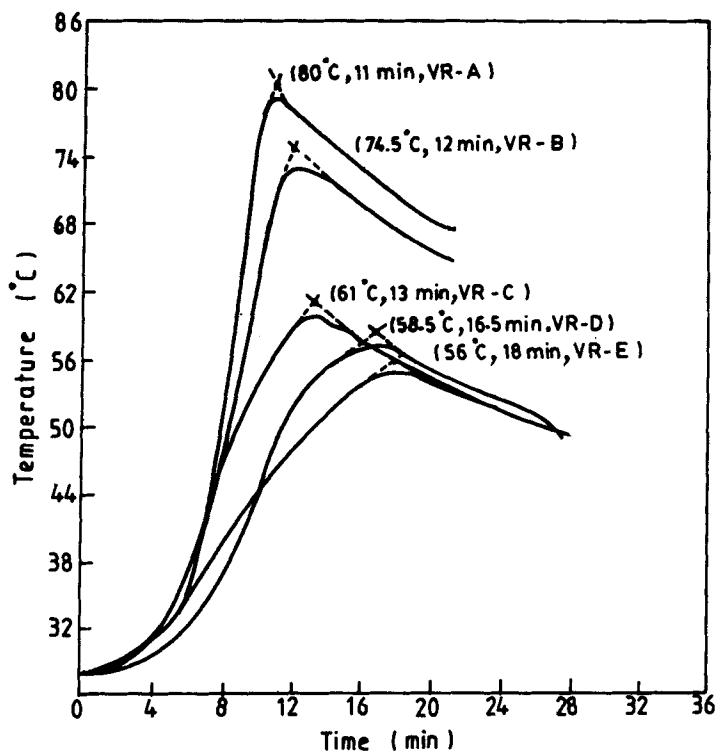


Figure 1. Gel point determination of VR resin in presence of different wt% of styrene (initiator benzoyl peroxide and N,N-dimethyl aniline).

Table 2. Effect of α -methyl styrene (α -MS) on cure characteristics of styrenated vinyl ester resin.

VR (%, w/w)	Styrene (%, w/w)	α -MS (%, w/w)	Gel time (min)	Exotherm peak temp. ($^{\circ}$ C)
50	50	0	18	56
50	48	2	20	51
50	45	5	22	43
50	40	10	> 8 h	—

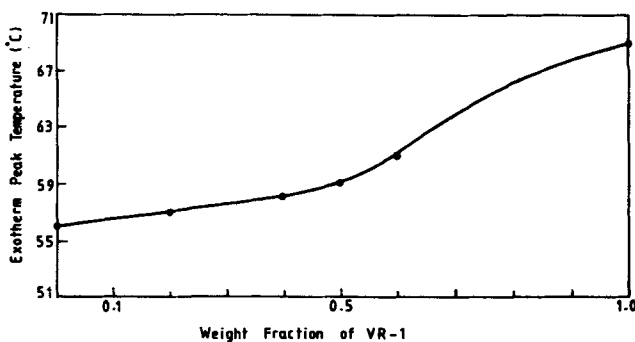


Figure 2. Effect of VR-1 content on exotherm peak temperature of VR:VR-1 resin formulation containing 50 wt% of styrene (initiators-benzoyl peroxide and N,N-dimethyl aniline).

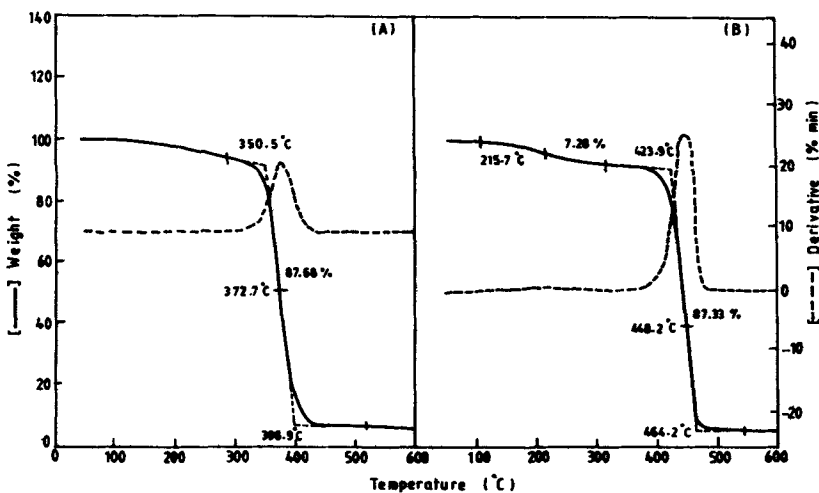


Figure 3. TG traces of (A) VR-1A and (B) VR-A resin sheets in N_2 atmosphere.

Table 3. Thermal behaviour of cured vinyl ester resin sheets.

Decomposition temp. (°C) (% wt loss)	VR-A	VER-P	VER-R	VER-T	VR-1A
	T_{i1}	160	170	168	150
T_{m1}	215	230	223	226	-
T_{f1}	315	290	270	270	-
(% wt loss)	(7.3)	(6.9)	(6.3)	(5.0)	-
T_{i2}	424	377	336	356	350
T_{m2}	448	415	389	378	372
T_{f2}	464	437	410	404	397
(% wt loss)	(87)	(87)	(81)	(88)	(87.7)

Table 4. Mechanical properties of cured vinyl ester resins.

Resin designation	Property				
	TS (MPa)	TM (GPa)	FS (MPa)	FM (GPa)	Limiting oxygen index (%)
VR-A	30.78	1.05	78.18	3.42	19.9
VER-P	30.56	1.32	77.83	3.57	20.8
VER-Q	34.08	1.53	76.88	3.57	21.2
VER-S	35.95	1.45	75.76	3.69	22.4
VR-1A	34.81	1.48	67.70	3.55	23.0

Table 5. Mechanical properties of vinyl ester resin composites.

Resin designation	Property			
	Resin content	FS (MPa)	FM (GPa)	ILSS (MPa)
VR-A	37.71	377.16	21.96	38.42
VER-P	37.25	418.80	21.28	39.79
VER-R	38.09	353.92	21.05	33.33
VER-T	40.37	308.72	20.24	26.71
VR-1A	39.20	323.12	20.51	28.68

The viscosity of VR containing different weight% of styrene and of VR : VR-1 resin containing 50 wt% of styrene are given in table 1. As expected, the viscosity of VR resin decreased by increasing styrene content in the formulation. The viscosity of VR-A resin (containing 50 wt% of styrene) was almost three times that of VR-1A resin (50 wt% styrene).

Gel time determination studies of VR resin in presence of different weight fraction of styrene are shown in figure 1. An increase in styrene content resulted in an increase in gel time and a decrease in exotherm peak temperature. Styrene, being a monofunctional monomer, reduces the cross-link density, thereby increasing the time for onset of gelation. A decrease in exotherm peak temperature and an increase

in time of gelation was observed by partial replacement of styrene in VR-A resin by α -methyl styrene (α -MS) (table 2).

Therefore from the gel time studies, it can be concluded that the gelation is reduced in presence of α -MS. The lower reactivity of α -methyl styrene may be explained on the basis of the greater stability of the tertiary propagating radical and hence reduced tendency for propagation.

The gel time decreased from 18 to 14 min by addition of VR-1 resin to VR (styrene content 50 wt%). The exotherm peak temperature increased from 56°C to 69°C (figure 2).

The density of cured specimen of VR-A and VR-1A were found to be 1.115 g/cm³ and 1.25 g/cm³ respectively.

The DSC scans of neat resin sheets showed absence of exothermic transition indicating thereby the absence of residual monomers/oligomers in the cured samples. These samples were stable up to 200°C. A weight loss of 5–8% was observed above this temperature (figure 3). However the major weight loss was above 420°C in VR-A and above 350°C in VR-1A. The lower decomposition temperature in VR-1A is due to the scission of C–Br bond which is thermally labile. The TG results of various resin samples are summarized in table 3.

The mechanical properties and oxygen index (LOI) of the neat sheets are given in table 4. The tensile strength of VR-1A was higher than VR-A. The tensile strength and LOI of VER-Q and VER-S resin formulation were found to be better than VR-A. Flexural strength of VR-A was higher than VR-1A. This may be due to high molecular weight epoxy resin used for the synthesis of VR-A resin. The limiting oxygen index of VR-1A was highest and it decreased by increasing VR-A content in the formulation. These results thus indicate that VER-Q and VER-S resins have good mechanical properties and flame resistance.

The glass fabric reinforced VR samples having 38.5 \pm 1.5% resin, exhibited good properties (table 5). The flexural strength, flexural modulus and ILSS was higher in VR-A. An increase of VR-1A in the resin formulation resulted in a decrease in ILSS and flexural properties.

Thus the vinyl ester resin based on high molecular weight epoxy resin have better flexural strength and modulus. Addition of 20–30 wt% of brominated vinyl ester resin to this VR resin increases the LOI without affecting the mechanical properties.

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