Methacrylate/Acrylate Terminated Derivatives of Diglycidyl Hexahydrophthalate: Synthesis, Structural, and Thermal Characterization

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ABSTRACT: Mono- or di(meth)acrylate-terminated derivatives of diglycidyl hexahydrophthalate (ER) were prepared by reacting 1 : 1 or 1 : 2 M ratio of ER and methacrylic acid or acrylic acid. These vinyl ester (VE) resins were characterized by determining epoxy equivalent weight, acid number, and molecular weight by gel permeation chromatography. Structural characterization was done by FTIR and ^{1}H NMR spectroscopy. In the ^{1}H NMR spectra of acrylate-terminated VE resins, three proton resonance signals were observed in the region 5.8–6.4 ppm due to vinyl group while in methacrylate-terminated VE resins only two proton resonance signals due to vinylidene protons were observed at 5.6–6.1 ppm. The Brookfield viscosity (room temperature (25 ± 2)°C) of these resins diluted with varying amounts of MMA was determined at 20 rpm. Curing behavior was monitored by determination of gel time and differential scanning calorimetry. An exothermic transition was observed in the DSC scans in the temperature range of (81–150)°C. Isothermal curing of MMA-diluted VE resins containing AIBN as an initiator was done at 60°C for 2 h in N_2 atmosphere, and then heating for another 2 h in static air atmosphere. Thermal stability of isothermally cured resins in N_2 atmosphere was evaluated by thermogravimetric analysis. All cured resins decomposed above 310°C in single step. Thermal stability of the cured resins having acrylate end caps was marginally higher than the resins having methacrylate end groups. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2414–2420, 2006

Key words: cycloaliphatic vinyl ester resin; curing; thermal properties

INTRODUCTION

Vinyl ester (VE) resins, introduced in the late 1960s, have made large strides in reinforced plastics applications. Originally developed for their high corrosion resistance performance, VE now find use in building and construction, coatings (UV and thermal curing systems, ranging from paper and card overprint varnishes, wood coatings, and solder resist inks for printed circuit boards), and automobile structural parts.

VE resins are the addition product of an epoxy resin and an unsaturated carboxylic acid such as acrylic or methacrylic acid (MAA), having pendant hydroxyl groups and double bonds (unsaturation) at terminal positions. Since the epoxy resin generally contains two oxirane groups, therefore by changing the molar ratio of unsaturated carboxylic acid (methacrylic/acrylic acid) with respect to epoxy resin, VE resins having one or two pendant hydroxyl group and (meth)acrylate end groups can be prepared. The hydroxyl groups enhance polarity and facilitate adhesion and pigment wetting properties.[1]

Different types of VE resins can be prepared by changing the epoxy resin and the acid used. The epoxy backbone provides toughness and flexibility to cured VE films, while the carbon–carbon and ether bonds of the resin improve the chemical resistance. The epoxy resins generally used in the preparation of VE resin are diglycidyl ether of bisphenol A and its oligomers.[2–5] Some work on bisphenol C [1,1′-bis(4-hydroxy phenyl)cyclohexane] based epoxy resin has also been reported.[6,7] Neat VE resin having aromatic groups have high viscosity, thereby wetting of the fibers and substrates is very difficult. Therefore, VE resins are diluted with vinyl monomers such as styrene or methyl methacrylate (MMA), and the curing is done by using free radical initiators. The vinyl monomers reduce the viscosity and facilitate preform impregnation. The major disadvantage of di(meth)acrylate derivative of DGEBA diluted with styrene is poor exterior durability. Most aromatic compounds are inherently susceptible to UV absorption and subsequent degradation. Because of the high energy of radiation at these wavelengths, photo-oxidation can cause chemical
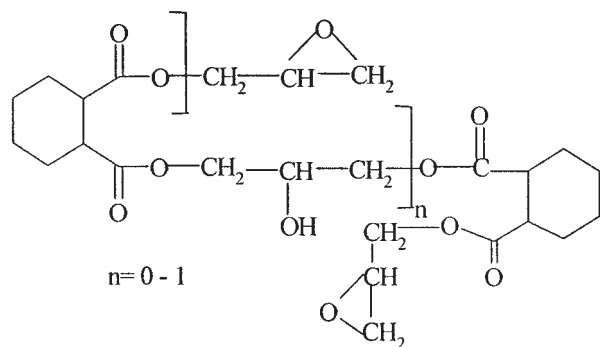
Figure 1 Structure of cycloaliphatic epoxy resin.

Figure 2 Structure of VE resin.

and physical changes in polymers and their networks. It is therefore desirable to use VE resins based on aliphatic or cycloaliphatic epoxy resins.

Cycloaliphatic epoxide coatings offer excellent weatherability, mechanical, and electrical insulating properties compared with those conventional epoxy resins based on bisphenol-A. They have been developed for many applications such as barrier coatings for polyolefin substrates, protective coatings for can ends, and conformal coatings for the electronic industries.[8,9]

Very few studies are reported on VE resins based on cycloaliphatic epoxies.[2] Kinetics of esterification of cycloaliphatic epoxies—diglycidyl ester of hexahydrophthalic anhydride or 3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexyl carboxylate with MAA—has been reported recently.[10] We now report the synthesis, characterization, and properties of (meth)acrylate-terminated cycloaliphatic epoxy resins. Our earlier studies have indicated that curing characteristics are affected by the presence of oxirane groups in VE resins.[11,12] The oxirane functionality in the resin also provides an additional site for reaction with amines[13] or carboxylic acids.[2] Higher interlaminar shear strength of glass fiber reinforced laminates was observed when resins containing oxirane rings were used.[13] Therefore, synthesis and characterization of mono(meth)acrylate resins prepared by reacting equimolar amounts of ER and unsaturated carboxylic acid was also carried out. The main objective of these studies was to synthesize, characterize, and evaluate thermal behavior of the VE resins containing cycloaliphatic moieties. MMA was used as the reactive diluent.

EXPERIMENTAL

Materials

Diglycidyl ester of hexahydrophthalic anhydride (cycloaliphatic epoxy) resin (referred to as epoxy resin in subsequent text) (Fig. 1) (supplied by Atul limited, Vad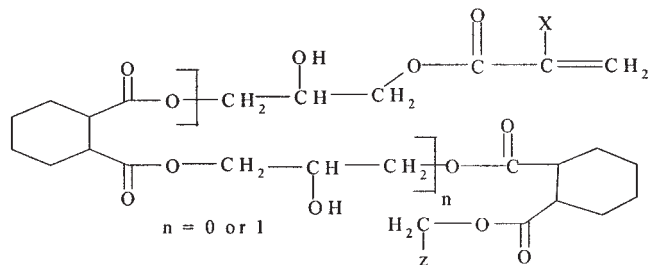odara) was used as such for the synthesis of VE resin. Other materials used were methacrylic acid (MAA) (G. S. Chemicals, Mumbai, India), acrylic acid (AA), methyl methacrylate (MMA), methanol (all from Qualigens, Mumbai, India), imidazole, and 2,2'-azobisisobutyronitrile (AIBN) (Loba Chemie, Mumbai, India). Inhibitor was removed from MMA by washing with 10% NaOH solution followed by washing with distilled water till neutral, and then drying over anhydrous sodium sulfate. The washed and dried monomer was distilled under reduced pressure. AIBN was recrystallized using chloroform.

Synthesis of mono or bis-acrylate/methacrylate terminated epoxy resin (VE resin)

The synthesis of four different VE resins was carried out in the present work. The VE resin obtained by reacting 1 : 1M ratio of epoxy resin and MAA or AA have been designated as resin A or C, respectively, while VE resins prepared by using 1 : 2M ratios have been designated as B or D, respectively, (Fig. 2, Table I).

The synthesis was carried out in a four necked reaction kettle equipped with a mechanical stirrer, an oxygen inlet, and a condenser. In a typical reaction 0.3 mol of epoxy resin and AA or MAA (0.3 mol or 0.6 mol), respectively, were introduced in the kettle and stirred. Imidazole catalyst (0.004–0.005 mol) was then added followed by thorough mixing of the contents. The reaction was carried out at 80–90°C in oxygen atmosphere and was monitored by determination of acid number till it reached a value <10. The resin was then cooled and stored at low temperature

TABLE I
Sample Designation for VE Resins

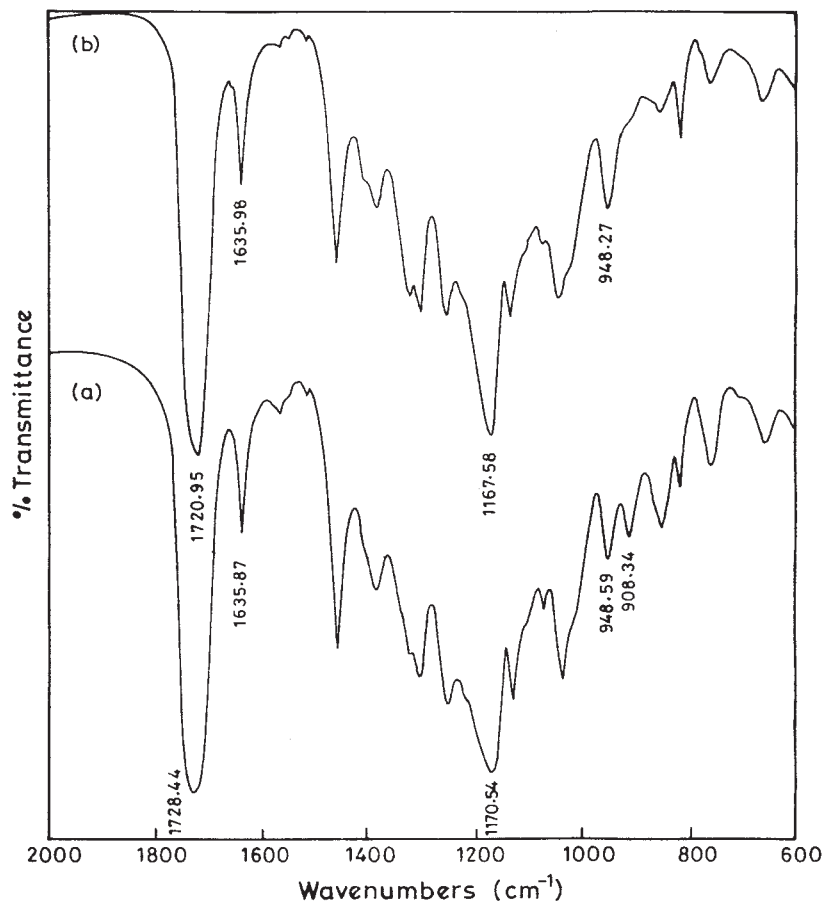| Sample designation	X	Z
A	CH$_3$	
B	H	
D	CH$_3$	
C	H	

Figure 3 FTIR spectra of VE resins (a) sample A and (b) sample B.

The VE resins thus obtained were diluted with MMA (20–40 phr).

Characterization

The epoxy resin was characterized by determining epoxy equivalent weight. The molecular weights were determined by gel permeation chromatography, using a high pressure liquid chromatography pump (Bischoff HPLC pump 2200) and a refractive index detector (Waters 410). The eluting solvent was tetrahydrofuran (THF) with a flow rate of 1 mL/min. Poly-(methyl methacrylate) standards were used for calibration purposes.

The acid number was determined volumetrically. The structural characterization of resins was done by recording IR spectra in thin film over KBr discs, using Nicolet FTIR spectrometer. ^{1}H NMR of resins were recorded on Brucker spectrospin 300 spectrometer using CDCl$_3$ as solvent and tetramethyl silane as an internal standard.

The neat VE resins were diluted with 20, 30, or 40 phr of MMA, and the samples have been designated by appending a numerical suffix of 2, 3, or 4 after the letter designation of resin sample. For example, sample A diluted with 20, 30, or 40 phr of MMA have been designated as A-2, A-3, and A-4, respectively. Similarly samples B, C, and D have also been designated. A Brookfield Synchroelectric Viscometer having spindle No. 3 and 7 (RV type) was used to determine the viscosity of these resin formulations at room temperature (25°C ± 2°C). Brookfield viscosity was determined at 20 rpm.

Thermal behavior of VE resins

A TA 2100 thermal analyzer having a 910 DSC module was used to evaluate the curing behavior of VE resins in presence of 1 phr AIBN (temperature range 50–300°C). A heating rate of 10°C/min and a sample mass of 10 ± 1 mg were used for recording DSC scans in static air atmosphere. The curing exotherm, observed in DSC scans, was characterized by determining the following parameters.

T_{onset}, temperature of onset of exotherm obtained by extrapolating the steepest portion of the exotherm; T_{final}, the endset temperature of the exotherm. This was taken as the temperature where the exotherm levels off with the base line at the final stage of cure. T_{exo}, peak position of the exotherm. ΔH, heat of curing
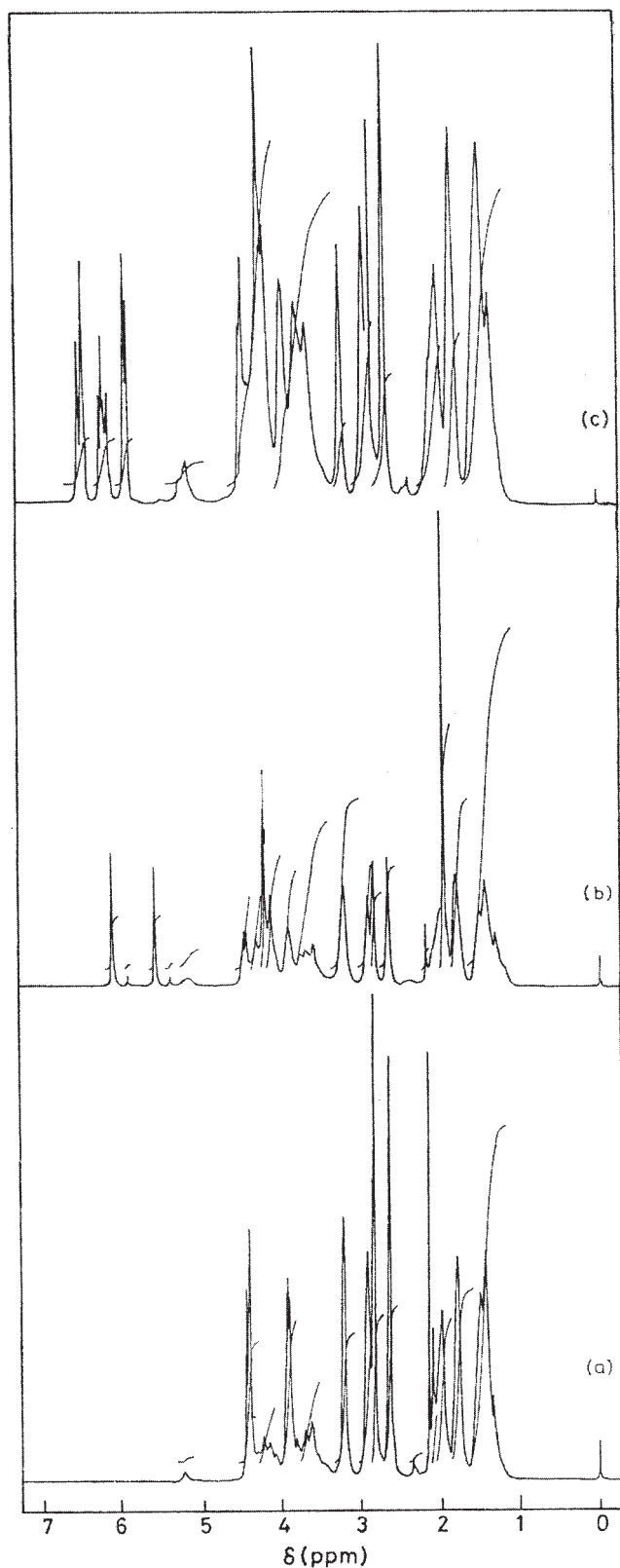
Figure 4 ¹H NMR spectra of epoxy and VE resin (a) epoxy resin (b) sample A and (c) sample C.

TABLE II
Brookfield Viscosity of VE Resins at 20 rpm at Temperature (25±2)°C

Sample designation	MMA content (phr)	Viscosity (cps) at RPM 20
A	0	3,375
A-2	20	100
B	0	22,000
B-2	20	250
C	0	3,475
C-2	20	150
D	0	24,000
D-2	20	475

reaction, obtained from the area under the exothermic transition.

Gel time of VE samples at 60°C in the presence of varying amounts of MMA was determined using AIBN (1 phr) as an initiator. VE resin (6 ± 1 g) containing different phr of MMA was placed in a tube kept in a constant temperature water bath maintained at (60 ± 1)°C. Nitrogen was bubbled through the solution and when resin attained the temperature of the water bath, 1 phr AIBN was added. The solution was stirred continuously. A gradual increase in temperature was observed initially, followed by a sharp increase in temperature. Rise in temperature of the samples as a function of time was plotted and gel time was determined by extrapolation.

Isothermal curing of resins was carried out by heating resin samples containing AIBN (1 phr) at 60°C in N_2 atmosphere in a water bath for 2 h, and then in air oven at 60°C for another 2 h.

A Du Pont 2100 thermal analyzer having a 951 TG module was used to assess the relative thermal stability of isothermally cured VE resins diluted with MMA. A heating rate of 10°C/min and a sample mass of 10 ± 1 mg was used. The relative thermal stability of the cured resins was evaluated by comparing initial decomposition temperature (T_i), temperature of maxi-

TABLE III
Effect of MMA Content on Gel Time of VE Resins

Sample designation	MMA content (phr)	T_{gel} (s)[a]
A-2	20	726
A-3	30	606
B-2	20	612
B-3	30	612
B-4	40	612
C-2	20	1176
C-3	30	894
D-2	20	1380
D-3	30	1188
D-4	40	360

[a] Determined at 60°C using 1 phr AIBN.
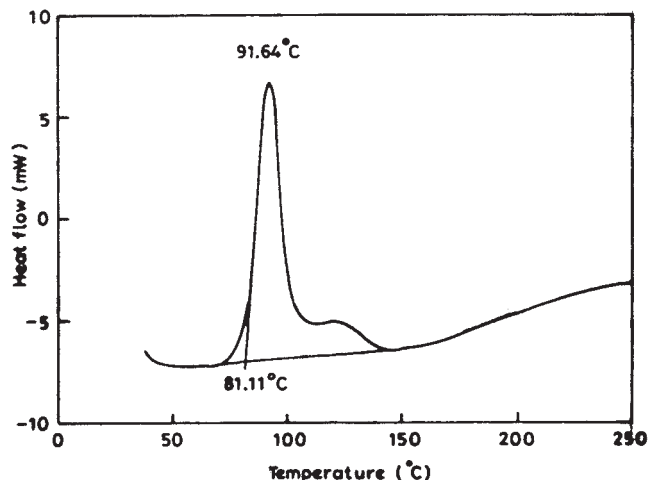
(a)
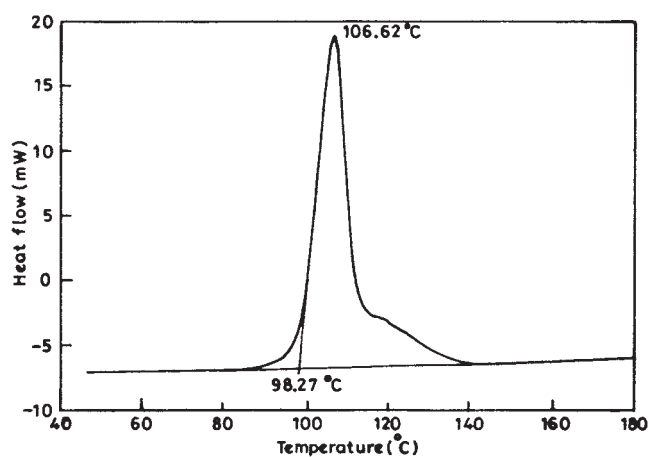
(b)

Figure 5 DSC scans of VE resin (a) sample A and (b) sample B.

mum rate of mass loss (T_{max}), final decomposition temperature (T_f), and char yield at 600°C.

RESULTS AND DISCUSSION

During the reaction of epoxy resin with unsaturated carboxylic acid, a significant decrease in acid number was observed in the first 90 min. The acid number

TABLE IV
Effect of Structure on the Curing Characteristics of VE Resin (DSC)

Sample designation	T_{onset} (°C)	T_{exo} (°C)	T_{final} (°C)	ΔH (kJ/mol)
A	81.1	91.6	126.3	61
B	98.3	106.6	140	90
C	83.4	92.3	141.3	66
D	92.9	1024	147.3	122

TABLE V
Results of Thermogravimetric Analysis of Isothermally Cured VE Resins

Sample designation	T_i (°C)	T_{max} (°C)	T_f (°C)	Char yield[a]
A-2	361	422	451	5.8
A-3	367	432	455	4.0
B-2	383	428	455	2.3
B-3	380	428	451	2.9
B-4	384	430	456	3.3
C-2	390	433	454	2.3
C-3	393	426	445	4.5
D-2	396	428	449	2.3
D-3	399	429	453	2.1
D-4	416	432	438	2.6

[a] Residual weight at 600°C.

decreased slowly after that and a value less than 10 was obtained after 3–5 h of reaction.

The epoxy equivalent weight of ER was found to be 192 g/g equiv. The calculated value for ER ($n = 0$) is 142 g/g equiv (Fig. 1). The molecular weight (M_n) of the VE resins were determined by GPC and were found to be 465, 575, 477, and 503 for resins A, B C, and D, respectively. The theoretical values based on the molecular weight of epoxy resin should have been 470, 556, 456, and 528 for resins A, B, C, and D, respectively.

In the FTIR spectrum of epoxy resin, the absorption peaks at 908 (characteristic of the epoxy group), 1728, and 1170 cm^{-1} (stretching and bending vibrations due to ester linkages) were observed. In the FTIR spectra of VE resin (A–D), strong absorption peak at 1728 cm^{-1} due to ester group of VE and epoxy resin were present and an additional peak was observed at 1636 cm^{-1} due to the terminal double bonds of VE resin. The absorption band at 945 cm^{-1} corresponds to out of plane bending of CH bonds in the VE oligomer. In sample A and C, absorption peak at 908 cm^{-1} (due to the oxirane) was present. This indicates that sample A and C contained (meth)acrylate end group as well as oxirane end groups. In sample B and D, the absorption peak at 908 cm^{-1} was absent (Fig. 3), indicating thereby that all epoxy end groups reacted with the acids.

Figure 4 shows the ^{1}H NMR spectra of epoxy resin and VE resins. In the ^{1}H NMR spectrum of epoxy resin, proton resonance signals due to methine and methylene protons of oxirane ring were observed at 3.19 and 2.6–2.8 ppm, respectively. The resonance signals due to the methylene protons of cyclohexane rings were observed at 1.3–1.8 ppm and for methine protons of cyclohexane ring at 2.8–2.9 ppm. The vinyl protons in acrylate-terminated VE resins (samples C and D) are magnetically nonequivalent and three proton resonance signals were observed at 5.8–6.4 ppm. In methacrylate-terminated VE resins (sample A and
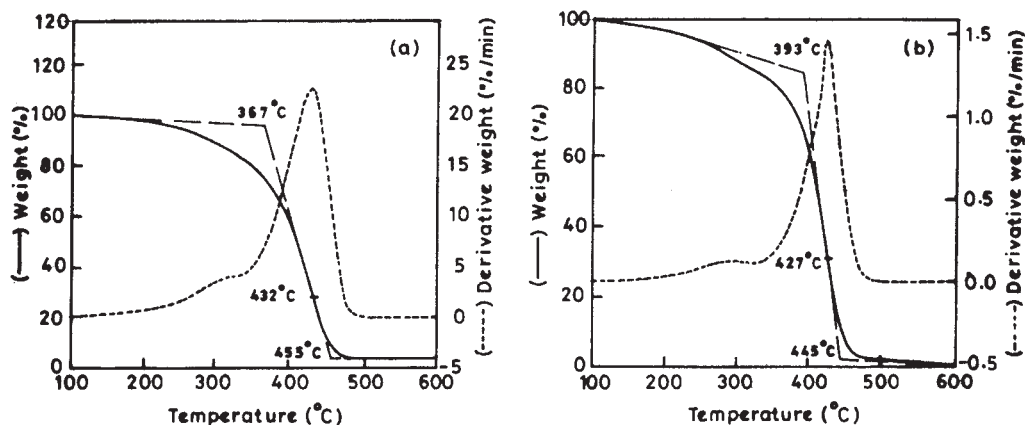
Figure 6 Thermogravimetric traces of isothermally cured VE resins in N_2 atmosphere (a) sample A-3 and (b) sample C-3.

B), only two proton resonance signals due to vinylidene protons were observed at 5.6–6.1ppm. The methyl protons of methacrylate unit (sample A and B) appeared at 1.8–1.9 ppm. The other protons of cyclohexane rings were observed at the same position as in ER. These studies thus confirmed the structure of VE resins and showed that oxirane groups were present in resin A and C and absent in resin B and D.

The viscosity of epoxy resin at 20 rpm was 1025 cps. The viscosity of VE resin samples A, B, C, and D was found to be 3375, 22,000, 3475, and 24,000 cps, respectively, at 20 rpm. Thus an increase in viscosity takes place by introducing (meth)acrylate end caps in epoxy resin. This may be attributed to high molecular weight of VE resin and intermolecular hydrogen bonding of hydroxyl group generated during the reaction of epoxy with (meth)acrylic acid. The viscosity of samples B and D was even greater than that of A and C. The viscosity decreased significantly upon dilution with MMA (Table II).

A decrease in gel time was observed with increasing content of MMA in sample A, C, and D, while in sample B dilution had no effect on gel time (Table III). Acrylate-terminated VE resins (sample C and D) have higher gel time as compared with methacrylate-terminated VE resin.

The DSC scans of VE resins (sample A and B) recorded in presence of 1 phr AIBN are shown in Figures 5(a) and 5(b). The results are summarized in Table IV. A very sharp exothermic transition was observed in the DSC traces in the temperature range of 81–125°C. The curing appears to be very fast initially, but at later stage a tailing effect is observed. This tailing effect (in the temperature range of 120–150°C) may be due to reduction in rate of curing because of increased viscosity of the resin. The process may be diffusion controlled at later stages. An increase in T_{onset} and T_{exo} was observed when di(meth)acrylate resins were cured (B and D) compared with corresponding mono(meth)acrylate resins (A and C). Our

earlier studies have shown that presence of oxirane group facilitates the curing behavior.[14]

The ΔH values for resins A (methacrylate end cap) and C (acrylate end cap) were 61 and 66 kJ/mol, respectively. The ΔH values for methacrylate resins are lower than that of acrylate resins. The curing of double bond in these methacrylate- or acrylate-terminated resins may be compared with that observed in vinyl monomers. For example the heat of polymerization of MMA and methyl acrylate has been reported as 56 and 78 kJ/mol, respectively.[15] This difference has been attributed to the effect of substituents at the double bond. The observed higher ΔH value in acrylate-terminated VE resin can thus be explained.

In di(meth)acrylate resins B and D, the ΔH was 90 and 122 kJ/mol, respectively. If the ΔH is associated only with the polymerization of double bonds of acrylate or methacrylate end caps, then, it is expected that in di(meth)acrylate-terminated resin the ΔH should be twice than that of the mono(meth)acrylate-terminated resins. In resin D, ΔH is 122 kJ/mol whereas the expected value should be 132 kJ/mol. In resin B, the observed value is 90 kJ/mol, which is significantly lower than the expected value of 122 kJ/mol. It is quite likely that oxirane group and hydroxyl group present in resins A and C also participated in the curing reaction. This will lead to the higher value of ΔH in resins A and C compared with resins B and D.

Thermal stability of isothermally cured resins A, B, C, and D containing different phr of MMA was evaluated by thermogravimetric analysis and the results are summarized in Table V.

All the resins were stable upto 310°C and decomposed in a single step above this temperature. Major mass loss was observed above (350 ± 10)°C [Figs. 6(a) and 6(b)]. The initial decomposition temperature (T_i) of resin samples containing the same amount of MMA was higher when acrylate end-capped resins were used instead of methacrylate end caps. For example in

sample A-3, T_i was 367°C whereas corresponding acrylate end-capped resin C-3 decomposed above 393°C. Similarly, the T_i of D-4 was higher (416°C) compared with that of B-4 (393°C). A marginal increase in T_i was observed with increase in MMA content (example A-2 and A-3; B-3, B-4 and C-2, C-3). These results also show that resin containing vinyl end caps (i.e., B or D) were more stable than those containing vinyl and oxirane end caps (resins A and C). The temperature of maximum rate of mass loss (430°C ± 8°C) and the final decomposition temperature (445°C ± 10°C) were marginally affected by the structure of VE resins.

CONCLUSIONS

The synthesis of VE resins using cycloaliphatic epoxy resins and unsaturated carboxylic acids (such as methacrylic/acrylic acids) were successfully carried out in oxygen atmosphere at 80–90°C in presence of imidazole. The viscosity of neat VE resin was higher than that of the parent epoxy resin due to increase in molecular weight as well as intermolecular hydrogen bonding. The heat of curing of acrylate end-capped resins was higher than methacrylate end-capped resin. Thermal stability of cured resins having acrylate end caps was marginally higher than the resins having methacrylate end groups.

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