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Polyester dimethacrylate oligomers and networks

B. Starr, E. Burts, J.R. Upson, J.S. Riffle*

Department of Chemistry, Virginia Polytechnic Institute and State University, 2018 Hahn Hall, Blacksburg, VA 24061-0344, USA

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Abstract

Dimethacrylate matrix resins and composites are becoming increasingly important in structural and coating components in the development of civil infrastructure. Service lives in excess of 50 years in outdoor environments are desirable for these materials. Aliphatic matrix resins derived from cycloaliphatic epoxies and dicarboxylic acids are under investigation as a means of obtaining coatings and fiber reinforced composites with such extreme durability to sunlight. The cycloaliphatic backbone shows reduced ultraviolet adsorption relative to bisphenol-A/epichlorohydrin resins. A series of new dimethacrylate resins and networks were prepared with 800 and 1200 g/mol oligomers and different concentrations of methyl methacrylate as the reactive diluent. Their thermal and mechanical properties have been compared to the bisphenol-A/epichlorohydrin-based dimethacrylate resins, which have either styrene or methyl methacrylate as the reactive diluent. The molecular weight between crosslinks was controlled by both the oligomer molecular weight as well as the amount of the reactive diluent to tailor network properties. The aliphatic networks exhibit glass transition temperatures ranging from ≈ 93–115°C with the higher T_gs associated with lower molecular weight oligomers and higher network densities. The aliphatic networks, in general, also have lower fracture toughness and higher hardness values as compared to networks prepared from bisphenol-A/epichlorohydrin oligomers. The fracture toughness, K_{1C}, increases with the percentage of methacrylate diluent due to the increase in the molecular weight between crosslinks. However, networks cured with styrene as the reactive diluent show the reverse trend in fracture toughness. © 2001 Published by Elsevier Science Ltd.

Keywords: Aliphatic dimethacrylate; Aliphatic vinyl ester; Vinyl ester

1. Introduction

Polymer composites in civil structures are of interest where long service lives (50 or more years) are desirable due to their potential for improved environmental resistance over more traditional materials such as concrete or steel. Commonly used matrices for fiber-reinforced composites include unsaturated polyesters and vinyl esters (Fig. 1a and b) [1–8]. Both of these classes of materials are diluted with a monomer, then copolymerized using free radical chemistry. Typical dimethacrylate resins, the so-called 'vinyl esters', are based on methacrylate terminated aromatic oligomers diluted with styrene. The oligomers generally have molecular weights between 700 and 2000 g/mol and the styrene lowers the viscosity below ≈2000 cps. This low viscosity at 25°C facilitates preform impregnation and fiber wetting during fabrication of fiber reinforced composites in continuous processes such as pultrusion. The dimethacrylate oligomers and styrene copolymerize to form void-free networks.

Most aromatic compounds are inherently susceptible to UV absorption and subsequent degradation. The UV region of terrestrial sunlight ranges from 290 to 400 nm [9,10]. Due to the high energy of radiation at these wavelengths, photo-oxidation can cause chemical and physical changes in polymers and their networks [11,12]. This paper reports the design, synthesis and properties of a new class of resins comprised of aliphatic oligomers (Fig. 2) and methacrylate diluents to minimize UV absorption and degradation. Poly(methyl methacrylate) is far more resistant toward photo-oxidative weathering than polystyrene [13]. In this study, a series of cycloaliphatic networks have been prepared with systematically varied percentages of methyl methacrylate to evaluate their UV adsorption and mechanical properties when compared to the aromatic bisphenol-A-based dimethacrylate networks.

2. Experimental

2.1. Materials

Bisphenol-A-based dimethacrylate (vinyl ester) resin (Fig. 1B) was kindly donated by the Dow Chemical Co.

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* Corresponding author. Tel.: +1-540-231-8214; fax: +1-540-231-8517.
E-mail address: judyriffle@aol.com (J.S. Riffle).

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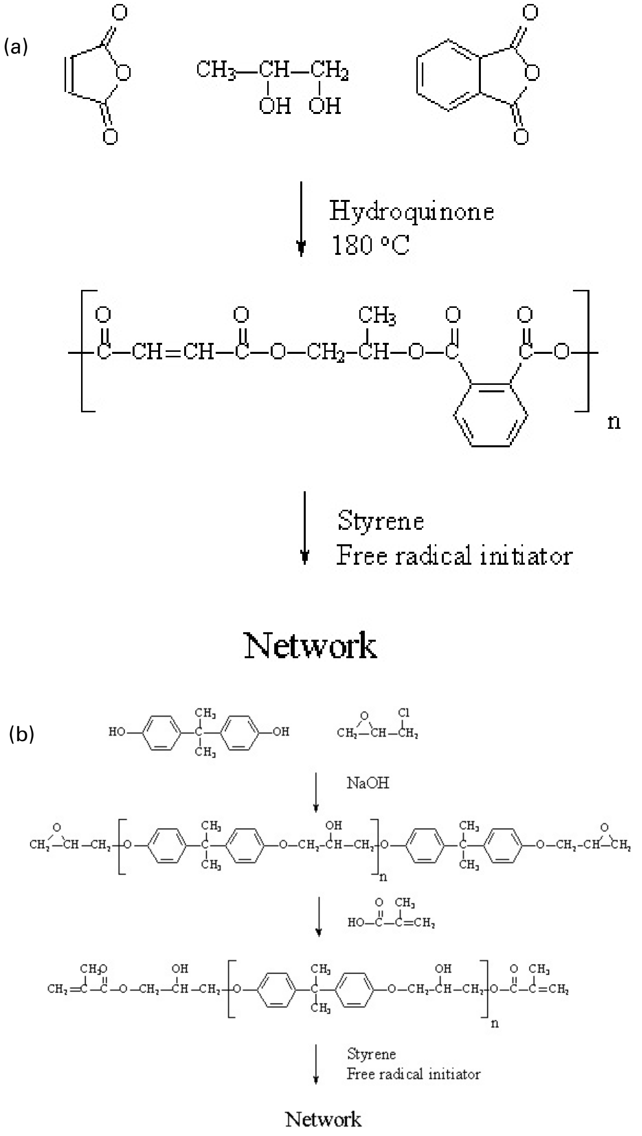

Fig. 1. (a) Synthesis of an unsaturated polyester. (b) Vinyl ester oligomer prepared from bisphenol-A and epichlorohydrin, then endcapped with methacrylic acid.

ERL-4221, a cycloaliphatic diepoxide, was donated by Union Carbide. It was purified by fractional distillation at 175°C/1 Torr. The phosphine oxide, sulfonyl, and hexafluoroisopropylidene diepoxides were prepared by reacting epichlorohydrin with the corresponding bisphenol under basic conditions [14]. Cobalt naphthenate (53 wt% in mineral spirits (6 wt% Co)) was obtained from Alfa Aesar and used as received. All other reagents were obtained from Aldrich.

2.2. Methods

2.2.1. Synthesis of the cycloaliphatic dimethacrylate oligomer

The aliphatic oligomers were prepared in melt, one-pot but two-step synthetic sequences involving nucleophilic epoxy ring opening with carboxylates. An exemplary synthesis for a 1000 g/mol methacrylate terminated oligomer is provided. 3,4-Epoxycyclohexylmethyl 3,4-epoxycyclohexylcarboxylate (ERL-4221) (0.07143 mol, 18.0000 g) was 'pre-reacted' with methacrylic acid (0.05714 mol, 4.9142 g) to form an endcapping reagent. 1.5 mol% triphenylphosphine (0.002143 mol, 0.5614 g) was used with respect to the number of epoxy equivalents, and 500 ppm hydroquinone (0.0146 g) was used as an inhibitor. The reaction was carried out in a three-neck 100 ml round bottom flask at 90°C for 1 h. The remaining epoxies were subsequently reacted with glutaric acid to yield controlled molecular weight, methacrylate terminated, all aliphatic oligomers (Fig. 3). Glutaric acid (0.04286 mol, 5.6572 g) was added to the flask and the temperature was increased up to 98°C to melt the acid, then lowered to 90°C and maintained for 1 h.

2.2.2. Network formation from the cycloaliphatic dimethacrylate oligomer and methyl methacrylate

Systematically varied percentages of methyl methacrylate were added to the oligomer to prepare a series of resins for copolymerization studies. An example of a cure reaction is provided using a 1000 g/mol oligomer and methyl methacrylate. A resin containing 40 wt% methyl methacrylate was prepared by charging a reaction vessel with 30.0000 g of a 1000 g/mol oligomer and 20.0000 g of methyl methacrylate. Accelerators and initiators were added in the following order and the mixtures were stirred well between additions: 0.15 wt% cobalt naphthenate (0.0750 g) in mineral spirits, 0.035 wt% dimethylaniline (DMA) (0.0175 g), and 1.125 wt% methyl ethyl ketone peroxide (MEKP) (0.5625 g). This initiator and accelerator concentration allowed about 20 min working time at 25°C once the MEKP was added. The mixture was poured into silicone mold and cured at 25°C for 24 h, then post-cured at 115°C for 2 h.

2.2.3. Aromatic network formation

Systematically varied percentages of styrene were added to a bisphenol-A-based dimethacrylate (vinyl ester) oligomer to prepare resins for the copolymerization studies. A 40 wt% styrene resin was prepared by charging a stirred reaction vessel with 30.0000 g of the bisphenol-A-based vinyl ester and 20.0000 g of styrene and co-dissolving

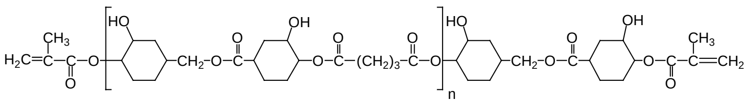

Fig. 2. Cycloaliphatic vinyl ester oligomer (CAVE).

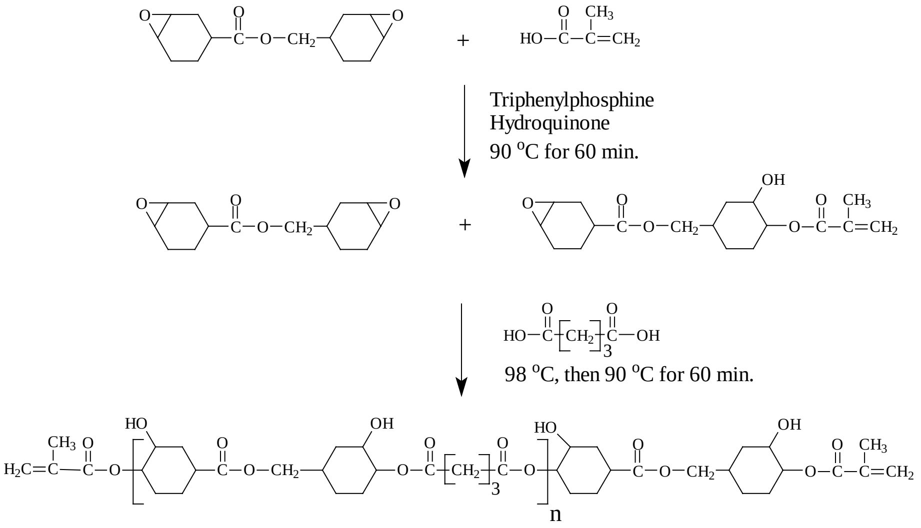

Fig. 3. Synthesis of the cycloaliphatic dimethacrylate. A one-pot reaction done in two steps.

them in the presence of oxygen at 55°C for 2 h. The mixture was cooled to room temperature, then accelerators and initiators were added in the following order and mixed well between additions: 0.15 wt% cobalt naphthenate (0.0750 g) in mineral spirits, 0.035 wt% DMA (0.0175 g), and 1.125 wt% MEKP (0.5625 g). This mixture was poured into a silicone mold and cured at 25°C for 24 h, then post-cured at 115°C for 2 h. Networks cured with methyl methacrylate were prepared analogously and cured under the same conditions.

An alternative curing procedure was also investigated for comparison. Analogous mixtures as described above were charged to a reaction vessel and co-dissolved with 1.1 wt% benzoyl peroxide (0.5500 g). The resin mixture was degassed by mild vacuum at 25°C for about 1 min, then cured in a silicone mold at 140°C for 1 h.

2.3. Measurements

^{1}H NMR was collected on a Varian Unity 400 MHz instrument with a frequency of 399.954 MHz. A 22° pulse angle was used with an acquisition time of 3.7 s and a recycle delay of 1 s. ^{13}C NMR was obtained using the same instrument but with a frequency of 100.578 MHz. A 45° pulse angle was used with an acquisition time of 1.2 s and a recycle delay of 1 s. d$_6$-DMSO was normally used as the NMR solvent. However, the spectra in Fig. 6 were recorded in dimethylacetamide (DMAc) to resolve the acid carbonyl from the ester carbonyl of the epoxy monomer.

Gel permeation chromatography (GPC) was conducted using a Waters GPC 150C at 60°C. The flow rate was 1 ml/min of 0.02 M P_2O_5 dissolved in *N*-methylpyrrolidone. A refractive index and viscosity detector were used. However, the signal to noise ratio was too low to obtain an absolute molecular weight using a universal calibration.

Glass transition temperatures were measured using a Perkin Elmer Pyris 1 differential scanning calorimeter. Because these oligomers exhibit glass transition temperatures near room temperature, all DSC samples were run from −50 to 100°C at 10°C/min. Results are reported from the second heating scans.

Thermal analysis of the networks was investigated using a Perkin Elmer DMA7e Dynamic Mechanical Analyzer. A three-point bend probe was used with a span of 10 mm. Glass transition temperatures were measured from the peak of the tan δ plot with a heating rate of 2°C/min. Elastic moduli were determined according to ASTM D 5934-96. A three-point bending attachment was used with a span of 15 mm. Sample dimensions were 1.50 mm × 2.50 mm × 15.00 mm. A static force scan of 50 mN/min was done isothermally at $T_g + 50$°C to generate the slope of the load versus displacement data. Molecular weights between crosslinks (M_c) were also calculated for the CAVE (cycloaliphatic vinyl ester) 808 and CAVE 1200 series. M_c was calculated from the rubbery modulus E' as shown in Eq. (1), where R is the gas constant (8.314 J/K mol), T (K) is $T_g + 50$°C, and ρ the density at $T_g + 50$°C [15]. Densities at $T_g + 50$°C were estimated by using the room temperature density (measured with a Mettler-Toledo AG204 balance adapted with a Mettler-Toledo density kit) and the coefficient of thermal expansion (CTE) below and above T_g to estimate the new density at $T_g + 50$°C. The CTE was measured above and below T_g using a quartz probe with a heating rate of 3°C/min.

UV–Vis absorption spectra were recorded on the epoxy functional oligomers to compare the backbone absorptions of the vinyl esters. A Hewlett Packard spectrometer 8452A was used with ethanol as the solvent. Acetonitrile was used for obtaining the spectra of the sulfonyl diepoxide.

Network formation was monitored by FTIR using a Nicolet Impact 400 coupled with a thermostatically

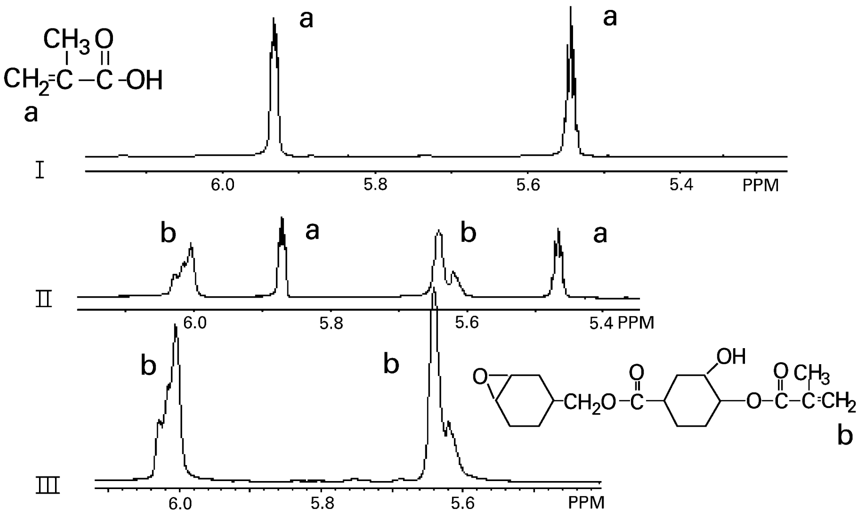

Fig. 4. ^{1}H NMR of the first synthetic step. The reaction of methacrylic acid and ERL-4221 shows a downfield shift of the vinyl protons as methacrylic acid becomes an ester: (I) spectrum of methacrylic acid; (II) spectrum of the 10 min reaction sample; (III) spectrum of the 60 min reaction sample.

controlled IR cell. For the samples cured at 25°C, the reaction was conducted over the 24 h period in a dessicator between salt plates between recording of the IR spectra. The 2 h post-cure was then monitored in situ in the FTIR instrument.

Fracture toughness measurements were conducted according to ASTM D5045-91. An Instron model 4204 was used with a crosshead speed of 1 mm/min, and a three-point bend attachment set to a span of 1 in. All samples were 0.250 in. × 0.125 in. × 1.50 in.

Vickers microhardness was used to compare the hardness of the vinyl ester networks. Microhardness values were measured using a Tukon microhardness tester with a pendulum weight of 1100 g and a repeatability value within 2%.

3. Results and discussion

Durable vinyl ester composites with long service lives, desirably over 50 years, are under investigation for use in civil infrastructure. This study involves the synthesis and structure–property relationships of an aliphatic vinyl ester network and its comparison to aromatic dimethacrylate/styrene networks. It was reasoned that the aliphatic networks should have superior resistance to sunlight damage since they do not absorb radiation in the range where sunlight has the highest intensities (>290 nm). Moreover, it is well known that coatings containing cycloaliphatic epoxides exhibit excellent environmental resistance against sunlight than those containing aromatic glycidyl ethers [16–18].

3.1. Oligomer synthesis and characterization

The synthesis of the cycloaliphatic dimethacrylate terminated oligomer is a one-pot reaction done in two steps (Fig. 3). Both steps in the synthesis are reactions of a carboxylic acid with an epoxide, catalyzed by triphenylphosphine. It is hypothesized that TPP ring opens an epoxy group forming an alkoxide anion, which rapidly abstracts an acidic carboxylic acid proton. The resulting carboxylate then acts as the propagating nucleophilic species. The cycloaliphatic diepoxide starting material was pre-reacted with methacrylic acid to form an endcapping reagent. Thus, the amount of methacrylic acid used relative to the other monomers, calculated using the Carother's equation, determined the oligomer molecular weight [19,20].

The progress of this first step was monitored by ^{1}H NMR and ^{13}C NMR as shown in Figs. 4 and 5, respectively. The chemical shifts of the vinyl protons were monitored by ^{1}H NMR as the methacrylic acid was converted to an ester. The vinyl protons of methacrylic acid (I) have chemical shifts of 5.93 and 5.54 ppm. As the methacrylic acid reacts and becomes an ester, these peaks shift downfield to 6.01 and 5.64 ppm, respectively (II), showing full conversion after 60 min at 90°C. ^{13}C NMR is also useful to follow the synthesis of the first step, formation of the endcapping reagent. The acid carbonyl of methacrylic acid disappears at 170.4 ppm and shifts farther upfield to 166.0 ppm. As with ^{1}H NMR, ^{13}C NMR also shows complete conversion after 60 min at 90°C.

The second step of the dimethacrylate oligomer synthesis chain extends the oligomer with glutaric acid to form the corresponding dimethacrylate. Glutaric acid was chosen due to its relatively low melting point versus adipic acid. NMR peak overlap in d_6-DMSO of the reactants in the chain extension step made it necessary to use DMAc as a solvent for ^{13}C NMR to monitor this step (Fig. 6). The glutaric acid carbonyl carbon resonance was resolved from the ester carbonyl of the epoxy monomer using DMAc versus d_6-DMSO as the solvent for ^{13}C NMR. The ^{13}C NMR spectrum

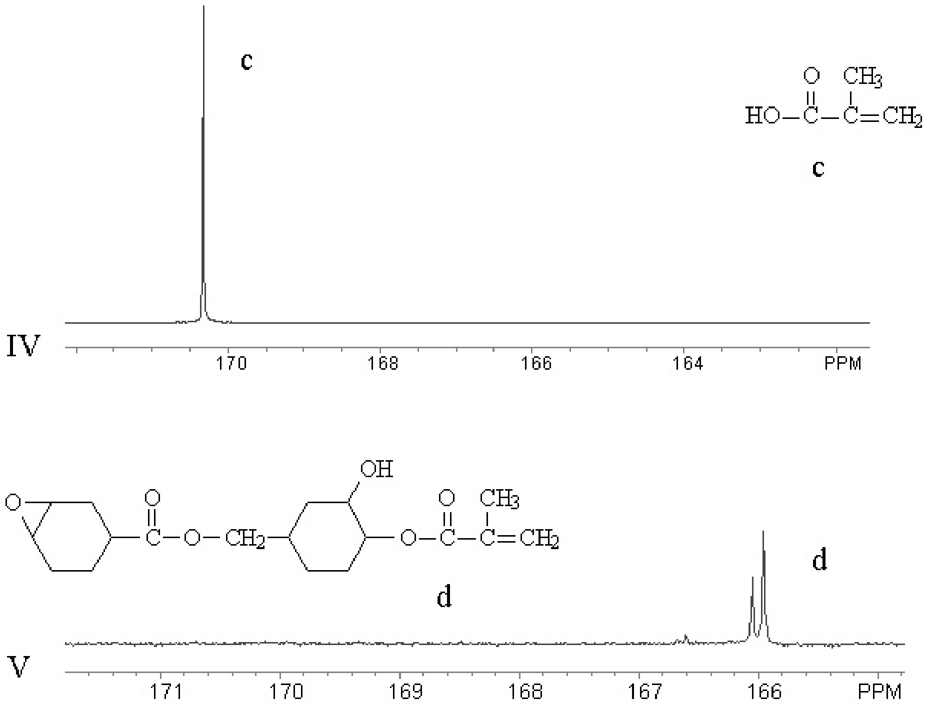

Fig. 5. ^{13}C NMR of the first synthetic step shows the appearance of the newly formed ester carbonyl with the complete disappearance of the methacrylic acid carbonyl: (IV) spectrum of methacrylic acid; (V) spectrum of the 60 min reaction sample.

confirms quantitative conversion to form the controlled molecular weight dimethacrylate oligomer.

The molecular weights of the dimethacrylate oligomers were qualitatively characterized by GPC in NMP using a refractive index detector and polystyrene standards (Fig. 7). The molecular weight range of interest for these matrix materials was between 700 and 2000 g/mol. These molecular weights provided reasonable resin viscosities when diluted with reactive monomers and desirable network crosslink densities. As expected, shifts to lower retention volumes with increasing target molecular weights were consistently observed. Several GPC detector types were

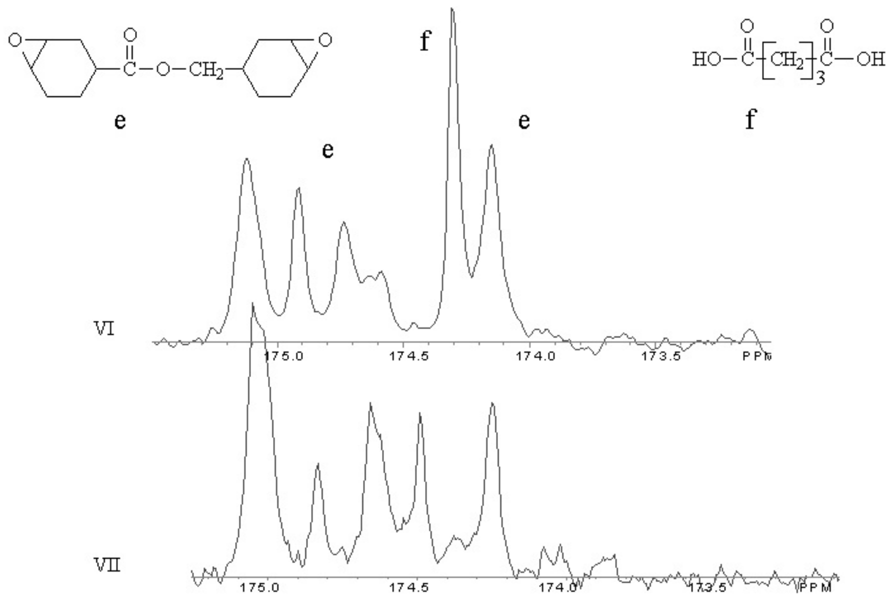

Fig. 6. ^{13}C NMR shows the disappearance of the glutaric acid carbonyl (f) (174.3 ppm) as it becomes an ester (172 ppm).

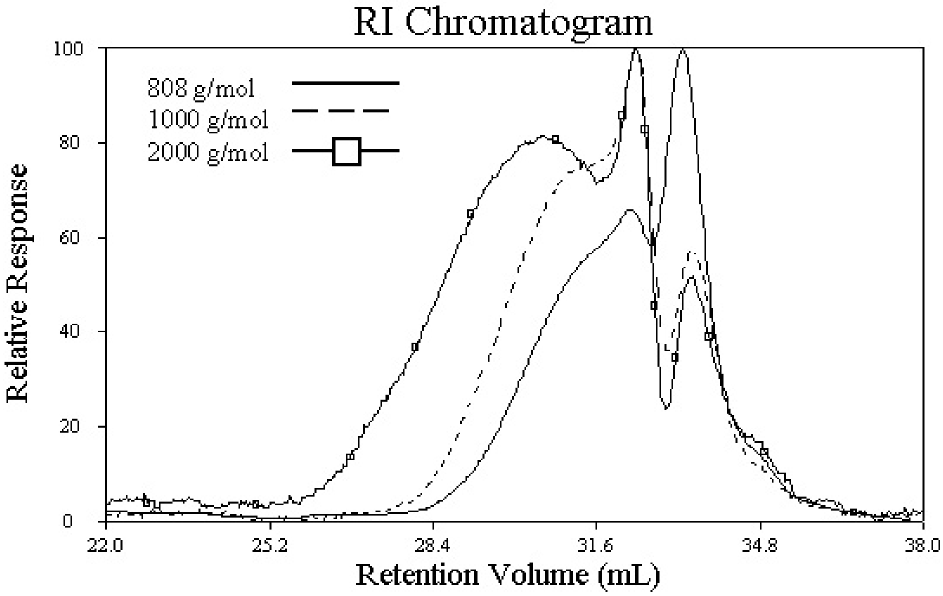

Fig. 7. GPC of three different molecular weight aliphatic dimethacrylate oligomers: (—) 2000 g/mol; (- - -) 1000 g/mol; (–□–) 808 g/mol.

tried to evaluate their utility for these measurements. Refractive index detection provided better sensitivity than either a viscosity or multi-angle light scattering method. Low signal to noise ratios with the latter types were encountered due to the low molecular weight range being investigated. Because these are low molecular weight oligomers, we were not able to use the viscosity detector to obtain an absolute molecular weight with universal calibration curves.

Glass transition temperatures ranged from 29 to approximately 40°C for a series of molecular weights (Table 1). For a given molecular weight, the transition temperatures were similar to those observed for the analogous dimethacrylate series prepared from the bisphenol-A/epichlorohydrin-based vinyl ester oligomers.

UV absorption spectra of oligomers terminated with epoxy groups (i.e. not endcapped with methacrylates to avoid absorbance due to conjugated methacrylate bonds) were investigated at equivalent concentrations (Fig. 8). Ideally, their absorption would be minimal within the sunlight range to reduce the probability of degradation. UV spectra for an acid terminated cycloaliphatic polyester (Fig. 8A) were compared to spectra for four aromatic epoxy oligomers containing isopropylidene, phosphine oxide, sulfonyl and hexafluoroisopropylidene groups (Fig. 8B–E). The cycloaliphatic polyester had minimal absorption in the wavelength range of terrestrial sunlight from 280 to 400 nm. The phosphine oxide diepoxide, although not as promising as the aliphatic structures, had the least absorption in this range of the aromatic oligomers. As expected, the bisphenol-A-based diepoxide had a $\lambda_{\max}$ at 284 nm, which tailed off into the region of sunlight. This polymer, as well as the oligomers containing sulfonyl and hexafluoroisopropylidene groups, absorbed energy strongly in this region.

3.2. Network formation

The so-called vinyl esters and unsaturated polyesters are diluted with reactive diluents to bring the glass transition temperatures down below room temperature for composite fabrication. This provides a sufficiently low viscosity for fiber wetting and preform impregnation under ambient conditions. The CAVE was diluted with methyl methacrylate due to its well-known resistance to UV degradation as compared to styrene. The cycloaliphatic resin diluted with methyl methacrylate was cured between salt plates in a heated cell and monitored by FTIR. The disappearance of the vinyl band at 1638 cm^{-1} was monitored to assess the extent of cure (Fig. 9). The vinyl band corresponds to the methacrylate double bond of both the vinyl ester endgroup and the reactive diluent, methyl methacrylate. As the resin cures at room temperature, there is a small excess of unreacted methacrylate groups that converts into the network upon post-curing at 115°C for 2 h. After post-curing under these conditions, all the methacrylate groups are reacted.

3.3. Network properties

A series of cycloaliphatic dimethacrylate networks

Table 1
Glass transition temperature of the dimethacrylate oligomers

	T_g (°C)
CAVE (g/mol)	
808	29
1000	39
2000	40
Bis-A VE (g/mol)	
700	5

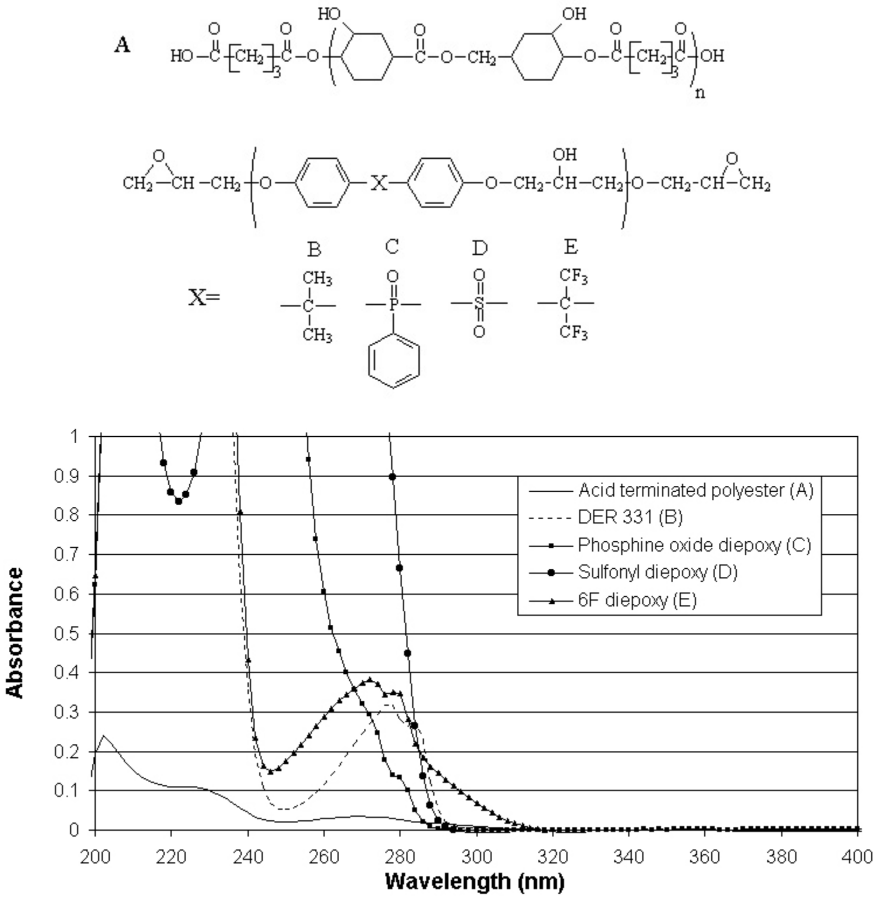

Fig. 8. UV spectra of the acid terminated cycloaliphatic polyester (A), DER 331 (B), phosphine oxide diepoxide (C), sulfonyl diepoxide (D), and hexafluoroisopropylidene diepoxide (E).

prepared from systematically varied percentages of methyl methacrylate were compared to the bisphenol-A dimethacrylate–styrene networks. One advantage of using methyl methacrylate is that reactivity ratios for the methacrylate oligomer and diluent should be similar, whereas the dimethacrylate–styrene reactivity ratios are significantly different [21].

The cycloaliphatic networks with varied percentages of methyl methacrylate exhibit similar network T_gs compared to the bisphenol-A-based dimethacrylate/styrene network T_g of ~115°C [22]. As the molecular weight of the vinyl ester was increased, networks T_gs decreased. This trend was expected since higher molecular weight oligomers produce networks with lower crosslink densities. However, the percent methyl methacrylate had little effect on the network T_gs (Fig. 10).

According to the theory of rubber elasticity, the rubbery moduli of polymer networks should be proportional to the crosslink densities, Eq. (1) [15]. The molecular weights between crosslinks were calculated from the rubbery moduli determined from the slope of the force versus displacement curve in the rubbery region at $T_g + 50$°C and the density at $T_g + 50$°C. Eq. (1) was derived to apply to active network chains only (not meant for chains with dangling ends or unconnected ends) and has four basic assumptions: (1) the chains have Gaussian statistics, (2) the material deforms affinely, (3) the internal energy of the system is independent of the conformations of the individual chains, and (4) the

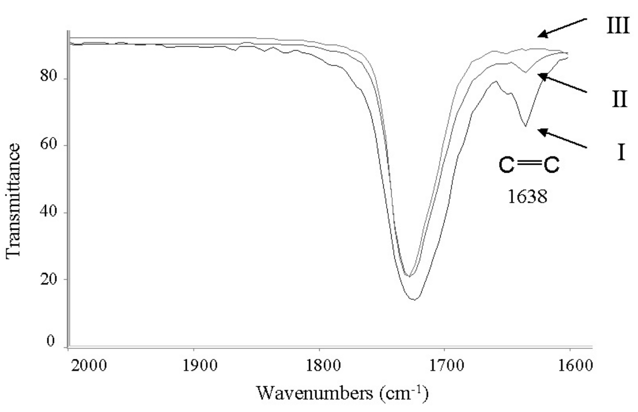

Fig. 9. FTIR of the aliphatic vinyl ester cure. Monitoring the disappearance of the carbon–carbon double bond (1638 cm^{-1}): after adding the initiators (I), after 24 h at room temperature (II), after post-curing at 115°C for 2 h (III).

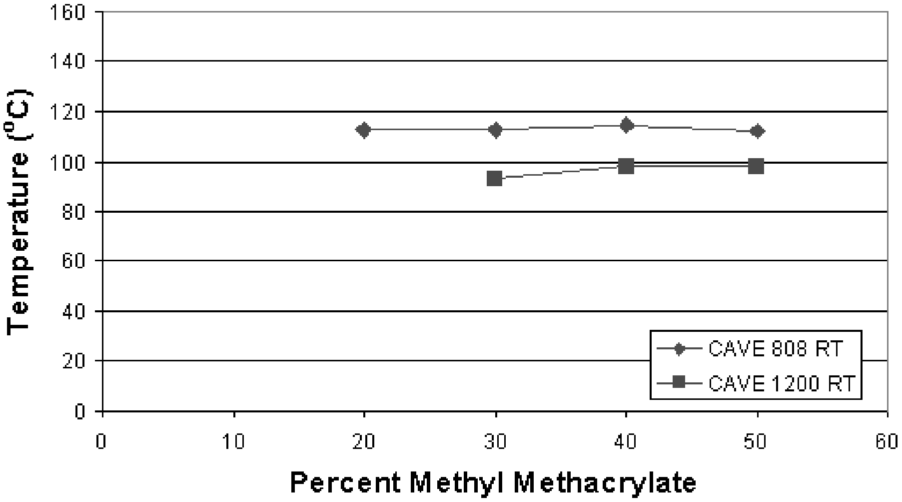

Fig. 10. Network T_gs of two molecular weight CAVEs as a function of percent methyl methacrylate: (A) 1200 g/mol; (B) 808 g/mol.

chains are treated as phantom networks (no excluded volume) [15,22,23]. The experimental trends in M_c followed the expected trend, Fig. 11. As the molecular weight of the oligomer was increased from 808 to 1200 g/mol so did M_c. In both cases, as the percent reactive diluent was increased so did M_c.

$$M_c = \frac{3RT\rho}{E'} \tag{1}$$

Fracture toughness of the CAVE networks was slightly lower than the aromatic materials derived from bisphenol-A for the oligomer molecular weights investigated (Fig. 12). It should be noted that all the materials discussed so far have been cured at room temperature then post-cured at 115°C. Curve (D) in Fig. 12 depicts fracture toughness for materials derived from bisphenol-A vinyl esters and styrene that were cured at 140°C. Interestingly, this suggests that the properties are dependent on the cure path, and that care should be taken to compare networks cured under similar conditions.

The CAVE networks and the bisphenol-A networks increased in toughness as the weight percentage of the methyl methacrylate reactive diluent was increased. This was expected since the molecular weight between crosslinks should increase along this series [24,25]. By contrast, however, toughness of the bisphenol-A vinyl ester–styrene networks decreased as the weight percentage of styrene was increased. This was considered unusual since the molecular weight between crosslinks should also have increased along that series of materials. The decrease in toughness with increasing styrene could be attributed to a compositional effect as well as a difference in reactivity ratios between the methacrylate endgroup and the reactive diluent styrene. A difference in reactivity ratios could lead to a variance in copolymer composition as a function of the extent of cure.

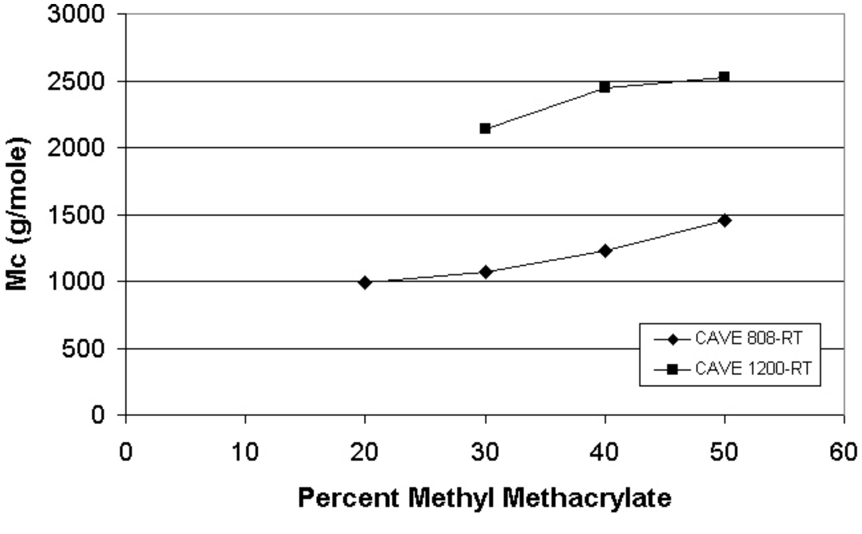

Fig. 11. M_c versus percent methyl methacrylate.

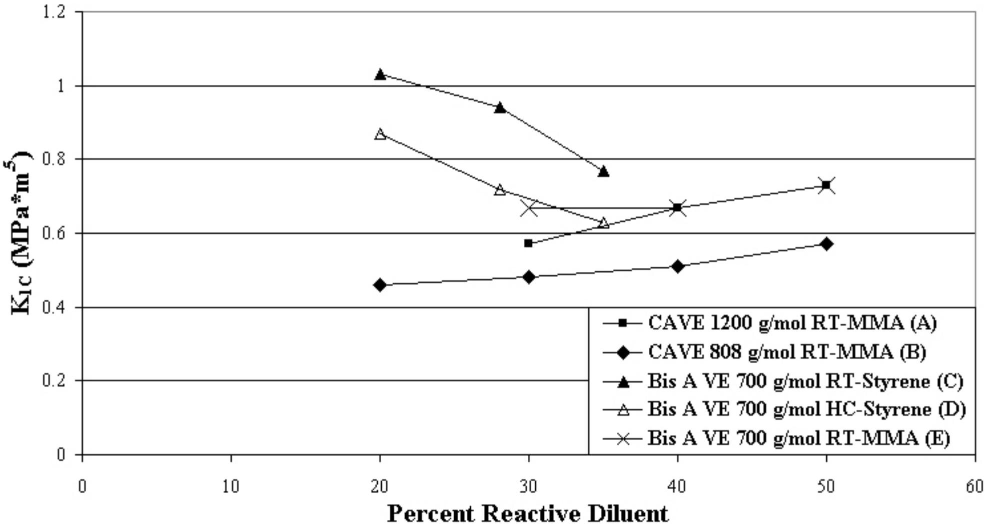

Fig. 12. Fracture toughness (K_{1C} values) of the CAVE–methyl methacrylate networks ((A) and (B) both cured at room temperature and post-cured at 115°C), the bisphenol-A-based vinyl ester (bis-A VE)–styrene networks ((C) cured the same as the aliphatic vinyl esters, and (D) is heat cured at 140°C), and the bisphenol-A-based vinyl ester-methyl methacrylate networks (E) cured under the same conditions as the CAVE networks.

Vickers microhardness was also studied to compare these series of networks (Fig. 13). The cycloaliphatic dimethacrylate networks were harder and the hardness decreased as the percent methyl methacrylate was increased. Thus, as the molecular weight between crosslinks increased, the hardness decreased. The bisphenol-A vinyl ester–styrene networks showed the opposite effect. Hardness values were lower, but increased as the percent styrene was increased. In all cases, decreases in hardness were associated with increases in K_{1C} fracture toughness.

4. Conclusions

Aliphatic dimethacrylate networks have been prepared using methyl methacrylate as the reactive diluent in a one-pot melt reaction conducted in two steps. As expected, these networks showed significantly reduced ultraviolet adsorption throughout the sunlight region of the spectrum. Thus, it is reasonable to expect improved durability in outdoor environments relative to aromatic analogs. Currently, the cycloaliphatic networks and the aromatic networks are being aged under a xenon arc lamp in accelerated aging studies. These studies will be the focus of another publication.

The cycloaliphatic and bisphenol-A networks exhibited increased fracture toughness as the molecular weight between crosslinks increased due to the incorporation of the methacrylate diluent. Microhardness also decreased under these conditions. The aromatic bisphenol-A vinyl esters cured with styrene displayed the reverse trend as styrene was increased. This may be due in part to the difference in reactivity ratios.

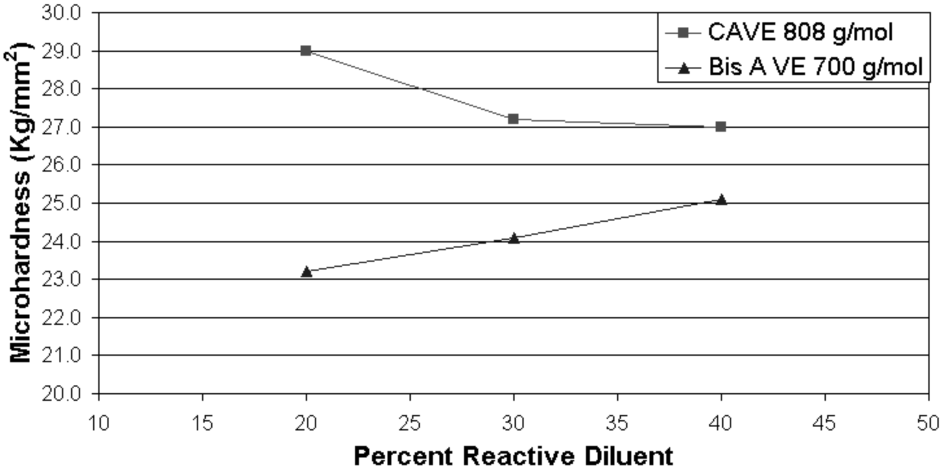

Fig. 13. Vickers microhardness of the CAVE–methyl methacrylate networks and the bisphenol-A vinyl ester (bis-A VE)–styrene networks.

Acknowledgements

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