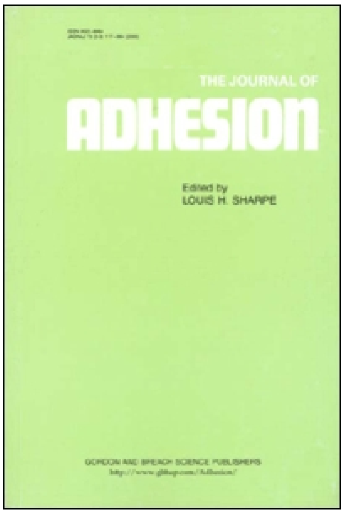

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Poly(propylene oxide) Modified Dimethacrylate Networks

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Poly(propylene oxide) Modified Dimethacrylate Networks

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A series of methacrylated poly(propylene oxide)/reduced styrene content/ dimethacrylate resin systems have been prepared. These modified vinyl esters may be ideal for coatings, toughened matrix resins for fiber-reinforced composites, bridge deck wear surface resins, and structural adhesive applications. Network systems cured with room-temperature and elevated-temperature cure methods have been studied. The network morphologies were investigated by DMA and TEM analyses. The K_{1c} *values of the adhesives increases when systems were cured with the room-temperature cure package. The lap-shear strength of these systems were investigated for structures including composite-to-composite, composite-to-steel, and composite-to-concrete following ASTM D1002. Lap-shear adhesive strengths of all of the adhesives, which had appropriate viscosities on composite substrates, were in the structural regime with values of* ~*13.8 MPa. Room-temperature cure schedules (with and without a postcure) resulted in good adhesive strength on the composite and aluminum substrates, displaying values up to 15.2 MPa.*

Keywords: Modified dimethacrylate resins; Poly(propylene oxide); Reduced volatile content; Free radically cured networks; Fiber-reinforced polymer composite substrate; Structural adhesive

INTRODUCTION

Fiber-reinforced polymer-matrix composites were introduced into construction and infrastructure applications more than half a century

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ago. These materials can display higher strength-to-weight ratios compared with conventional steel and concrete structures, and modular composite components have the potential for leading to reduced construction times. Over the past few decades, there has been an increase in their utilization in infrastructure designs [1]. An upsurge in consumption has recently been predicted because of the aging and environmental deterioration of a large number of structures in the United States. Approximately 4–10% of bridges in the United States are considered structurally deficient and require immediate repair [2, 3], and an average of 150 to 200 bridges in the United States partially or completely collapse each year [4]. The significance of the problem has led scientists and engineers to investigate improved matrix resins for fiber-reinforced composites and improved structural designs. Related to this is the need for the design of load-bearing adhesives for such structures. Conventional mechanical fasteners can cause stress concentrations that can diminish the strengths and lifetimes of polymeric composite structures [5, 6].

The research described herein begins to address some of the issues regarding the design and synthesis of matrix resins and adhesives with potential applications in construction and characterization of those materials. Desirable properties of civil structural matrix resins or adhesives include (1) low viscosities to enhance surface wetting of adhesives to substrates or to enhance fiber preform impregnation, (2) reduced organic volatile content, (3) sufficiently high T_g of the cured networks to avoid creep under environmental conditions, (4) moisture resistance and good weatherability, (5) good adhesion to substrates, and (6) sufficient durability to cyclic deformation to meet the requirements necessary for structural applications.

Unsaturated polyesters and vinyl esters are two classes of polymer-matrix resins utilized in construction and infrastructure [1]. The so-called “vinyl esters” are low-molecular-weight polyhydroxyether oligomers that have been terminated on both ends with methacrylate groups. These dimethacrylate oligomers are commonly diluted with styrene in concentrations up to $\sim$50 weight percent to yield resin mixtures that have low viscosities at room temperature. Vinyl ester/styrene systems are one of the most promising families of matrix resins for infrastructure applications because of these low viscosities at ambient temperature combined with adjustable free-radical cure profiles. The vinyl ester networks have T_gs that can approach 150°C and display excellent moisture resistance and hydrolytic stability [1, 7, 8]. One undesirable feature is that the cure reaction of such resins causes 6–8% shrinkage because of the rather high styrene content [8].

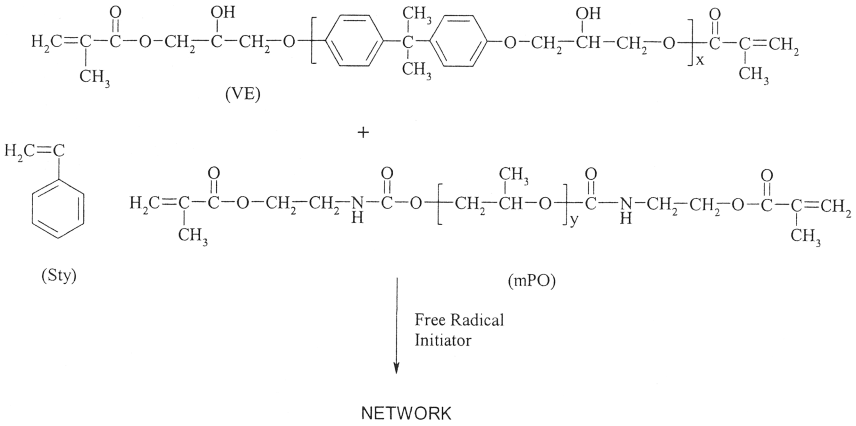

FIGURE 1 Dimethacrylate oligomer-styrene network formation *via* free radical crosslinking copolymerization.

This article reports the synthesis and some of the properties of a series of matrix resins and adhesives composed of methacrylate terminated polyhydroxyethers, methacrylate terminated poly(propylene oxide), and styrene (Figure 1). The resin compositions contain significantly reduced styrene concentrations relative to conventional vinyl ester resins, yet retain the desirable structural network properties. These modified vinyl esters may be ideal for coatings, matrix resins for fiber-reinforced composites, bridge deck wear surface resins, and structural adhesives. The reduced concentration of volatile monomer is also of interest to enhance worker safety because coatings and adhesives from these materials are often applied in the field.

Poly(propylene oxide) was investigated as a component of these resins because of its relatively low viscosity, nonvolatility, and amorphous morphology. The poly(propylene oxide) oligomers are miscible with the vinyl esters at ambient temperature in the compositions investigated herein. Other reactive oligomers such as acrylate terminated poly(acrylonitrile-*co*-butadiene) have previously been investigated as modifiers for unsaturated polyesters and vinyl esters [9, 10]. It was reasoned that the miscibility of the methacrylate terminated poly(propylene oxide)s with the vinyl ester–styrene resins would promote incorporation of the modifier into the networks during cure.

The concentration of styrene in the resins described herein was reduced relative to conventional vinyl esters. These resins contained 20 weight percent styrene as opposed to the ~35–50 weight percent often utilized in commercial vinyl esters. The methacrylate functionalized poly(propylene oxide) (mPO) and polyhydroxyether (vinyl ester) oligomers, and styrene resin compositions were miscible in their uncured states. Their curing behavior and network properties have been studied to identify materials with reduced volatile monomer content that retain or surpass the network properties of conventional vinyl esters.

EXPERIMENTAL

Materials

Dow Chemical (Freeport, TX, USA) kindly provided methacrylate terminated polyhydroxyether oligomers (vinyl ester, VE oligomers) with number average molecular weights of ~700 and 1000 g mol^{-1} (Figure 1). Bayer kindly donated a poly(propylene oxide) (PO) oligomer with a number average molecular weight of 4200 g mol^{-1}, which was prepared with a coordination catalyst that allowed for low unsaturation (0.0034 mEQ/g) and good hydroxyl termination (Pittsburgh, PA, USA). The poly(propylene oxide) was dried under reduced pressure at 70°C overnight prior to derivatization with methacrylate groups. Isocyanatoethyl methacrylate purchased from Aldrich (Milwaukee, WI, USA) was fractionally distilled under reduced pressure at ~110°C and then stored in a flame-dried, brown bottle in the refrigerator until used. Methyl ethyl ketone peroxide (MEKP) was kindly donated by Witco Corporation (Middlebury, CT, USA) and used as received. Benzoyl peroxide, dimethylaniline, dibutlytin dilaurate, and styrene were purchased from Aldrich Chemicals and used as received. Cobalt naphthenate was purchased from Alfa Aesar (Ward Hill, MA, USA) as a 53% solution (6% Co) in mineral spirits and used as received. Dichloromethane, utilized for the swelling investigations, was purchased from Burdick and Jackson (Muskegon, MI, USA) and used as received.

Functionalization of the Telechelic, Hydroxyl Terminated Poly(propylene oxide) Oligomer with Methacrylate Terminal Groups

Dried poly(propylene oxide) with a number average molecular weight of 4200 g mol^{-1} and with hydroxyl endgroups on each end (50 g), isocyanatoethyl methacrylate (3.36 mL, 0.024 mol), and dibutyltin dilaurate (0.025 mL, 500 ppm) were charged to a 100-mL round-bottom flask equipped with a mechanical stirrer. The reaction mixture was purged with dry air and reacted at 40°C for 6 h with stirring. The reaction was monitored by observing the disappearance of the isocyanate peak at 2260 cm^{-1} via Fourier transform infrared spectroscopy (FT-IR). Upon completion, the functionalized oligomer was cooled to

TABLE 1 Resin Compositions Investigated in This Research

Styrene (weight %)	Methacrylate terminated poly(propylene oxide) (weight %)	Methacrylate terminated polyhydroxyether (VE) (weight %)
20	20	60 wt. %, 700 g mol^{-1}
20	20	60 wt. %, 1000 g mol^{-1}

room temperature, hydroquinone (0.591 g, 100 ppm) was added, and the material was stored in the refrigerator under N_2.

Resin Preparation and Network Formation

A series of resin mixtures were prepared with the 700 and 1000 g mol^{-1} methacrylate terminated polyhydroxyether (vinyl ester) oligomers, the methacrylate terminated poly(propylene oxide), and styrene (Table 1). The resins were mixed with a mechanical stirrer at 40–45°C until transparent miscible blends were obtained. The resins were degassed under mild vacuum at 35–40°C prior to network formation to remove oxygen.

Networks prepared in two sets of curing conditions were explored: (1) 25°C for 16 h followed by a postcure at 100°C for 1 h and (2) 150°C for 1 h. The materials that were initially reacted at 25°C were initiated with methyl ethyl ketone peroxide (MEKP) (0.0905 mol/mol vinyl) combined with 0.002 mol cobalt naphthenate/mol vinyl and 8.5×10^{-4} mol dimethylaniline/mol vinyl as accelerators. The higher temperature curing reaction was conducted with 9.31×10^{-3} mol benzoyl peroxide/mol vinyl. Samples prepared by this method were then cooled to 25°C in the oven.

Methods

Dynamic Viscosity

The dynamic viscosities of the resin mixtures were measured using a Bohlin VOR Rheometer (Laboratory Products, Southborough, MA, USA) in oscillation mode at a frequency of 1 Hz. The parallel plate gap was set at $\sim$1 mm and the temperature was ramped from 25–50°C at 2.5°C/min.

FT-IR

The functionalization reactions of the poly(propylene oxide) oliogomers with isocyanatoethyl methacrylate and the curing reactions were studied using a Nicolet Impact Model 400 Fourier transform infrared spectrometer (Madison, WI, USA). A drop of the reaction mixture was sandwiched between salt plates and placed in a temperature-controlled demountable heat cell to obtain these measurements as functions of time.

Swelling Experiments

Swelling measurements were carried out in dichloromethane (CH_2Cl_2) at room temperature. The dimensions of network specimens were small blocks ($3 \times 3 \times 5$ mm). Specimens were immersed in the CH_2Cl_2 until swelling equilibrium was obtained (appropriately two weeks). The swelling equilibria were determined by weighing the samples periodically until constant weights were observed. After equilibrium was achieved, the specimens were weighed in the swollen state and then in the dried state, which was achieved by drying the specimens under reduced pressure at 150°C for three days to a constant weight.

DMA

Network morphologies were investigated using a Perkin-Elmer DMA (Shelton, CT, USA) at 1 Hz with no controls applied in the three-point bending mode. The temperature range was –130 to 225°C at 3°C/min with liquid N_2 as the coolant.

TEM (Transmission electron microscopy)

Imaging of the network morphologies was performed using a Philips 420T TEM (FEI Company, Salem, MA, USA) run at 100 kV. The samples were cryotomed on a Reichert-Jung Ultracut-4E Ultramicrotome with a FC-4D cyroattachment at –100°C and imaged without staining (Sciscope Instrument Company, Iowa City, IA, USA).

Cloud Points

Cloud points of the resins were determined without initiator using an Olympus BX50 Optical Microscope (Dulles, VA, USA) with a photodiode array. A Linkam TMS 93 hot stage (Tadworth, UK) was used to ramp the temperature of the sample from 25 to 150°C at 10°C/min.

SALS

Small-angle light scattering was investigated utilizing a He-Ne laser with a wavelength of 632.8 nm. The sample-to-film distance was 13.5 cm unless otherwise stated. The light scattering was investigated in the V_v mode where the polarization direction of the incident beam was parallel to the analyzer. Phase-separation behavior was monitored at 55°C as a function of time using a THM 600 Linkam hot stage.

K_{1C}

Plane-strain fracture toughness of the networks was investigated following ASTM 5045. Opaque networks were precracked using a modified procedure to ASTM 5045 [11]. The K_{1C} analysis was performed on a 5500R Instron model 1123 instrument (Canton, MA, USA) in the three-point bending mode with a 2.27-kg load cell at a compression rate of 1.0 mm/min.

FE-SEM

The surfaces of the fracture toughness samples were imaged using a LEO 1550 field emission scanning electron microscope (FE-SEM) (Carl Zeiss MicroImaging Inc., Thornwood, NY, USA). Fracture toughness specimens were embedded in epoxy and sputter-coated with gold prior to imaging.

Lap Shear Strengths

The average lap-shear strengths of the adhesively bonded materials were determined following ASTM D1002 and D3136 in triplicate. The lap-shear analysis was performed on a 5500R Instron model 1123 instrument (Canton, MA, USA) with a 2.27-kg load cell at an extension rate of 1.27 mm/min. The substrates investigated were aluminum (60–61), Derakane 411-350 (Dow Chemical, Freeport, TX, USA) vinyl ester reinforced with E-glass woven fabric, and steel (grade A36). The substrates were surface pretreated prior to bonding. The Al (60–61) was cleaned and underwent a P-2 etch [12] and the composite and steel substrates were grit blasted, sonicated, rinsed with acetone, and oven dried at 115°C for 15 min.

RESULTS AND DISCUSSION

Methacrylation of Telechelic Poly(propylene oxide) Oligomer Modifier

The objective was to design toughened dimethacrylate resins with a workable viscosity and reduced volatile diluent content to serve as structural adhesives. The nature of the modifier is therefore an important consideration in the design of such materials. It was reasoned that the poly(propylene oxide) would be suitable for this application because of its low viscosity and miscibility with the uncured vinyl ester resin. Figure 2 shows the reaction scheme for the methacrylation of the hydroxyl endgroups of the poly(propylene oxide) oliogmer *via* urethane chemistry.

The reaction was performed in the melt to limit side reactions of the isocyanate moiety. A tin catalyst (dibutyltin dilaurate) was used to promote hydroxyl attack on the carbonyl. The degree of reaction completion was determined by observing the disappearance of the isocyanate peak at 2260 cm^{-1} using FT-IR.

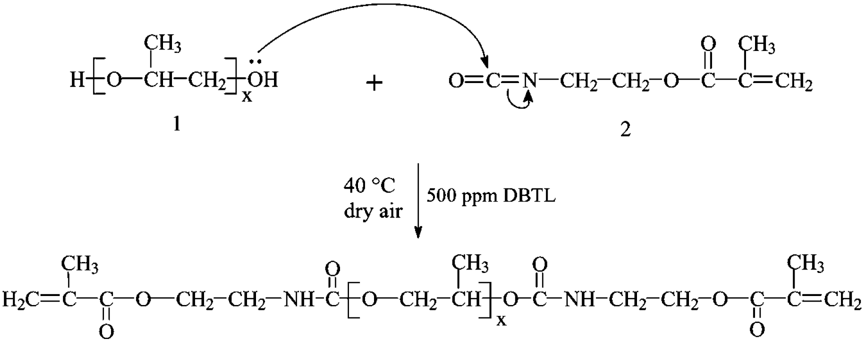

FIGURE 2 Methacrylate termination of poly(propylene oxide) using isocyanatoethyl methacrylate in a melt reaction.

Formulation of Modified Vinyl Ester Resins

The relatively low viscosity of the methacrylate terminated poly (propylene oxide) oligomer (mPO) compared with the dimethacrylate resins (VE) allowed for compositions to be prepared with reduced styrene levels. Viscosity is a significant factor in the design of a structural adhesive for application and joint filling at a construction site. Commercial structural adhesives, such as Plexus® (Danvers, MA, USA), have viscosities of ~40–60 Pa·s at ambient temperatures. Table 2 shows that the dynamic viscosities of these mPO-containing matrix resins were determined in a temperature range between 25°C and 50°C (Table 2).

The viscosity values ranged from ~10 to 125 Pa · s at 30°C, depending on the resin composition, suggesting that these are all in a workable range. However, in actual practice, the slightly lower viscosity displayed by the sty/mPO/VE resins composed of the 700-g/mol vinyl ester might require an additional filler to decrease any flow out of the adhesive joints. The 1000-g/mol vinyl ester oligomers without

TABLE 2 Dynamic Viscosities of Resin Mixtures at Expected Application Temperatures

	Dynamic viscosity (Pa · s)		
Resin composition (wt. %)	30°C	40°C	50°C
20% styrene/20% mPO/60% VE (700)	9.0	3.4	1.6
20% styrene/20% mPO/60% VE (1000)	125	64.2	44.4

added styrene were too viscous to be prepared. Miscibility and the appropriate viscosity allows for a uniform distribution of the modifier throughout the styrene/vinyl ester resin. During the polymerization, the methacrylate terminated poly(propylene oxide) chemically reacts with the vinyl ester and styrene *via* the methacrylate functional endgroups.

Free Radical Cure of Modified VE Resin Systems

The two cure methods were investigated. The room temperature study was important to help assess the viability of the modified vinyl ester resin to serve as a structural adhesive applied at the construction site. However, a postcure at 100°C for 1 h was investigated to quantify the extent of conversion at ambient temperatures. Alternatively, the elevated temperature cure method (150°C for 1 h) is applicable to the preparation of preformed structures. The cross-linking of the functional groups in the resins can be monitored by observing the disappearance of the styrene vinyl groups (943 cm^{-1}) and **both** the methacrylate groups of the vinyl ester and the methacrylate terminated poly(propylene oxide) (910 cm^{-1}) *via* FT-IR (Figure 3). The extent of conversion was monitored in real time for a resin mixture cured at room temperature followed by a postcure at 100°C. The resin-containing initiator was placed in a temperature-controlled cell and the room-temperature cure was monitored as a function of time for 16 h.

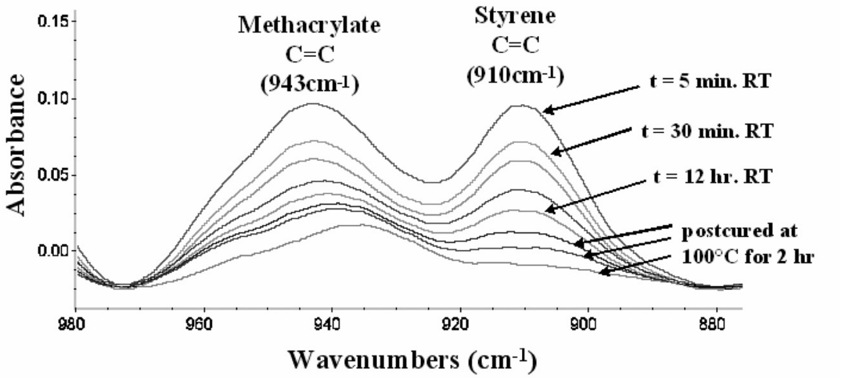

FIGURE 3 Room temperature conversion monitored *via* FT-IR with a 100°C postcure, observing the disappearance of the methacrylate and styrene double bonds at 943 and 910 cm^{-1}, respectively.

A postcure was introduced after the 16-h room-temperature cure period, where the cell was ramped quickly to 100°C and monitored for 1 h. Peak heights of the methacrylate vinyl groups (out-of-plane bending of CH group) at 943 cm^{-1} and the styrene vinyl group (wagging of CH_2 group) at 910 cm^{-1} were normalized using the vinyl ester backbone peak at 830 cm^{-1} as an internal normalization peak. Earlier investigations have shown that the methacrylate double bond peak overlaps with a peak in the vinyl ester backbone in the 943 cm^{-1} region, which accounts for the residual peak absorption [7, 8].

The backbone absorbance was removed by subtracting a fully cured system's FT-IR spectrum from the normalized spectra. The fully cured network used in these corrections was obtained with a cure at 150°C using benzoyl peroxide (BPO) initiator. It had been previously established, using FT-IR and solid-state ^{13}C NMR spectroscopy, that these conditions lead to full cure [8]. Using this procedure, after 16 h, the room-temperature conversion of the methacrylate vinyl groups and styrene double bonds for a 20% styrene/20% mPO/60% VE (700) resin was determined to be approximately 71% and 88%, respectively. When the sample was postcured at 100°C for 1 h, the conversion proceeded to 92% and 98% for the methacrylate and styrene groups, respectively. These investigations suggest that the room-temperature cure may not provide sufficient conversion for application of these resins at a construction site. However, the near-complete conversion obtained after a 100°C postcure suggests that the introduction of an external heat treatment onsite may be a means to ensure consumption of the volatile monomer reactants.

Modified Vinyl Ester Network Physical Properties

Swelling Index

The chemical resistance of the networks was investigated by swelling experiments in dichloromethane at room temperature. As stated in the experimental section, the specimens (3-mm thick) were immersed in dichloromethane until they obtained swelling equilibrium and then dried in a vacuum oven at 150°C until they reached a constant weight. Dichloromethane was chosen as the swelling liquid because it is a good solvent for all of the resin components. Therefore, any extractables would be assessed by the gel fraction analysis. Networks cured by two different cure methods were investigated in terms of the degree of swelling or swell indices (Equation 1) and gel analysis. The swell index is defined in terms of the weight of gel in the swollen state (W_{SW}), weight of the gel in the dry state (W_d), density of the gel (ρ_g), and the density of the solvent (ρ_s). A swell index of one corresponds to no swelling of the network. The gel fraction is the ratio of the weight of a swollen extracted gel and the initial weight of the network prior to swelling:

$$\text{Degree of swelling} = 1 + \frac{[(W_{\text{sw}} - W_{\text{d}})(1/\rho_{\text{s}})]}{[W_{\text{d}}(1/\rho_{\text{g}})]}. \tag{1}$$

Swelling experiments were performed on the modified networks containing 20% wt. styrene, 20% wt. mPO, and 60% wt. vinyl ester (700 or 1000 g/mol) oligomer cured by the two different cure methods (Figure 4). In addition, an unmodified 700 g/mol vinyl ester network containing 20% wt. styrene (sample 1) cured at room temperature, reported by Burts, was used as a comparison [13]. All of the networks containing the lower M_n vinyl ester resin (700 g/mol) exhibited relatively low swelling in dichloromethane, which is a solvent for all resin components. The swelling of the unmodified vinyl ester (700 g/mol VE) network is comparable with the mPO modified networks containing the same M_n vinyl ester. The networks containing 1000-g/mol vinyl ester resin oligomers show higher swelling, which is expected because of the lower cross-link density obtained with the higher M_n VE oligomer.

Despite the extent of swelling observed, high gel fractions were observed for all of the toughened networks in dichloromethane (Table 3). The FT-IR analysis and gel fraction analyses both indicate that the networks are significantly cured by either of the two curing procedures utilized.

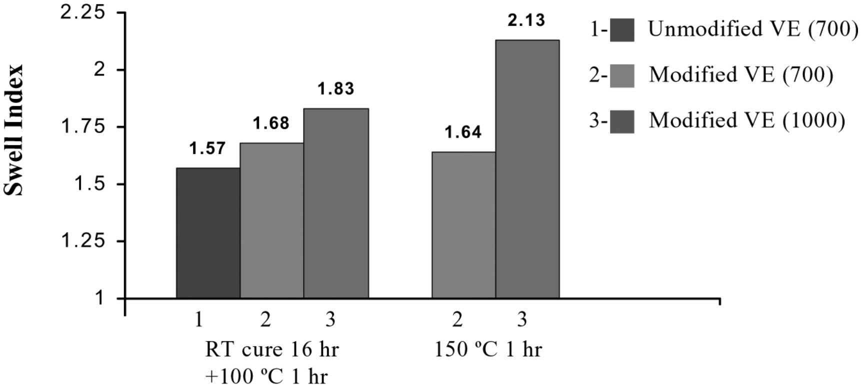

FIGURE 4 Swelling index of an unmodified network and mPO modified networks in dichloromethane. Modified networks are comprised of 20 wt.% styrene/20 wt.% mPO/60 wt.% VE (700 or 1000 g/mol).

TABLE 3 Gel Fractions of Modified Vinyl Ester Networks Investigated by Immersion in Dichloromethane Solvent

Network composition	Cure method	% gel
20% sty/20% mPPO/60% VE (700)	16 h rt + 100°C 1 h	93.4 ± 0.7
	150°C	97.6 ± 0.3
20% sty/20% mPPO/60% VE (1000)	16 h rt + 100°C 1 h	89.7 ± 2.8
	150°C	97.5 ± 0.6

Morphological Studies in Relation to Network Properties

Interestingly, these modified networks formed by the two different cure methods produced networks with extremely different morphologies. When cured at 150°C with BPO, the once-transparent mixture of liquid reactants turned opaque. However, all room-temperature reacted systems remained transparent after cure. DMA was used to assess whether any type of phase separation occurred during cure by determining the occurrence of a second glass-transition temperature (Table 4).

The DMA thermograms of the 25°C cured materials followed by a postcure at 100°C displayed only one distinct T_g in the range of ~85–100°C. It should be noted that the T_gs of these networks approached the postcure temperature (100°C) where vitrification occurred. In contrast, the thermogram curve of the opaque networks (resins cured with BPO at 150°C) displayed two T_gs. The lower temperature T_g is associated with the mPO component whereas the higher temperature T_g is associated with the vinyl ester/styrene domain (see Table 4). Hence, in view of the T_g data and the lack of optical clarity of the sample, it can be stated that macrophase separation developed in the thermally cured networks composed of the two components (mPO and vinyl ester/styrene).

Morphology studies using TEM indicate a structural periodicity of the networks cured with BPO at 150°C (Figure 5B and D). The dark

TABLE 4 T_g Values Determined by Dynamic Mechanical Analysis for Modified Vinyl Ester Resins Cured by the Two Different Methods

	Tan delta (°C)		
		150°C 1 hr	
Network compositions	25°C 16 hr + 100°C 1 hr	T_{gmPO}	T_{gVE}
20% sty/20% mPO/60% VE (700 g/mol)	96	−70	137
20% sty/20% mPO/60% VE (700 g/mol)	87	−34	135

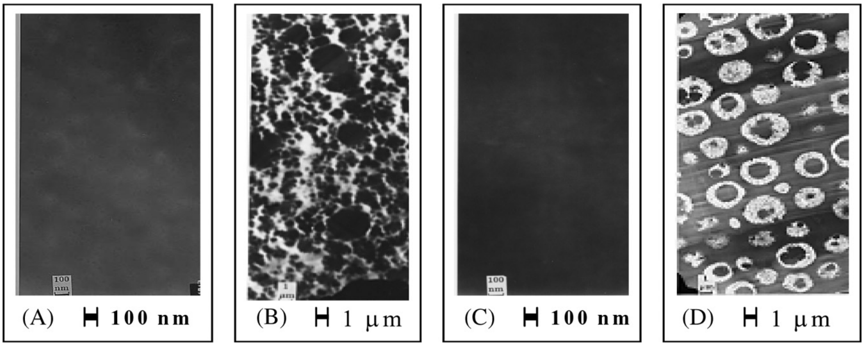

FIGURE 5 TEM images of resins cured with MEKP at ~25°C for 12 h followed by a postcure at 100°C for 1 h (A and C) and resins cured with BPO at 150°C for 1 h (B and D). The resin compositions all contain 20 wt.% styrene/20 wt.% mPO/60 wt.% VE (X) where X = 700 g/mol for A and B and X = 1000 g/mol for C and D.

regions of the TEM images correspond to the vinyl ester/styrene regions and the lighter areas represent the poly(propylene oxide) modifier. Interestingly, it appears that the molecular weight of the vinyl ester resin affects the location of the phase-separated poly (propylene oxide) modifier in the networks cured at the elevated temperature. The poly(propylene oxide) modifier appears as the continuous phase of the network containing the lower M_n vinyl ester oligomer (Figure 5B), whereas the reactive thermoplastic modifier forms domains in the network containing 1000-g/mol vinyl ester. TEM analysis of the networks cured at ambient temperature with MEKP and a postcure at 100°C for 1 h showed no significant structure or multiphase nature (Figure 5A and C), which helped us to understand the origin of the single T_g values observed for the networks cured by this specific route.

Lower Critical Solution Temperature (LCST) of Resin Mixtures

Optical Microscopy and Cloud Point

Phase separation of initially miscible rubber modified resins during cure has been extensively investigated [14–19]. In epoxy-based resins, phase separation was attributed to hydrogen-bonding effects between the rubber modifier and the epoxy resin backbone using various techniques [16]. In contrast to the promotion of phase separation through molecular weight build-up as is common in many of the rubber modified epoxy-based resins, we have noted from cloud point analysis studies that LCST behavior plays an important role. In brief, LCST considerations were suggested based on the fact that our resin mixtures with modifier became turbid very early on at high temperatures, suggesting that they may phase-separate even before molecular weight build-up occurs through cross-linking. To verify this, thin films of the resins were studied by an optical microscope equipped with a hot stage. Inducement of phase separation was monitored during a temperature ramp by measuring the intensity of transmitted light. When the cloud point temperature was reached, a large decrease in transmitted light occurred. To be certain that molecular weight build-up was not the cause of the onset of turbidity, the cure reaction was inhibited by the addition of 500 ppm of hydroquinone. From the hot stage optical measurements, the resin mixture containing 20% styrene/ 20% mPO/60% VE (1000) was found to exhibit a cloud point at 60°C or above (Figure 6).

The cloud point of the same adhesive composition (containing BPO initiator) was also investigated during cross-linking and it became turbid at 55°C. These investigations suggest that the resin mixtures cured at 150°C are phase-separated prior to or during the very early stages of polymerization and lead to opaque phase-separated networks.

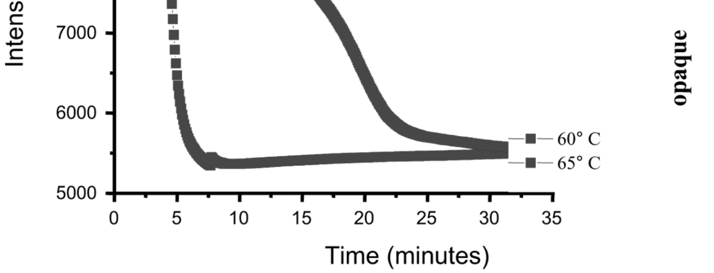

FIGURE 6 Cloud point analysis of resin containing 20 wt.% styrene/20 wt.% mPO/60 wt.% VE (1000) without initiator as a function of time *via* optical microscopy. The cloud point was observed at 60°C.

Small Angle Light Scattering

Use of small angle light scattering (SALS) is a well-known method to help monitor reaction-induced phase separation of polymer blends or a mixture of low-molecular-weight oligomeric reactants [17–19]. For this work, SALS was used to study the resin morphology as the transparent mixture proceeds from a single phase through phase separation to a two-phase system above the cloud point temperature. The scattering study of a mPO modified 1000-g/mol VE resin was monitored as a function of time at 60°C, which was the cloud point for the resin (Figure 7). The SALS pattern shown on the left in Figrue 7 displays a maximum in scattered intensity with scattering angle that in turn moves to smaller angles with cure time. This behavior indicates that the structural periodicity arising from phase separation is increasing with time. The periodicity was estimated using Bragg's law (Equation 2), given by

$$d = \frac{\lambda/n}{2\sin\frac{\theta}{2}} \tag{2}$$

where λ is the wavelength (632.8 nm), n is the refractive index (assumed to be 1.5), θ can be determined using the arctan (B/sample-to-film distance), and B is the radius of the scattering ring. The interdomain distance of the resin was determined using Equation (2) from the scattering patterns produced by the resin held isothermally at 55°C. From this analysis, the periodicity increased from $\sim$1.7 μm at 12 min to 3.3 μm at 31 min. Phase separation of an amorphous polymer blend that occurs where the peak maximum appears at a finite

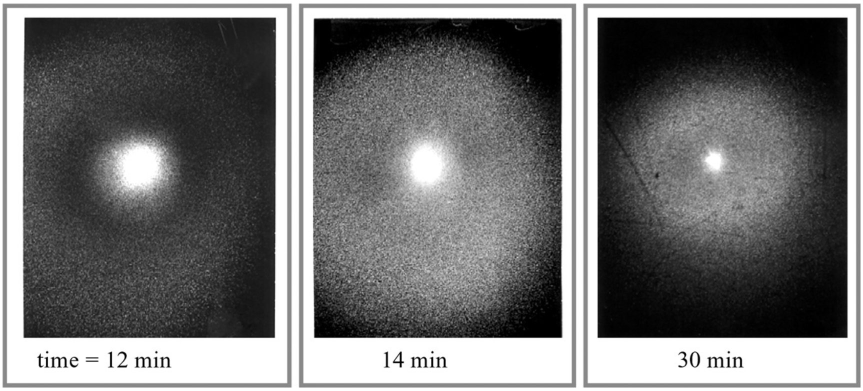

FIGURE 7 The V_v scattering pattern of a resin comprised of 20 wt.% styrene/20 wt.% mPO/60 wt.% VE (1000) and BPO held isothermally at 55°C as a function of time.

distance and moves to smaller distances is often indicative of spinodal decomposition. Further evidence for the fact that this behavior is spinodal decomposition versus nucleation and growth behavior is provided later in this article. These observations are comparable with those reported for rubber modified epoxy systems [18, 19].

By contrast, the room-temperature-cured materials remain well below the cloud point while the molecular weight builds. It is proposed that phase separation does not occur during the 100°C postcure because the poly(propylene oxide) PO is already "locked" into the network as a result of the prior network formation that occurs at the initially lower cure temperature. The resins cured at elevated temperatures displayed multiphase morphology, as observed using TEM and SALS. It was expected that the presence of two T_gs of these materials would influence the fracture toughness.

Fracture Toughness, K_{1C}

Yoon *et al.* were among the first, to introduce the use of reactive thermoplastic oligomers to toughen networks. Those researchers also found that above a critical concentration of reactive thermoplastic modifier in epoxy resins, the cured network will display a phase-inverted morphology where the covalently linked thermoplastic is the continuous phase. Furthermore, they showed that these morphologies, produced by the presence and copolymerization of the reactive thermoplastics, displayed significant increases in fracture toughness. Since then, a variety of reactive thermoplastic oligomers have been reported to modify epoxies and other thermosetting resins [21–24].

The fracture toughness produced by the incorporation of methacrylate terminated poly(propylene oxide) within the styrene/dimethacrylate network compositions was investigated using a three-point bending method. For each test specimen, a load-versus-displacement curve was obtained. The toughness values were determined in terms of the plane strain critical stress intensity factor (K_{1C}). The K_{1C} values were calculated from the load causing crack propagation in each prenotched sample using a relationship established on the basis of elastic stress analysis [25] (Equation 3):

$$K_{1C} = \frac{p}{BW^{3/2}} \frac{3(X)^{1/2}[1.99 - X(1-X)(2.15 - 3.93X + 2.7X^2)]}{2(1+2X)(1-X)^{3/2}}. \qquad (3)$$

In this relationship, p is the load, B is the specimen thickness, W is the specimen width, a is the crack length, and $X = a/W$. Networks cured at room temperature then postcured at 100°C exhibited high fracture toughness ($1.08 \pm 0.16\,\mathrm{MPa \cdot m^{1/2}}$, $1.4 \pm 0.08\,\mathrm{MPa \cdot m^{1/2}}$) relative to the same resin compositions cured at elevated temperatures with BPO (Figure 8). The room-temperature-cured materials, which gave high K_{1C} values, also displayed single-phase morphologies. The low fracture toughness values of the networks containing 700 g/mol of vinyl ester oligomer cured at elevated temperature are believed to be due to the phase separation of the PO caused by the low cloud point temperature. The lack of PO incorporation into the styrene/vinyl ester domain makes these resulting networks flexible and weak. Unexpectedly, the networks composed of 1000 g/mol of vinyl ester oligomer cured at elevated temperatures, where the vinyl ester is the matrix phase and the mPO modifier is the domain phase (Figure 5D), displayed lower fracture toughness values than the unmodified network. Moreover, the room-temperature-cured, single-phase materials containing mPO modifier also have significantly higher fracture toughness than an unmodified vinyl ester/styrene network formed with similar viscosity and styrene content (Figure 8). However, the fracture toughness is similar to or slightly lower than butadiene–acrylonitrile-based copolymer liquid rubber modified vinyl

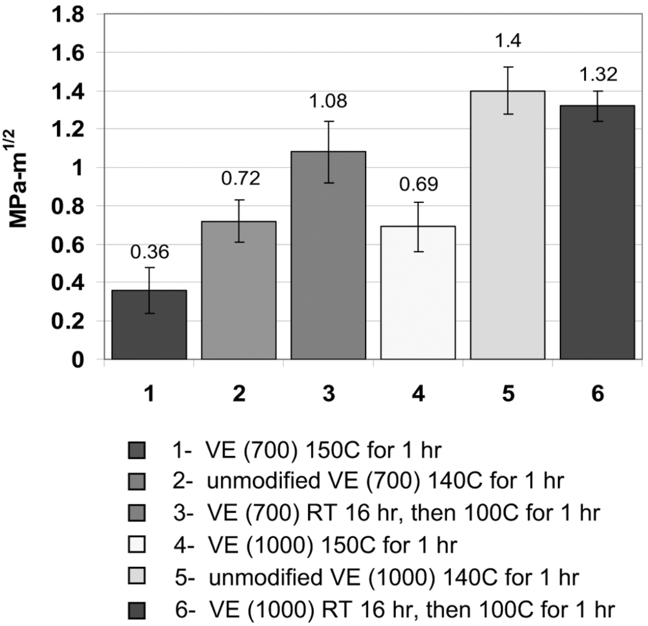

FIGURE 8 Fracture toughness by three-point bending test of mPO modified networks containing 20 wt.% styrene/20 wt.% mPO/60 wt.% VE (700 or 1000 g/mol) and unmodified styrene/vinyl ester networks.

esters reported in the literature [26]. To better understand the toughness results and interpret how the modifier is incorporated into the network, additional experiments to study the stress relaxation and rheology of the network during cross-linking are necessary. Nonetheless, the observed relationship between phase morphology and fracture toughness suggests that optimal properties may be obtained by curing slightly below the cloud points of the resins. This approach may allow for incorporation of a large portion of the PO into the network prior to phase separation.

The fracture surface created by the three-point bending test was imaged using scanning electron microscopy (Figure 9). The fracture surface for the single-phase room-temperature-cured material shows a uniform network morphology (Figure 9A). However, the images of the phase-separated high-temperature-cured networks further suggest that the polymerization above the cloud point inhibits incorporation of the methacrylate groups of the poly(propylene oxide) thermoplastic modifier with the styrene and vinyl ester oligomer. In fact, the cavitations observed compare well with the interdomain or structural periodicity determined by TEM and SALS studies. As noted in the TEM micrograph for the higher-temperature-cured material (Figure 9B), it is very clear that this morphology displays an interconnected texture of high periodicity, which is highly suggestive of its formation by spinodal composition. This micrograph gives further proof of the earlier statements made in this paper that the observed SALS

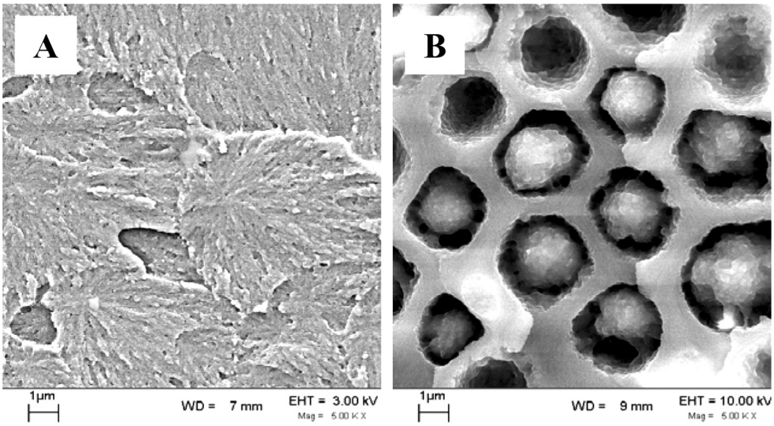

FIGURE 9 SEM imaging the fracture surface of the three-point bending samples of networks comprised of 20 wt.% styrene/20 wt.% mPO/60 wt.% VE (1000) cured at A) rt for 16 h followed by 100°C for 1 h and B) 150°C for 1 h, where the vinyl ester/styrene represents the majority of the matrix phase and the poly(propylene oxide) modifier the domain.

periodicity that shifted to smaller angles with time arises from the spinodal decomposition behavior displayed by this higher-curing-temperature condition. However, the phase-separated regions create a final material that is not tough. The mechanism of toughening reported by Yoon and McGrath, obtained by a phase inversion, is not observed in these networks [24]. It was anticipated that the covalent bond formed between the reactive groups of the mPO and the resin would improve the toughness without diminishing the thermomechanical properties of the network, as it would when a nonfunctional thermoplastic is used as a modifier [24]. The lack of improved toughness observed in the networks cured at elevated temperatures appears to be due to a distinct separation in the location of the methacrylated PO relative to the styrene/dimethacrylate components above the cloud point temperature of the resin.

Lap Shear

Adhesive strengths of the networks were investigated by single lap-shear analysis. All of the adhesives contained 20 wt.% styrene, 20 wt.% mPO (4200 g/mol), and 60 wt.% vinyl ester oligomer (700 or 1000 g/mol). The adhesives were bonded to aluminum–aluminum, steel–steel, and vinyl ester-based composites and cured by the same cure methods previously described. The adhesives containing the 1000-g/mol vinyl ester oligomer cured with BPO at 150°C exhibit structural strength on aluminum and composite substrates (23.5 ± 1.5 and 18.1 ± 1.2 MPa, respectively) (Figure 10). The high adhesion strengths of the networks cured at elevated temperatures further suggest that these adhesive compositions may find utility in the construction of preformed composite structures.

In addition, the adhesives containing the lower M_n vinyl ester oligomer (700 g/mol) were reacted at room temperature following two different cure schedules: (1) room temperature cured for 1 week without a postcure, and (2) room temperature cured for 16 h followed by a postcure at 100°C for 1 h. Both cure schedules yielded adhesive bonds with similar strengths (15.4 ± 1.4 and 13.7 ± 0.4 MPs, respectively) (Figure 10).

The room-temperature-cured aluminum substrate bonds show higher adhesive strength than the same resin mixture cured above the lower critical solution temperature, suggesting that the phase-separated modifier component leads to a more flexible than tough matrix. The higher adhesion strength value obtained for the 1000-g/mol VE cured at elevated temperatures suggests that the flexible nature is balanced by the better mechanical properties of the higher-molecular-weight dimethacrylate resin.

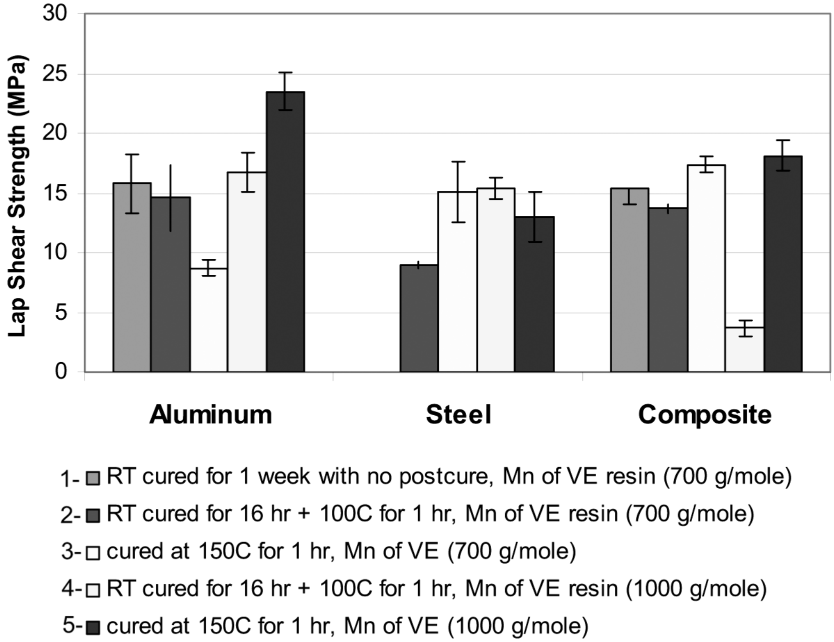

FIGURE 10 Lap shear strength of 20 wt.% styrene/20 wt.% mPO/60 wt.% VE (700 or 1000 g/mol) bonded aluminum-to-aluminum, steel-to-steel, and composite-to-composite structures (I = interfacial failure, C = cohesive/adhesive failure, M = mixed mode failure, and S = failure in the composite).

The low adhesive value of the 1000 g/mol cured at room temperature is a result of the high viscosity of that particular resin. This resin did not appear to wet the composite surface and resulted in interfacial failure. All other adhesives bonded to the vinyl ester/glass fiber weave composite substrates resulted in failure in the surface veil of the composite. These investigations help to suggest that the methacrylated poly(propylene oxide) modified styrene/vinyl ester resins display structural strength when cured at room temperature, with the appropriate viscosity. The relatively high fracture toughness of the room-temperature-cured networks may also enhance the performance of these materials as structural adhesives designed for polymer composite substrates.

CONCLUSIONS

Cloud point analysis of the mPO modified resins confirmed LCST behavior, which is tentatively suggested to arise as a result of hydrogen bonding between the vinyl ester hydroxyl groups and the PO ether oxygens [14–16]. The room-temperature cure conditions were well below the cloud points and, thus, allowed for good incorporation of the mPO thermoplastic into the dimethacrylate-styrene networks. Phase separation did not occur during the 100°C postcure because the PO was already "locked" into the networks established during lower temperature cure. These mPO modified room temperature cured networks (followed by a postcure) were single phase and had high fracture toughness. By contrast, the resins cured above their cloud points phase separated prior to or early in the polymerization and, hence, the PO modifier was not well incorporated into the vinyl ester/styrene. The spacing between the phase separated regions of the mPO toughened resin cured at 150°C containing 1000 g/mol VE oligomer was calculated to be *ca.* 4.2 μm from the SALS behavior. This dimension compared well with that observed for the general structural periodicity also noted within the TEM images of the same network, which are believed to arise because of spinodal decomposition. It is also recalled that this periodicity was a time-dependent function at constant cure temperature. Unfortunately, these phase-separated networks did not improve the fracture toughness.

Lap-shear adhesive strengths of all of the adhesives, which had appropriate viscosities, on composite substrates were in the structural regime (~13.8 MPa). Both room-temperature-cure schedules (with and without a postcure) resulted in good adhesive strength on the composite and aluminum substrates (~15.2 MPa). The fact that the adhesive resins cured solely at room temperature (without an elevated temperature postcure) showed similar adhesive strengths to those finished at higher temperatures is significant. This is important to the potential use of such adhesives in the construction industry because they will be applied at the construction site.

To optimize the structure property relationships, it may be necessary to cure these mPO-modified networks at higher temperature, yet below the cloud point temperature of any given resin composition. Elevating the cure temperature of the resins, while maintaining a single phase, may further increase the fracture toughness performance of these systems by promoting a higher degree of cure in the network. However, the FT-IR analysis and swelling experiments suggests that the room-temperature-cured networks that were postcured for 1 h at 100°C already display a significant conversion.

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