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Copolymerization behavior and properties of dimethacrylate–styrene networks

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Abstract

Dimethacrylate oligomers diluted with styrene (commonly known as vinyl ester resins) are important matrix resins for fiber-reinforced composites used in construction, marine craft, and transportation vehicles. These comonomers react via free radical copolymerization to yield void-free thermosets. The inter-relationships among copolymerization kinetics, physical properties of the networks, and cure temperatures for a 700 g/mol dimethacrylate oligomer with systematically varied styrene concentrations were investigated. FTIR was used to monitor the reactions of the carbon–carbon double bonds of the methacrylate (943 cm^{-1}) and styrene (910 cm^{-1}). Reactivity ratios were determined via a non-linear method at four cure temperatures. The data were analyzed using the integrated form of the copolymerization equation and assuming a terminal reactivity model to predict copolymer compositions throughout the reactions. The results indicated that at early conversion more styrene was incorporated into the networks at lower cure temperatures. The experimental vinyl ester–styrene network compositions agreed well with those predicted by the integrated copolymer equation at early and intermediate conversion. Mechanical properties of dimethacrylate–styrene networks were determined for materials cured at room temperature and at 140 °C. Materials cured at room temperature were tougher and had lower rubbery moduli than those cured at 140 °C.

Keywords: Vinyl ester; Dimethacrylate; Reactivity ratios

1. Introduction

The network formation mechanism via free radical polymerization remains an area of interest for many polymer scientists. The complexity of the reactions introduces structural heterogeneities into the resultant polymer networks and creates several challenges for developing an absolute description of the network formation and structure. Since many thermosets with large application potentials polymerize by a free radical mechanism, understanding the steps leading to a polymeric network would enable the design of materials with improved performance.

Currently, it is widely accepted that the formation of crosslinked networks from multi-functional (i.e., >2) oligomers diluted with reactive monomers in free radical copolymerizations begins with microgels [1–6]. Microgels are compact areas of high crosslink density, and likely high cyclization, that begin to form at low conversion. Gelation occurs when these dense regions connect via intermolecular crosslinks to form a macrogel, which eventually leads to a three-dimensional network at later reaction stages.

One thermosetting class of resins of particular interest consists of dimethacrylate oligomers (so-called "vinyl esters") diluted with styrene (Fig. 1). Their low viscosities coupled with rapid cure schedules and low resin cost make them ideal candidates for structural composites. However, the mechanical behavior of these systems is sensitive to the cure conditions. Thus, probing the chemistry of this cure reaction is important for understanding the physical and mechanical properties of

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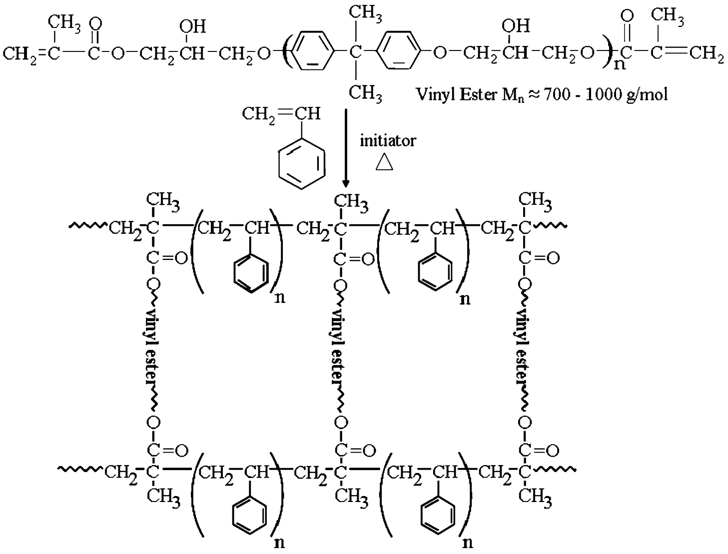

Fig. 1. Free radical copolymerization of a dimethacrylate oligomer and styrene to form a crosslinked network.

these materials as well as for designing materials suitable for specific applications.

Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) can be employed to monitor the cure of vinyl ester resins. DSC has the advantage of simultaneously generating kinetic and thermal data for thermosetting systems. Previous studies have used both isothermal and scanning modes to measure various kinetic parameters of vinyl ester resins at different temperatures [7–10]. FTIR spectroscopy is a powerful technique that can be used to monitor the concentrations of the dimethacrylates on the oligomer and styrene separately during the reaction. Thus, the sequence distribution of the copolymer (at early stages of the reaction) can be determined using copolymerization theory. While there has been some work in this area, few have performed a thorough investigation of the impact different cure temperatures have on the microstructure and physical properties of such systems [11–14].

This paper focuses on determining relationships among the cure kinetics at different temperatures, and the thermal/mechanical properties of the networks. A dimethacrylate oligomer ($M_n = 700$ g/mol) with systematically varied styrene concentrations was used to determine the reactivity ratios at four temperatures. Variations in the network microstructure are discussed in light of early stage heterogeneities introduced by microgelation. The kinetic data were ultimately used to explain the observed properties of vinyl ester networks cured at room temperature and elevated temperatures.

2. Experimental

2.1. Materials

A bisphenol-A-based dimethacrylate (vinyl ester) oligomer was kindly supplied by the Dow Chemical Co. Additives such as inhibitors which had been added to the resin were not removed. Styrene monomer (Aldrich) was passed through a neutral alumina column to remove inhibitors before mixing with the vinyl ester oligomer. Benzoyl peroxide (BPO, Aldrich) was the free radical initiator for the high temperature curing reactions and was used as received. For the room temperature curing reactions, the initiating system consisted of cobalt naphthenate (CoNap), methyl ethyl ketone peroxide (MEKP), and *N*,*N*-dimethylaniline (DMA). CoNap (Alfa Aesar) and DMA (Aldrich) were used as reaction accelerators to promote the decomposition of MEKP, the initiator for the free radical copolymerization. These reagents were used as received.

2.2. Preparation and cure of dimethacrylate resins

The neat solid vinyl ester oligomer was diluted with systematically varied amounts of styrene ranging from 20 to 60 wt%. The oligomer was dissolved in styrene at 50 °C, then the mixture was allowed to cool to room temperature. After the resin mixture reached room temperature, 1.1 wt% of BPO was added, and the mixture was stirred until the initiator dissolved. Oxygen was removed using a freeze–thaw technique. The resin was cured at 60, 90, or 140 °C in a closed system.

For resins cured at room temperature, the following amounts of accelerators and initiators were added in the order listed: 0.15 wt% of CoNap, 0.04 wt% DMA, and 1.13 wt% of MEKP. After addition of each reagent, the mixture was stirred to obtain a homogeneous solution. The reaction mixture was allowed to react for 8 h, followed by a 93 °C postcure for 2 h.

2.3. Measurements

^{1}H NMR spectra were collected using a Varian Unity 400 instrument operating at 400 MHz. ^{1}H NMR confirmed that the molecular weight of the vinyl ester oligomer was approximately 700 g/mol. The integrals of the peaks corresponding to the methyl groups of bisphenol-A (1.65 ppm) and for the methacrylate end groups (2.0 ppm) were used to calculate these molecular weights. ^{1}H NMR was also used to verify the compositions of the resin blends based on the ratios of peak integrals for styrene vinyl protons (5.62 and 5.10 ppm) to methacrylate vinyl protons (6.02 and 5.46 ppm).

FTIR spectra were collected using a Nicolet Impact Model 400 instrument equipped with a controlled temperature cell (Model HT-32 heated demountable cell used with as Omega 9000-A temperature controller) [12,14–16]. One drop of the reaction mixture was placed between two NaCl plates, which were then placed in a preheated controlled temperature cell in the FTIR. The heights of the infrared absorbencies at 943 and 910 cm^{-1}, corresponding to the methacrylate and styrene double bonds respectively, were monitored quantitatively and used to calculate reaction conversion. A small background absorbance assigned to the vinyl ester backbone overlapped the absorbance at 943 cm^{-1} (about 20% of the initial absorbance at 943 cm^{-1}) [13]. Therefore, all spectra were subtracted by a spectrum where the conversion of methacrylate and styrene double bonds was complete.

Corrections for any changes in sample thickness during polymerization were made by normalizing the FTIR spectra to an absorbance of the polyhydroxyether backbone of the vinyl ester at 830 cm^{-1}. Reaction conversion ("a" in Eq. (1)) was determined from the change of the normalized absorbance after subtraction of the background where A_o and A_t are the normalized absorbances before the reaction and at reaction time t.

$$a = 1 - \frac{A_t}{A_o} \tag{1}$$

Glass transition temperatures (T_gs) of the vinyl ester networks were measured using a Perkin–Elmer DMA 7e Dynamic Mechanical Analyzer. A three-point bend probe was used with a span of 20 mm. Each thermogram was obtained using a 5 °C/min heating rate and 1 Hz frequency under amplitude control. The temperature at the maximum in the tan δ peak was taken as the T_g.

Elastic moduli were determined using a Dynastat calibrated with digital calipers accurate to 0.01 mm. The test specimens, with dimensions of $3.18 \times 6.35 \times 38.1$ mm, were placed on two flat supports with a span of 2.54 cm, in the three-point bend setup. The samples were heated to 40 °C above T_g to measure the elastic moduli. A small load (0.01 kg) was placed on the samples once the temperature was reached, and the displacement at equilibrium was measured. The load was increased by increments of 0.01 up to about 0.08 kg and at each load the equilibrium displacement was recorded. From these data the load versus displacement curves were generated and linear regression analyses were performed to determine the slopes of the lines. These slopes were used to determine the moduli according to Eq. (2):

$$E = (P/\Delta) \times g \times \left(L^3/48I\right) \tag{2}$$

P/Δ = slope of load versus displacement data;
g = gravitational constant = 9.81 m/s^2;
L = length between supports = 2.54 cm;
$I = (1/12)wh^3$;
w = width of sample;
h = height of sample.

Fracture toughness measurements were conducted according to ASTM Standard D 5045-91. An Instron model 4204 instrument was used with a cross-head speed of 5 mm/min and a three-point bend attachment set to a span of 1 in. All specimens had a thickness of 3.12 mm, a width of 6.28 mm, a notch depth of 2.2 mm and a notch width of 0.8 mm. The single-edge notch bending (SENB) method was used.

Tensile properties of the networks were measured according to ASTM Standard D 638-90. The dogbone specimens (cured in silicone rubber molds covered by a heavy aluminum plate) had dimensions for type I as defined in the ASTM standard. An Instron 4204 instrument operating at a constant extension rate of 5 mm/min was utilized.

3. Results and discussion

Dimethacrylate–styrene networks are one of the major classes of polymer matrix resins for structural composite applications because they are lightweight, durable, and strong. This study focuses on the inter-relationships among cure procedure and network properties for a 700 g/mol dimethacrylate oligomer cured with systematically varied concentrations of styrene. Two different cure conditions were investigated: a room temperature cure (8 h at room temperature followed by a 2 h 93 °C postcure), and a high temperature cure (30 min at 140 °C). Copolymerization kinetics were investigated to provide additional insight into the observed physical and mechanical properties of these materials.

3.1. Dimethacrylate–styrene network formation

Formation of the dimethacrylate–styrene networks was studied using FTIR (Fig. 2) [13,15–17]. The disappearance of the absorption bands at 943 and 910 cm^{-1}, corresponding to the out of plane stretching of the –CH group in the dimethacrylate oligomer and the wagging of the –CH$_2$ group in the styrene monomer, were monitored independently to assess the extent of cure. The conversion profiles for the room temperature and high temperature curing reactions of a resin comprised of 70 wt% of the dimethacrylate oligomer and 30 wt% styrene were significantly different (Fig. 3). For the room temperature cure, the initial conversion rate for the dimethacrylate oligomer was higher than styrene. Vitrification occurred 90 min into the cure, where conversions of 68% and 55% were reached for the dimethacrylate and styrene monomers, respectively. During the postcure, more styrene was converted relative to the dimethacrylate monomer reaching ultimate conversions of 92% and 87%, respectively. Moreover, the conversion of styrene monomer continued while the conversion of the dimethacrylate ceased, implying that long sequences of styrene were formed at later stages of the cure. For the high temperature cure, high conversions (~97%) were reached in ~2–3 min for both monomers. The high temperature cure

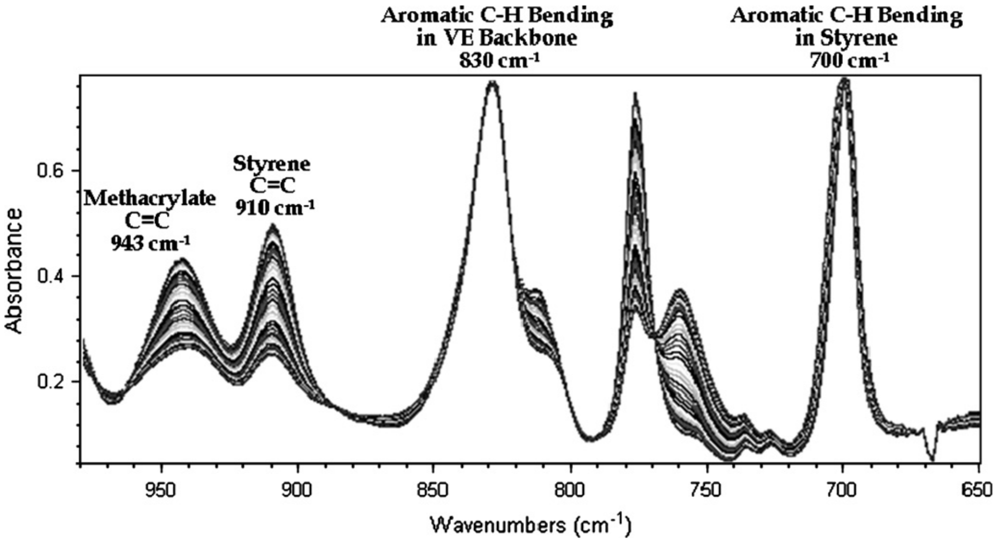

Fig. 2. FTIR spectra of a 700 g/mol dimethacrylate terminated oligomer with 28 wt% styrene cured at room temperature.

produced higher conversions compared to the room temperature cure.

3.2. Copolymerization kinetics

Monomer reactivity ratios were calculated from FTIR data obtained at early conversions to predict the azeotropic feed compositions (the monomer feed ratio where the copolymer composition should remain constant throughout the polymerization) and copolymer compositions during cure. The two double bonds in the dimethacrylate oligomer were assumed to have the same reactivity. Thus, any terpolymerization kinetic effects due to pendant double bonds were neglected. Copolymerization was assumed to obey a terminal model, meaning that only the monomer unit at the end of the propagating chain affected the kinetics. These assumptions allowed the simplest copolymerization equation to be employed (Eq. (3)) [18].

$$r_2 = \frac{[M_1]}{[M_2]} \times \left[\frac{\mathrm{d}[M_2]}{\mathrm{d}[M_1]}\right]^2 r_1 + \left[\frac{\mathrm{d}[M_2]}{\mathrm{d}[M_1]} - 1\right] \times \frac{M_1}{M_2} \tag{3}$$

where $[M_1]$ and $[M_2]$ are the initial concentrations of the monomers, $\mathrm{d}[M_1]/\mathrm{d}[M_2]$ (copolymer composition) is the ratio of the rates at which M_1 and M_2 enter the copolymer, and r_1 and r_2 are the reactivity ratios for M_1 and M_2. Note that $[M]$ in Eq. (3) refers to the equivalent concentration of double bonds rather than the molar concentration of monomers.

The compositions of the copolymers ($\mathrm{d}[M_2]/\mathrm{d}[M_1]$) at early reaction stages were determined from early conversion slopes of styrene consumption as a function of methacrylate consumption. The reactivity ratios were estimated by using the copolymerization equation (Eq. (3)) and plotting r_2 versus r_1. The point of intersection for the dimethacrylate–styrene compositions represents the estimated reactivity ratio pair for the dimethacrylate oligomer and styrene (Fig. 4 for the room temperature cure).

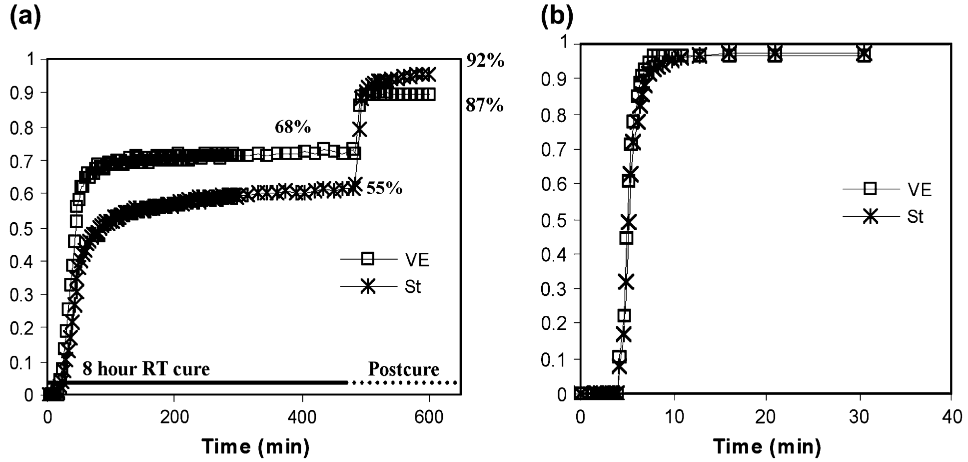

Fig. 3. Fractional double bond conversion of a 700 g/mol dimethacrylate terminated oligomer with 28 wt% styrene cured at (a) room temperature followed by a 93 °C postcure and (b) 140 °C.

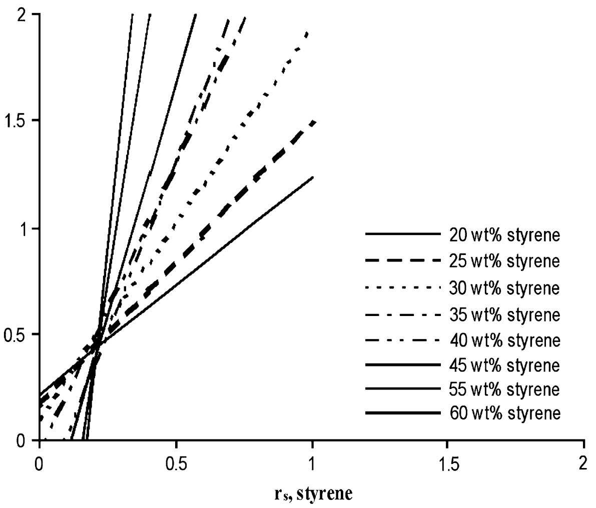

Fig. 4. Reactivity ratios for the dimethacrylate oligomer (r_m) and styrene (r_s) cured at room temperature using the Mayo–Lewis method of intersections.

Non-linear analyses are the most reliable statistical treatments of copolymer composition data. Linear methods, e.g. the Mayo–Lewis method, only offer a qualitative estimate of precision and require subjective weighing of the data. Tidwell and Mortimer [19,20] developed an iterative method based on non-linear least squares theory using the copolymer equation of the form:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{4}$$

where F_1 is the mole fraction of M_1 in the copolymer and f_1 and f_2 are the mole fractions of M_1 and M_2 in the feed.

The non-linear analysis uses initial estimates of the parameters r_1 and r_2 (derived from the Mayo–Lewis analysis in this study) to yield a pair of reactivity ratios that result in the minimum value of the sum of the squares (ss, Eq. (5)) between the experimental and theoretical copolymer composition (the composition derived from Eq. (4) using initial estimates of r_1 and r_2). The non-linear least squares analysis assumes that errors exist only in the dependent variable, F_1, and that this relative error is constant.

$$\mathrm{ss}(\lambda) = \sum_i w_i (y_i - f(x_i, \lambda_i))^2 \tag{5}$$

where y_i is the experimental F_1, $f(x_i,\lambda_i)$ is the theoretical F_1 as a function of $f_1 - (x)$ and the parameters r_1 and $r_2 - (\lambda_i)$, and w_i is the weighing factor:

$$w_i = \frac{1}{y_i^2} \tag{6}$$

Most statistical software packages determine the minimum of the sum of squares by iterative processes. A simpler algorithm has been developed by van Herk that involves calculating all the sums of squares in a specified region and then pinpointing the lowest sums of squares in that region [21]. A computer program can be applied to a variety of functions to yield optimum parameters and their 95% joint confidence intervals (Fig. 5).

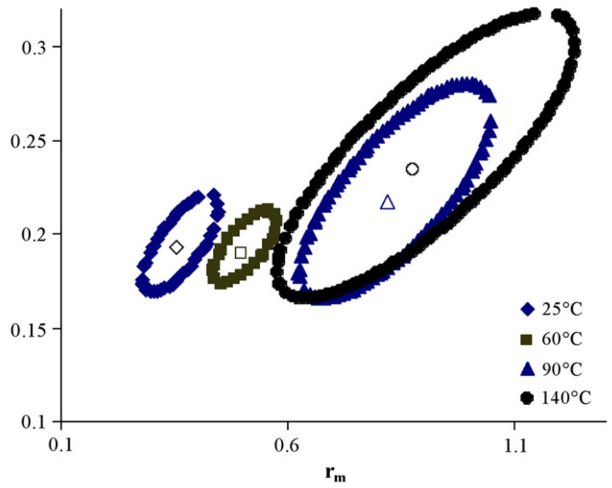

Fig. 5. Reactivity ratios for the dimethacrylate oligomer (r_m) and styrene (r_s) cured at 25, 60, 90, and 140 °C and their 95% joint confidence intervals via non-linear analysis.

A summary of the Mortimer–Tidwell reactivity ratios at the four different cure temperatures is shown in Table 1. The observed differences between the lower temperature cures (25 and 60 °C) and the higher temperature cures (90 and 140 °C) were significant since the 95% joint confidence intervals did not intersect (Fig. 5). As the cure temperature was increased, r_m increased while r_s remained relatively constant. In every case r_m was greater than r_s, indicating that the dimethacrylate monomer preferentially entered the copolymer at early reaction stages. The ratios of r_m to r_s provided additional insight into the network structure at early stages of conversion. Lower r_m/r_s ratios imply that more styrene was incorporated into the network at lower temperatures. As more styrene becomes incorporated, the molecular weight between crosslinks should increase. Therefore, the network crosslink density was increased as the cure temperature was increased.

The mole fractions of styrene in the feed and at early conversions in the networks were compared with respect to the azeotropic 45° line (Fig. 6). The azeotropic compositions (where the experimental data crosses the azeotropic line) were determined for all four cure temperatures (Table 2). It is anticipated that these particular vinyl ester–styrene compositions should yield networks where the composition of the network formed in early stages of polymerization should have the same composition as the network formed in latter stages. All of the azeotropic compositions were lower than the vinyl ester–styrene mixtures

Table 1
Reactivity ratios of the dimethacrylate oligomer (r_m) and styrene (r_s) at different cure temperatures

Temp (°C)	r_m	r_s	r_m/r_s
25	0.35	0.19	1.84
60	0.50	0.19	2.63
90	0.82	0.22	3.73
140	0.88	0.23	3.83

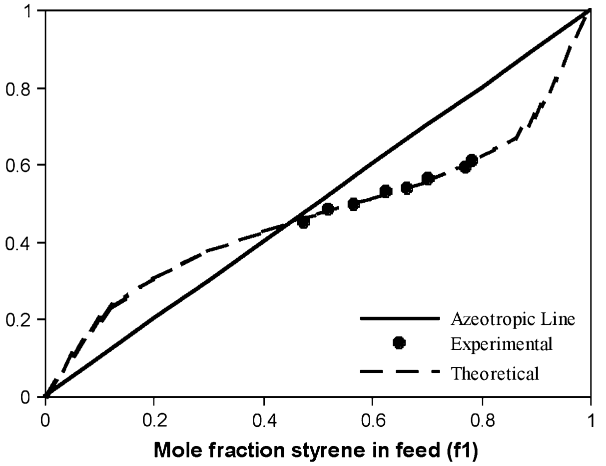

Fig. 6. Comparison of copolymer compositions with feed compositions for the dimethacrylate–styrene thermosets cured at room temperature showing the crossover point with the 45° line (azeotropic points).

Table 2
Azeotropic compositions at different cure temperatures

Temp (°C)	f_{az} (mole fraction of styrene)	Azeotropic weight percent of styrene
25	0.45	19
60	0.38	16
90	0.19	6.50
140	0.14	4.50

typically utilized commercially. As the temperature was increased, these copolymer mixtures had compositions further from the azeotropic points. A direct consequence is that feed and copolymer composition drift is greater when these materials are cured at higher temperatures.

Using the Mortimer–Tidwell reactivity ratios, the experimental copolymer compositions were compared to those predicted by the Meyer–Lowry integrated copolymer composition equation (Eq. (7)) for the room temperature and high temperature cures [22]. X corresponds to total monomer conversion, f_{1_o} is the initial mole fraction of monomer 1 (styrene) in the feed, and f_1 is the mole fraction of monomer 1 in the feed at a given conversion X.

$$\begin{aligned}
X &= 1-\left(\frac{f_1}{f_{1_o}}\right)^{\alpha}\left(\frac{(1-f_1)}{1-f_{1_o}}\right)^{\beta}\left(\frac{(f_{1_o}-\delta)}{(f_1-\delta)}\right)^{\gamma}\\
\alpha &= \frac{r_2}{1-r_2}\\
\beta &= \frac{r_1}{1-r_1}\\
\gamma &= \frac{1-r_1r_2}{((1-r_1)(1-r_2))}\\
\delta &= \frac{(1-r_2)}{(2-r_1-r_2)}
\end{aligned} \tag{7}$$

Computer programs developed by van Herk were also used to predict copolymer compositions throughout the reaction, including the latter stages where significant gelation had occurred. The 8 h room temperature cure and 2 h postcure were considered as separate reactions (Fig. 7). There is good agreement between the experimental and predicted data for the mixtures containing 30 and 40 wt% of styrene at early and intermediate conversion. Slight deviations occurred during the vitrification stage that became more pronounced as the weight percent of styrene was increased. For the 60 wt% styrene mixture, significant deviations began at 15% conversion. The fact that more styrene was incorporated into the copolymer than predicted may indicate that the styrene monomer is more reactive relative to the methacrylate monomer at early stages of conversion. This implies that another pair of reactivity ratios may better describe comonomer mixtures containing high amounts of styrene. For the postcure, unreacted double bonds at the vitrification step were taken as the initial feed compositions. The reactivity ratios failed to predict the

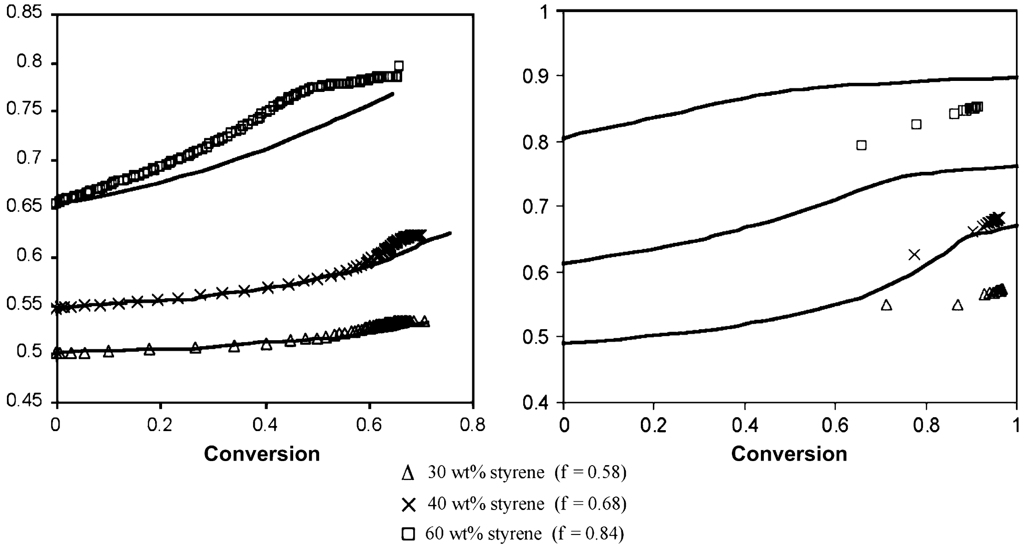

Fig. 7. Copolymer composition (F_s) as a function of overall double bond conversion for systematically varied mole fractions of styrene in the feed (f_s) cured at (left) 25 °C followed by (right) a 93 °C postcure. The lines represent the copolymer compositions predicted from reactivity ratios (non-linear analyses).

compositions of the networks in this stage for all comonomer mixtures. The predicted mole fractions of styrene in the copolymer were higher than the experimental data, suggesting that the reactivity ratios may have changed during the course of the polymerization.

Similar trends were observed during the high temperature curing reaction (Fig. 8). The experimental dimethacrylate–styrene network compositions agreed well with the theoretical curves at early stages of conversion for all three compositions. However, differences begin at intermediate stages of conversion, particularly with the compositions containing 30 and 60 wt% of styrene. At later stages, less styrene was incorporated in the network than was predicted for all three compositions due to a change in the relative reactivity of the dimethacrylate oligomer and the styrene monomer.

The deviations from the predicted copolymer composition curves can be understood by considering the network formation process. At low conversion, microgels develop as the pendant double bonds on a branched macroradical react to form multiple crosslinks, and possibly also react intramolecularly to form cyclic moieties. Several studies have indicated that cyclization reactions were favored as the crosslinking agent was increased, producing more compact microgel structures [3–6,23]. For both cure temperatures, the experimental data agreed well with the theoretical curves at early reaction stages (conversion <10%). If microgels had formed at this stage, any impact of their structures could not be discerned by the copolymerization kinetics.

Interestingly, the resin containing 60 wt% of styrene showed significant deviations in copolymer composition from the predicted values as early as ~15% conversion at both cure temperatures. Compared to the other resin compositions, the 60 wt% styrene mixture had less crosslinking agent and should therefore have generated microgels that were less dense. Based on previous studies, lower crosslink density of the microgel resulted from the decreased occurrence of cyclization [2–4,23]. Despite the decreased mobility of the pendant double bonds within the microgel, they were more accessible to the more mobile styrene monomer. This may be the reason why more styrene was incorporated into the copolymer than was predicted.

Significant deviations from the predicted network compositions were observed during the postcures at 93 °C. During the room temperature curing step, the microgels formed intermolecular crosslinks to produce a vitrified macrogel. Any unreacted double bonds on the dimethacrylate oligomers existed primarily as pendant double bonds within a macrogel that were swollen with unreacted styrene monomer. The high temperature in the postcure increased the mobility of the styrene, enabling it to react further with the pendant methacrylates or itself. With styrene being the more mobile and reactive monomer, the magnitude of its reactivity ratio could increase during this stage. Similarly, the reactivity ratio for the dimethacrylate oligomer could decrease due to its lower reactivity during this stage.

Another interesting phenomenon is that differences between experimental and theoretical curves become more pronounced with increasing cure temperature. Based on their studies of unsaturated polyester resins, Huang and Chen [24] and Grunden and Sung [25] postulated that enhanced microgelation and intramolecular crosslinking occurs at high cure temperatures (i.e., more compact microgels form), making styrene diffusion into the microgel more difficult. For a particular dimethacrylate–styrene mixture, the pendant methacrylates within the microgel may be less reactive when the mixture is cured at higher temperatures because the microgels are more dense. Compared to the room temperature cure, deviations from the predicted curves occurred much earlier for the 140 °C cure process.

3.3. Properties of dimethacrylate–styrene networks

A series of dimethacrylate–styrene networks containing systematically varied percentages of styrene ranging from 20 to 35 wt% were studied to assess the effects of crosslinking on glass transition temperatures, rubbery moduli, fracture toughness, and tensile strength. Two different cure procedures were of interest: (1) an 8 h room temperature cure followed by a 2 h postcure at 93 °C and (2) a 30 min cure at 140 °C. Glass transition temperatures and mechanical properties were expected to be functions of the amount of dimethacrylate oligomer relative to styrene in the chemical structure. The copolymerization kinetics indicated that more styrene was incorporated into the network at early conversion when these materials were cured at lower temperatures, resulting in a more open network structure. Moreover, it is believed that more structural heterogeneities exist within the networks formed at higher temperatures due to enhanced microgelation and the compositions of the copolymer mixtures being further from the azeotropic points. Thus, it was anticipated that dimethacrylate–styrene networks cured at room temperature would possess better physical properties than those cured at 140 °C.

The rubbery moduli as a function of weight percent of styrene are shown in Fig. 9 for the networks cured at room temperature and the higher temperature. As the styrene concentration

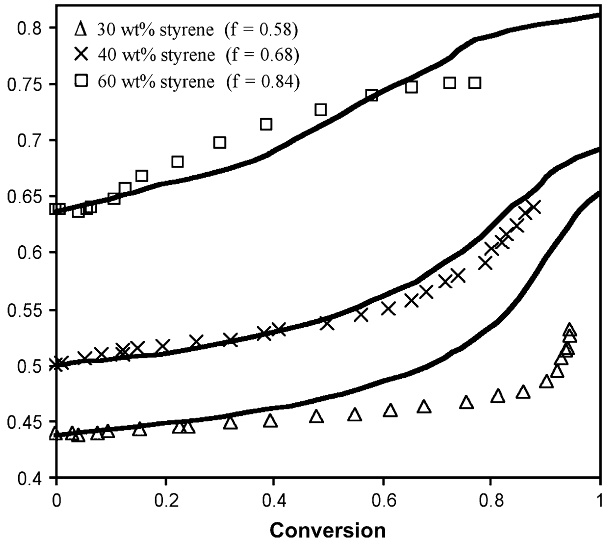

Fig. 8. Copolymer composition (F_s) as a function of overall double bond conversion for systematically varied mole fractions of styrene in the feed (f_s) cured at 140 °C. The lines represent the copolymer composition predicted from reactivity ratios (non-linear analyses).

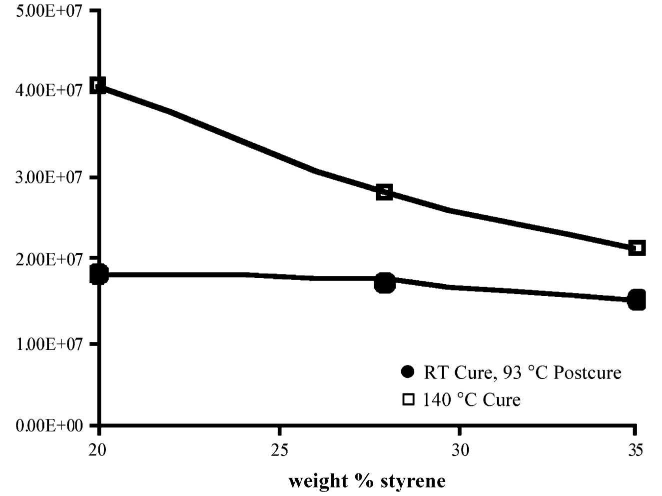

Fig. 9. Rubbery moduli versus weight percent of styrene.

was increased, the rubbery moduli decreased. Room temperature curing reactions produced networks with higher rubbery moduli than high temperature cures. Consequently, networks possessing lower crosslink density resulted when these materials were cured at lower temperatures.

The glass transition temperatures of dimethacrylate–styrene networks are strongly dependent on cure procedure (Table 3). The network T_gs were significantly lower when cured at room temperature, further confirming the openness of this network structure. Increasing the percent styrene had little effect on the network T_gs for either cure procedure. Since the glass transition temperatures of high molecular weight polystyrene and also the analogous high molecular weight polyhydroxyethers are both near 100 °C, the T_gs of the networks were expected to be relatively insensitive to changes in chemical composition, but sensitive to crosslink density.

A less dense network normally results in improved toughness and/or ductility in networks [26–28]. Pre-cracked three point bend measurements were used to measure the fracture toughness for dimethacrylate–styrene networks cured at room temperature and the high temperature (Table 4). It was anticipated that the networks cured at room temperature would be tougher since the kinetic data indicated that a more open network structure resulted. Surprisingly, the plane strain critical stress intensity factor (K_{1c}) consistently decreased as the styrene content was increased for both cure procedures. If all the reactive diluent was incorporated homogeneously into the network, then the toughness should increase with styrene concentration. The fact that toughness decreased as the styrene concentration increased may be attributed to copolymerization kinetics. The reactivity ratios for the comonomers predicted azeotropic compositions lower than the comonomer mixtures used in this study. Moreover, these mixtures have compositions further from the azeotropic points at higher temperatures, which results in greater drifts in the feed and copolymer composition. The heterogeneous incorporation of comonomers adversely affects the mechanical properties of network structure (Table 5). Generally, the networks cured at room temperature were stronger, tougher, and had higher elongations than those cured at 140 °C.

Table 3
Glass transition temperatures (°C) of dimethacrylate–styrene networks cured at room temperature and 140 °C

Styrene (wt%)	T_g	
	RT cure	140 °C cure
20	113	155
28	119	147
35	119	144

Table 4
Effect of styrene content and cure procedures on fracture toughness (K_{1c}) of dimethacrylate–styrene networks

Styrene (wt%)	K_{1c} (MPa $m^{0.5}$)	
	RT cure	140 °C cure
20	1.03 ± 0.04	0.87 ± 0.12
28	0.94 ± 0.09	0.72 ± 0.11
35	0.77 ± 0.05	0.63 ± 0.11

Table 5
Summary of thermal and mechanical properties for dimethacrylate–styrene networks (30 wt% styrene) as a function of cure procedure

	Room temperature cure followed by a postcure at 93 °C	High temperature cure at 140 °C
T_g (°C)	119	147
Tensile strength (ksi)[a]	13.29	5.50
% Elongation[a]	5.23	1.31
Fracture toughness (MPa $m^{0.5}$)	0.94 ± 0.09	0.73 ± 0.11

[a] Average % error < 2%.

4. Conclusions

The impact of cure procedure on the copolymerization kinetics and physical properties of dimethacrylate–styrene networks was investigated. The reactivity ratios were determined via a non-linear method at four different cure temperatures. The reactivity ratios indicated increased styrene incorporation at lower cure temperatures, resulting in a more open network structure. Copolymer compositions were further from the azeotropic points as the cure temperature was increased. Consequently, composition drift was greater at the higher cure temperatures. Experimental network compositions deviated significantly from those predicted by the Meyer–Lowry integrated copolymer equation at intermediate conversions. These differences occurred earlier for the high temperature cure, suggesting the production of a more heterogeneous network.

The physical properties of the networks provided further insight into their structures. Low temperature cures produced networks that were stronger and tougher, as expected for more open networks. Surprisingly, the fracture toughness decreased as styrene concentration increased for all cure conditions studied. This was attributed to the heterogeneous network structure produced at higher styrene concentrations, where composition drift was greater.

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