

Structure–Property Relationships in Photopolymerizable Polymer Networks: Effect of Composition on the Crosslinked Structure and Resulting Thermomechanical Properties of a (Meth)acrylate-Based System

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ABSTRACT: Photoinitiated polymer networks were formed by copolymerization of *tert*-butyl acrylate with di(ethylene glycol) dimethacrylate (DEGDMA) or poly(ethylene glycol) dimethacrylate (PEGDMA). The degree of crosslinking was systematically varied by modifying the weight fraction and molecular weight of the dimethacrylate crosslinking agent. An increase in effective crosslink density with increasing crosslinking agent concentrations was confirmed by decreasing equilibrium swelling ratios (q) and increasing rubbery moduli (E_R). Glass transition temperatures (T_g) varied from -22 to 124°C , increasing with increasing DEGDMA content and decreasing with increasing PEGDMA content. Tensile deformation behavior (at T_g) ranged from an elastomeric-like large-strain response for lightly crosslinked materials to a small-strain brittle response for highly crosslinked networks. At low crosslinking levels, the strain-to-failure of the network

polymers decreased quickly with increasing crosslinking agent concentration. The stress at failure demonstrated a more complex relationship with crosslinking agent concentration. The effect of composition on network structure and resulting properties (q , E_R , strain-to-failure) decreased as the crosslinking agent concentration increased. The results reveal trade-offs in T_g , E_R , strain-to-failure, and failure stress with composition and network structure, and are discussed in light of the wide range of potential applications suggested in the literature for (meth)acrylate-based photopolymerizable polymer networks including biomaterials and shape-memory polymers. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1559–1572, 2008

Key words: structure–property relations; photopolymerization; crosslinking; mechanical properties; glass transition

INTRODUCTION

Crosslinking has been shown to greatly influence the physical and mechanical properties of polymers. Crosslinked network polymers demonstrate enhanced creep resistance, improved dimensional stability, increased thermal stability, increased mechanical

strength, and increased resistance to solvent absorption^{1,2} compared with uncrosslinked linear polymers. Network polymers can be made via the secondary crosslinking of initially linear polymer chains or the single-stage polymerization of multifunctional monomers. Photopolymerization of multifunctional monomers as a means to create network polymers is of increasing interest because of the many advantages of photopolymerization such as spatial and temporal control, reaction speed, and the possibility of *ex vivo* or *in situ* polymerization for biomedical applications.^{2,3}

Photopolymerized networks produced from multifunctional (meth)acrylated monomers have been studied for use in a wide range of applications such as gas separation membranes,⁴ hydrogels,^{3,5,6} tissue engineering,⁷ orthopedics,⁸ drug delivery,⁶ dentistry,^{9–11} and shape-memory materials for cardiovascular applications.^{12,13} Such systems are produced by the copolymerization of mono-(meth)acrylate and

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multifunctional (meth)acrylated monomers or the homopolymerization of multifunctional monomers. Because of the complex nature of the polymerization kinetics and the resulting structure of such systems, processing/structure/property relationships are not always straightforward and need to be fully characterized for optimal use in a wide range of applications requiring different physical and mechanical properties. For example, photopolymers have been historically used in thin film coating applications and dentistry, which both require hard, deformation-resistant polymers achieved through high crosslink densities. However, emerging biomedical applications in tissue engineering or shape-memory polymers for minimally invasive surgery require soft, deformable polymers with tuned glass transition temperatures (T_g) over a wide range of crosslink densities. Moreover, biomedical applications demand a more fundamental understanding of mechanical properties beyond elastic modulus, which is the property typically presented in the photopolymer literature.

A number of studies have examined how photopolymerization kinetics and aspects of the resulting structure of (meth)acrylate-based systems are influenced by monomer properties and reaction conditions such as light intensity, reaction temperature, comonomer composition, monomer chain length between double bonds (monomer size), and monomer functionality.^{9,14–17} These studies have demonstrated that properties such as the rate of polymerization, pendant double-bond reactivity (heterogeneity) during polymerization, and final double-bond conversion of the resulting networks are dependent on various monomer and reaction parameters. Additionally, it has been shown that parameters such as comonomer composition, monomer size, and monomer functionality influence the effective crosslink density of the final network systems.^{15,18} Such changes in the crosslink density ultimately result in shifts of the physical and mechanical properties of the resulting networks.

Studies on the characterization and quantification of the evolution of properties such as swelling capacity, T_g , distribution parameter (a measure of heterogeneity), and elastic modulus with modifications to comonomer composition and monomer molecular weight (and inherently network structure) in photopolymerized (meth)acrylate systems have been reported.^{9,15,18–21} However, less attention has been given to the evolution of deformation behavior and corresponding mechanical properties of such systems across a wide compositional (and structural) range. Knowledge of such properties and their link to compositional and structural modifications, as well as more commonly reported properties such as T_g and elastic modulus, is important due to the varying physical and mechanical

requirements of the many possible applications for such materials.

The purpose of this study is to present a fundamental, systematic evaluation of the coupled structure/property evolution in photopolymerizable (meth)acrylate-based networks in terms of their comprehensive mechanical response, including stiffness, tensile strength, and deformation limits. Network structures were produced from the copolymerization of monoacrylate and dimethacrylate monomers. The concentration, as well as the length, of the dimethacrylate monomer was systematically varied with respect to that of the monoacrylate monomer as a means to control the resulting crosslink density. The structural evolution of the materials was characterized in terms of properties such as swelling capacity, shifts in T_g , and small-strain elastic rubbery modulus (E_R) development. The effect of structure on the resulting tensile deformation behavior to failure (at T_g) of the materials and corresponding mechanical properties such as strain-to-failure, stress at failure, and tensile toughness was also determined. This work will provide further insight into the property evolution of photopolymerizable polymer networks, as well as highlight and quantify the effect of composition and resulting structure on a broad range of mechanical properties. This will help to further demonstrate how simple modifications to polymerization conditions can be used to optimize the physical and mechanical properties of these networks for a wide range of potential applications.

EXPERIMENTAL

Materials

Network materials were prepared by the copolymerization of *tert*-butyl acrylate (tBA) with one of three dimethacrylate crosslinking agents: (1) di(ethylene glycol) dimethacrylate (DEGDMA), (2) poly(ethylene glycol) dimethacrylate (PEGDMA), $M_n = 550$ (PEGDMA550), or (3) PEGDMA, $M_n = 750$ (PEGDMA750). Monomer characteristics are presented in Table I and include the average number of repeat units (poly(ethylene glycol), i.e., PEG repeat

TABLE I
Monomer Characteristics

Monomer	Repeat units ^a	MW (g/mol) ^b
tBA	1	128
DEGDMA	2	242
PEGDMA(550)	9	550
PEGDMA(750)	13.5	750

^a Number of repeat units (PEG repeat units for the PEGDMA materials).

^b Average molecular weight (including methacrylate end groups when applicable).

TABLE II
Conversion from Weight Percent to Mole Percent
Crosslinker for the Three Crosslinking
Agents Used in This Study

Weight percent	Mole percent		
	DEGDMA	PEGDMA(550)	PEGDMA(750)
0	0.0	0.0	0.0
2	1.1	0.5	0.3
4	2.2	1.0	0.7
10	5.6	2.5	1.9
20	11.7	5.5	4.1
40	26.1	13.4	10.2
85	75.0	56.9	49.2
100	100.0	100.0	100.0

units for the three crosslinking agents) and molecular weights (MW), which are number-average molecular weights for the PEGDMA materials. The three crosslinking agents have similar backbone chemistries but differ in chain length (number of PEG repeat units). Comonomer solutions were produced by mixing varying weight percentages of one of the crosslinking agents with tBA. The compositions evaluated in this study are provided in Table II, where compositions are listed in terms of weight percent (wt %) and mole percent (mole %) crosslinking agent. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone was added to the comonomer solution at a concentration of 1 wt % of the total comonomer weight and mixed manually until fully dissolved. All materials used in the polymer synthesis were purchased from Aldrich (Milwaukee, WI) and used as-received.

Methods

Glass slides were coated with Rain-X (SOPUS Products, Houston, TX), which acts as a nonreacting release agent, prior to the addition of the comonomer solution. The comonomer-photoinitiator mixture was injected between two coated glass slides, which were separated by 1-mm spacers and secured by binder clips. The entire configuration was then exposed to UV light (Blak-Ray, B-100AP) for 10 min (intensity $\sim 8 \text{ mW/cm}^2$).

Near-infrared (NIR) spectroscopy (Nicolet 750 Magna FTIR Spectrometer, Madison, WI) was used to determine the conversion of a representative set of compositions (0, 4, 40, and 100 wt % crosslinking agent for all three crosslinking systems) subjected to the polymerization protocol. Spectra were acquired from 16 scans with a 2 wavenumber resolution. Samples were scanned pre- and post-photopolymerization and conversions were based on the =C-H absorption peak located at $\sim 6165 \text{ cm}^{-1}$.²² Percent conversions were calculated by subtracting the ratio

of the absorbance peak area after to before polymerization from one²³ and multiplying the final value by 100. All tested compositions demonstrate conversions $>90\%$, with the exception of the 100 wt % DEGDMA composition that reaches conversion levels of $\sim 80\%$.

Swelling experiments ($n \geq 2$) were completed by placing samples $\sim 3 \text{ mm} \times 3 \text{ mm} \times 1 \text{ mm}$ in size (cut from bulk slide samples with a precision saw) in $\sim 20 \text{ ml}$ of 2-propanol (Fisher Scientific, Pittsburgh, PA), a solvent for the tBA homopolymer. Samples were polished with 500–600 grit sandpaper prior to testing and initial weights (W_i) were measured prior to immersion into the solvent. Sample weights were then measured periodically until equilibrium (swollen) weights (W_s) were reached. The equilibrium (weight) swelling ratio (q) was calculated from the relationship:²⁴

$$q = \frac{W_s}{W_i} \quad (1)$$

Samples for dynamic mechanical analysis (DMA) were cut from bulk slide samples with a precision saw to final dimensions of $\sim 4 \text{ mm} \times 1 \text{ mm} \times 17 \text{ mm}$ ($n \geq 2$). Samples were polished with 500–600 grit sandpaper prior to testing and the ends were wrapped with aluminum foil to prevent failure at the grips during testing. Testing was performed using a TA Q800 DMA (New Castle, DE) under tensile loading with a dynamic strain of 0.1%, a frequency of 1 Hz, a force track of 150% and a heating rate of $5^\circ\text{C}/\text{min}$. The glass transition temperature is defined in this study as the peak of the $\tan \delta$ (or $\tan \delta$) curve obtained from DMA testing, where $\tan \delta$ is the ratio of the loss modulus to the storage modulus.²⁵

For strain-to-failure testing, flat dog-bone tensile samples were laser-cut from bulk slide samples. Sample geometry was adapted from dimensions stated in ASTM D 638-03, with a gage cross-sectional area of $3 \text{ mm} \times 1 \text{ mm}$ and a gauge length of $\sim 8 \text{ mm}$. Samples were polished with 500–600 grit sandpaper prior to testing to remove edge effects caused by the laser-cutting. Strain-to-failure tests were performed using an MTS Insight mechanical tester with a 100 N load cell. A thermal chamber (Thermcraft, Inc., Winston-Salem, NC model LBO-14-8-5.25-1X-J8249_1A) with liquid nitrogen cooling was used to control the isothermal test temperature. Each composition was tested at its respective T_g ($n \geq 2$). Once the thermal chamber reached the set temperature, a 10 min temperature hold was completed prior to sample elongation to ensure temperature equilibrium. Tests were run in displacement control at an extension rate of 1 mm/min. Strain was measured externally by a laser extensometer (LX300, MTS, Eden Prairie, MN). Laser tape was placed on the

extreme ends of the sample gauge section to measure overall gauge elongation. Initial tests were conducted to ensure that the tape did not influence the mechanical response (stiffness and strain-to-failure) of the samples. To allow the use of data from runs where the laser data were not usable, an effective gage length (dependent on grip type and elongation) was determined for each polymer composition and used to match strain determined by crosshead displacement to that of the laser extensometer for final determination of strain-to-failure values. The effective gage length was dependent on material composition and total elongation because when crosshead displacement data was compared with laser extensometer strain data, the softer samples (reaching higher elongation levels) experienced larger deformation contributions from the grip-to-gauge section (which increased as elongation levels increased), resulting in larger effective gage lengths.

The term crosslink density refers to the number of crosslinked chains per unit volume. The number average molecular weight of the polymer between crosslinks (\bar{M}_c) is inversely related to the crosslink density. From the theory of rubber elasticity the relationship between modulus and \bar{M}_c for an elastomeric network is²⁶

$$\bar{M}_c = \frac{3\rho RT}{E_R} \quad (2)$$

where ρ is the polymer density, R is the gas constant, E_R is the rubbery modulus, and T is the absolute temperature at which E_R is measured. This relationship loses accuracy at high crosslink densities because of the loss of a reasonable approximation of a Gaussian chain distribution. As can be seen in eq. (2), \bar{M}_c is proportional to the ratio of T over E_R or

$$\bar{M}_c \propto \frac{T}{E_R} \quad (3)$$

This relationship has been used in previous studies to gain an understanding of relative changes in the network structure of similar polymer systems.^{4,18} Because of the wide range of compositions and thus degrees of crosslinking evaluated in this study, the relationship given in eq. (3) is employed to gain a qualitative understanding of the evolution of network structure with changes in composition. The relationship given in eq. (2) is used briefly to present a more quantitative estimate of the actual crosslink spacing in the network polymers. However, the limitation of this relationship at high crosslinking levels is noted and calculated \bar{M}_c values should thus be considered as relative approximations. Data presented in figures are average values \pm one standard deviation (indicated by error bars) unless otherwise noted.

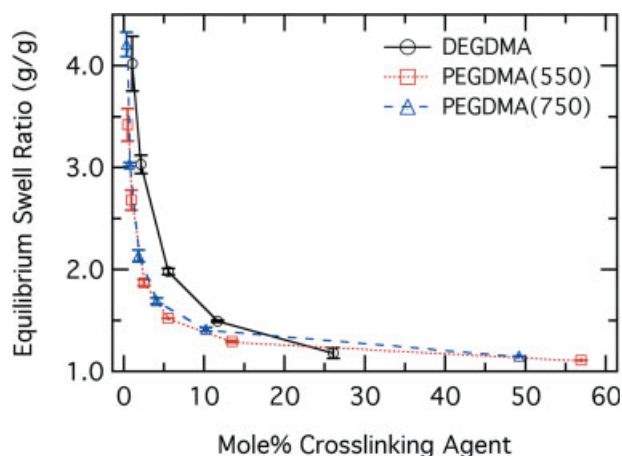


Figure 1 Equilibrium swelling ratios (q) of the three copolymer systems. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS

It is well established that the extent to which a polymer swells in the presence of a solvent can be related to the degree of crosslinking in the network structure, with the level of equilibrium swelling decreasing with increasing degrees of crosslinking.^{1,27,28} Swelling tests were completed as an initial method for determining the structure (extent of crosslinking) of the final polymer networks as a function of composition. The uncrosslinked polymer (100 wt % tBA) completely dissolves in 2-propanol, thus indicating negligible chemical crosslinking in the polymer formed from the pure linear monomer. For the remaining compositions, the equilibrium swelling ratios in 2-propanol decrease as the mole % crosslinking agent increases (Fig. 1). The trends in equilibrium swelling ratios as a function of crosslinking agent concentration for the two PEGDMA systems are similar and somewhat overlap. However, the equilibrium swelling ratios of the DEGDMA system are larger than those of the two PEGDMA systems for a given molar crosslinking agent concentration (except for the 26 mole % DEGDMA composition).

Dynamic mechanical testing was used to determine the thermomechanical properties of the network systems (Fig. 2). For the DEGDMA system, an increase in crosslinking agent concentration results in an increase in the temperature at which the transition from the glassy state to rubbery state occurs (i.e., T_g). Additionally, the breadth of this transition increases as the concentration of DEGDMA increases. The materials with the two highest DEGDMA concentrations (85 and 100 wt %) appear to evidence transitions at $\sim 140^\circ\text{C}$. However, these transitions are difficult to distinguish because of the

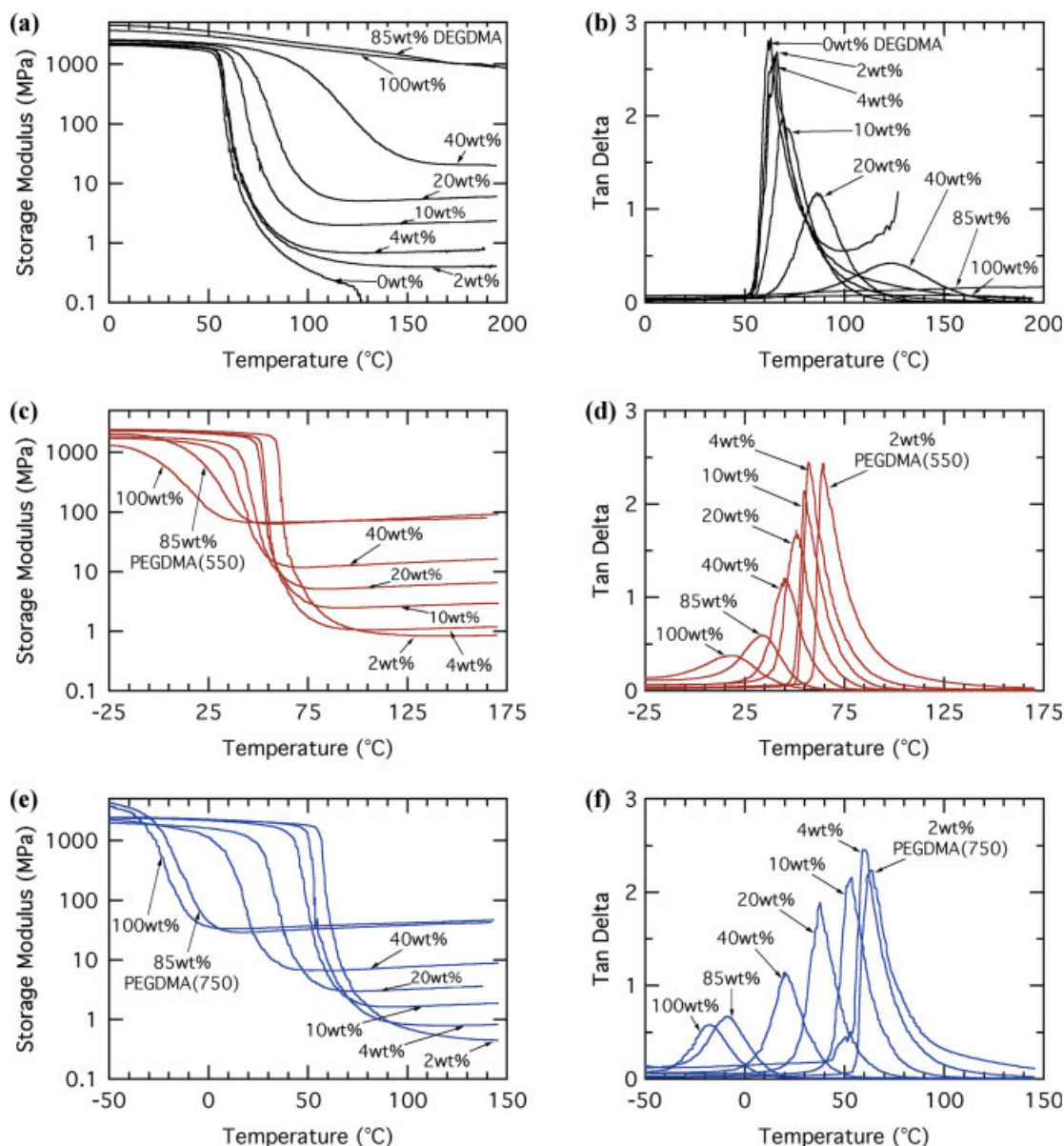


Figure 2 Representative curves from dynamic mechanical analysis (DMA) of the three network systems as a function of temperature, under tensile loading: (a, b) DEGDMAs; (c, d) PEGDMA(550); (e, f) PEGDMA(750). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

large breadth and reduced height of the corresponding $\tan \delta$ peaks. For the two systems with PEGDMA crosslinking agents, an increase in crosslinking agent concentration results in a decrease in the temperature at which the transition from the glassy state to the rubbery state occurs. Furthermore, the decrease in T_g occurs more rapidly for the PEGDMA with the higher molecular weight. The neat tBA material (0 wt % crosslinking agent) loses mechanical integrity at temperatures just above its glass transition range. As expected, the addition of a crosslinking agent results in the presence of a rubbery plateau region that enables the crosslinked polymers to maintain mechanical loading at temperatures

above their T_g regions. For all three systems studied, an increase in crosslinking agent concentration results in an increase in the magnitude of the rubbery modulus plateau.

The trends in the modulus-temperature data can be seen in Figure 3, where T_g and E_R are plotted as a function of mole % crosslinking agent. T_g values of the DEGDMA system increase in a near-linear manner with increasing mole % DEGDMA, with some deviation from linearity at low crosslinking levels [Fig. 3(a)]. The T_g values of the PEGDMA systems decrease monotonically with increasing mole % crosslinking agent. The rate of decrease in T_g with increasing PEGDMA concentration lessens at higher

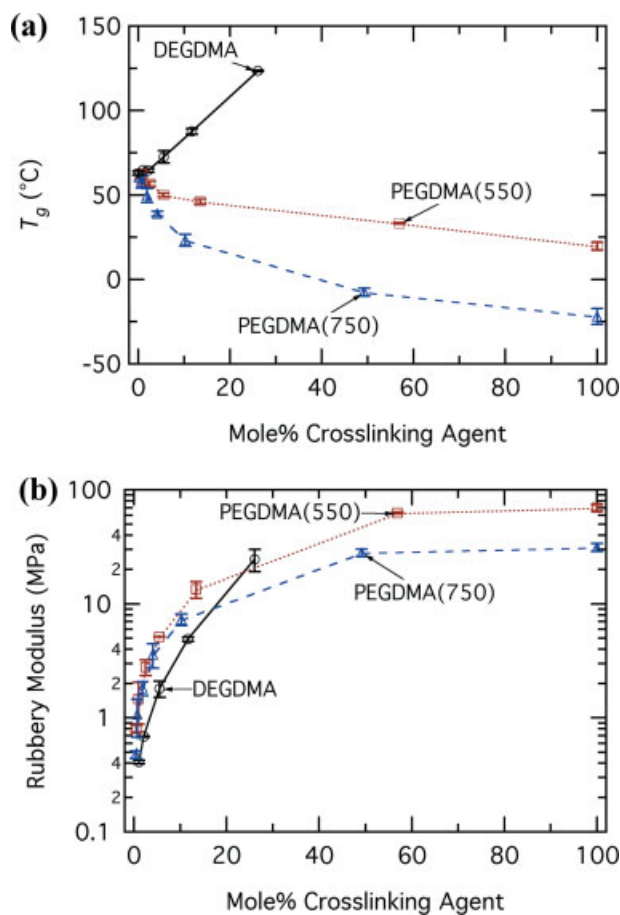


Figure 3 (a) T_g of the three copolymer systems as a function of mole % crosslinking agent, where T_g is defined as the peak of the $\tan \delta$ curve; (b) rubbery modulus (E_R) as a function of mole % crosslinking agent, where E_R values were taken from the rubbery plateau of the DMA curves shown in Figure 2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

crosslinking concentrations. The rubbery modulus values of all three systems increase with increasing mole % crosslinking agent [Fig. 3(b)]. No data are included for the uncrosslinked material because of the lack of a modulus plateau in the rubbery region. For the PEGDMA systems, the rubbery modulus values as a function of mole % crosslinking agent are similar at low levels of crosslinking. At higher crosslinking agent concentrations the rubbery modulus of the PEGDMA(550) system surpasses that of the PEGDMA(750) system, and the rubbery moduli of both systems approach asymptotic values as the mole % crosslinking agent increases further. The E_R values of the DEGDMA system for a given mole % crosslinking agent tend to be lower than that of the PEGDMA systems and do not reach a plateau in the tested composition range. Values of T_g and E_R for the two highest DEGDMA compositions (85 and 100 wt %) are not included in this analysis because of

their lack of a well-defined glassy to rubbery transition.

To gain a better understanding of the structural evolution (in terms of the extent of crosslinking) of the evaluated materials, the ratio given in eq. (3) (T/E_R) was determined as a function of composition. Figure 4 shows T/E_R as a function of mole % crosslinking agent for the three systems studied. Overall, the T/E_R ratio decreases with increasing crosslinking agent concentration. At small crosslinking agent concentrations, a small change in composition results in a large change in the T/E_R ratio. However at higher crosslinking agent concentrations, the molecular weight between crosslinks becomes less sensitive to composition, with T/E_R approaching an asymptotic value as a function of composition. For a given mole % crosslinking agent, the T/E_R values for the two PEGDMA

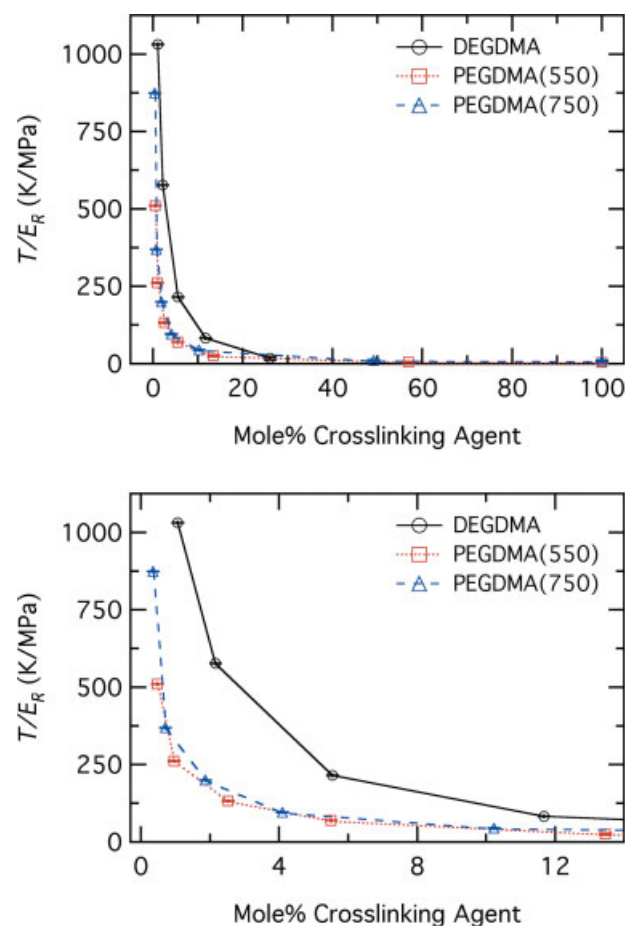


Figure 4 T/E_R ratio as a function of mole % crosslinking agent. T/E_R is assumed proportional to the number average molecular weight between crosslinks (\bar{M}_c), and thus can be used as a qualitative measure of the change in the distance between crosslinks as a function of mole % crosslinking agent. Top: full concentration range; bottom: low concentration range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

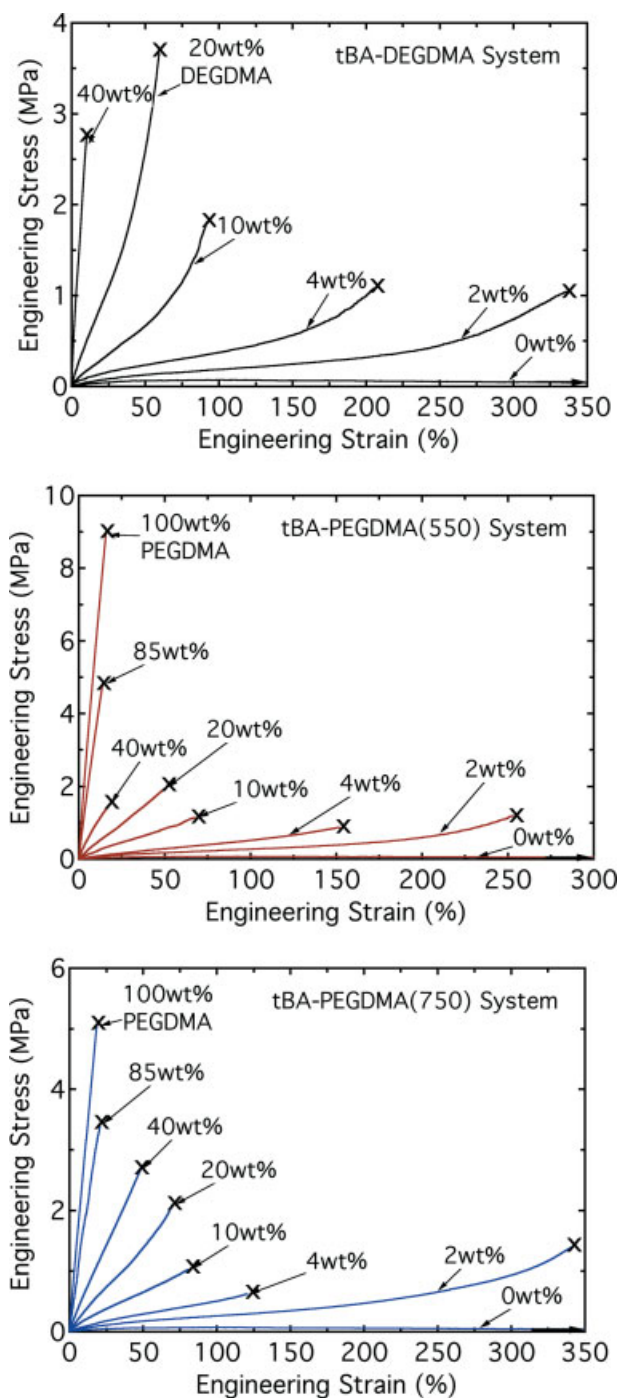


Figure 5 Tensile deformation behavior (to failure) of the three copolymer systems, where each composition is tested at T_g (representative curves shown). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

systems are similar but are larger for the DEGDMA system until ~ 26 mole % DEGDMA (40 wt %).

Representative tensile stress-strain curves (through fracture, indicated by an X) of the three network systems are shown in Figure 5. Each composition was tested at its determined T_g to control inherent differences in the stress-strain response due to shifts in the

relative T_g locations. Because the 85 and 100 wt % DEGDMA materials did not evidence a well-defined glass transition, they were not included in the strain-to-failure testing (where “failure” is considered the point of fracture). The uncrosslinked material (0 wt % crosslinking agent) reached the extension limits of the equipment prior to fracture. As crosslinking agent concentration increases, the stress-strain behavior of the material transitions from a “classic” elastomeric response to that of a stiff network with a pronounced brittle response. Overall strain-to-failure decreases with increasing mole % crosslinking agent (Fig. 6). The trends of strain-to-failure as a function of mole % crosslinking agent for the two PEGDMA systems are similar. However, the strains-to-failure for the DEGDMA system are noticeably larger than those of the PEGDMA systems for a given mole % crosslinking agent concentration. For all three systems, strain-to-failure is most sensitive to compositional changes at low crosslinking agent concentrations, where small changes in the mole % crosslinking agent result in

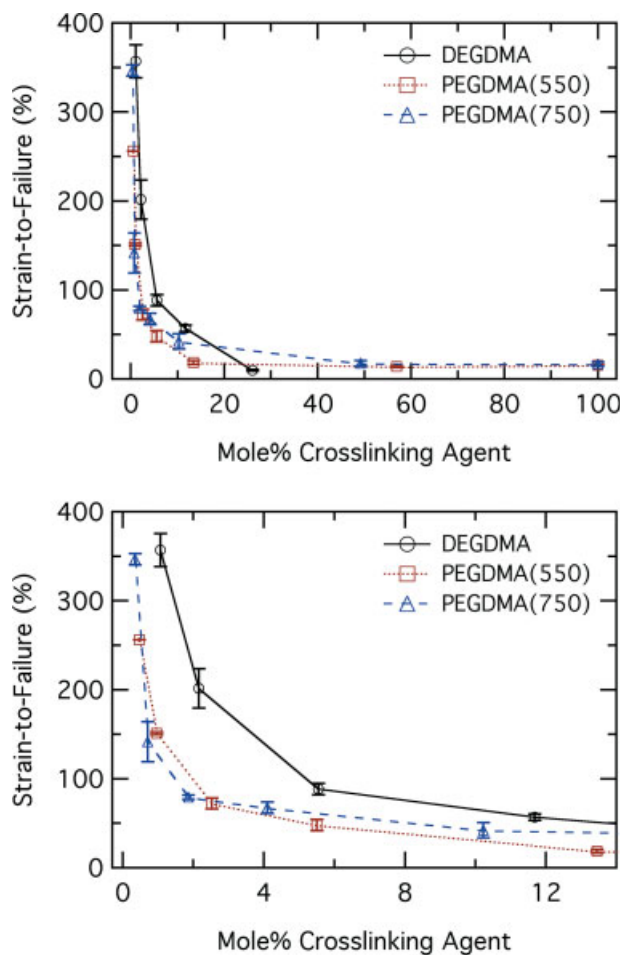


Figure 6 Failure strains at T_g as a function of mole % crosslinking agent for the three copolymer systems. Top: full concentration range; bottom: low concentration range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

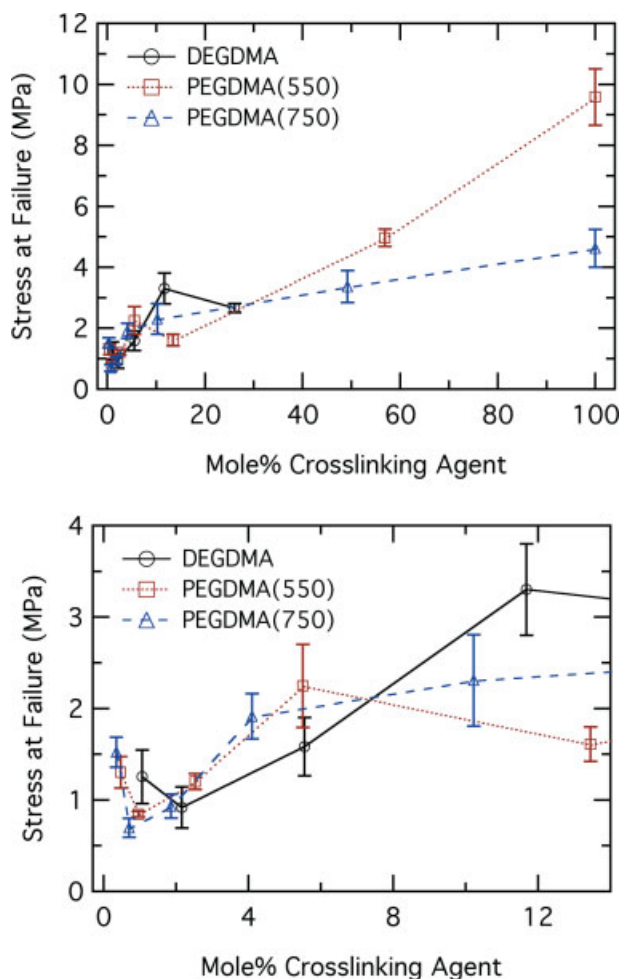


Figure 7 Stress at failure at T_g as a function of mole % crosslinking agent for the three copolymer systems. Top: full concentration range; bottom: low concentration range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

relatively large changes in strain-to-failure. This compositional sensitivity diminishes as the concentration of crosslinking agent increases.

At low crosslinking agent concentrations all three systems evidence an initial decrease and subsequent increase in the average values of stress at failure (tensile strength) with increasing concentrations of crosslinking agent (Fig. 7). Overall, average stress at failure values for the two PEGDMA systems continue to increase as the PEGDMA concentration increases. The stress at failure as a function of mole % crosslinking agent for the two PEGDMA systems is similar at low crosslinking agent concentration. At higher concentrations of PEGDMA crosslinking agent, the stress at failure of the PEGDMA(550) system becomes larger than that of the PEGDMA(750) system. For the DEGDMA system, at higher levels of crosslinking agent concentration, the stress at failure again decreases.

Tensile toughness (or work of fracture) values, at T_g , were determined from the area under the tensile stress-strain curves (Fig. 8). The tensile toughness of the three systems appears to decrease with increasing crosslinking agent concentration at very low crosslinking levels. Beyond that point, there is no clear trend in this property with increasing crosslinking agent concentration, aside from the increase in tensile toughness of the PEGDMA(550) at its compositional limit due to the increased value of stress at failure of that composition.

DISCUSSION

In this study the polymer structure, specifically the extent of crosslinking, was modified by systematically (1) varying the weight fraction of a dimethacrylate crosslinking agent relative to an acrylate base monomer, and (2) varying the size (MW or length) of the crosslinking agent used. This methodology results in a transition in both chemistry and

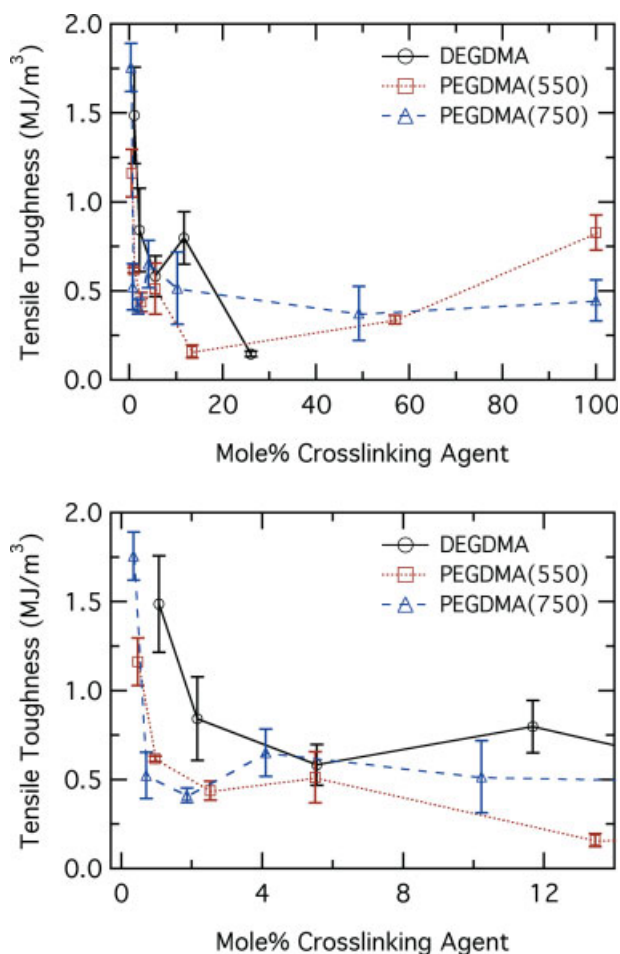


Figure 8 Tensile toughness at T_g as a function of mole % crosslinking agent for the three copolymer systems. Top: full concentration range; bottom: low concentration range. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

structure from a linear polymer (tBA chains) to a three-dimensional network structure (DEGDMA- or PEGDMA-based). This transition in structure should occur at the (compositional) point at which the crosslinking agent concentration is sufficiently high to statistically favor the interaction of crosslinking agent molecules with one another rather than with tBA molecules/chains. This compositional point should theoretically occur at a 1 : 2 ratio of the number fraction of dimethacrylate molecules to monoacrylate monomer molecules, i.e., 33 mole % crosslinking agent [48.5, 68, and 74 wt % crosslinking agent for DEGDMA, PEGDMA(550), and PEGDMA(750), respectively]. However, this point of transition should also depend on specific polymerization conditions as well as crosslinking agent reactivities and efficiencies.

As a consequence of this chemical and structural transition, the structure and property relationships determined in this study reflect both an increase in crosslink density and a change in chemistry. The eventual disappearance of the linear (tBA) chains in the network as the structure approaches that of the pure DEGDMA or PEGDMA homopolymers in the current systems implies that the extent of crosslinking or crosslinking density is ultimately limited by the MW (length) of the crosslinking agents employed and that the crosslink density of the systems should eventually saturate as the crosslinking agent concentration becomes sufficiently high. This behavior is demonstrated in Figure 4 where the T/E_R parameters for the PEGDMA systems approach asymptotic values at high crosslinking agent concentrations. This structural and chemical transition and crosslinking density limitation is most likely the underlying cause of the decrease in compositional sensitivity of a number of the tested physical and mechanical properties of these systems (such as q , E_R , and strain-to-failure) at high crosslinking agent concentrations.

The decrease and eventual plateau in equilibrium swelling ratio with increasing mole % crosslinking agent (Fig. 1) most likely confirms the expected increase and plateau in crosslink density (decrease/plateau in \bar{M}_c) with increasing crosslinking agent concentration. However, because of the change in chemistry from a tBA-based polymer to a PEGDMA-based polymer as crosslinking agent concentration increases, the decrease in equilibrium swelling could also be interpreted as being a consequence of a shift in the chemical compatibility between the network polymer and the chosen solvent. To check this possibility, samples of PEGDMA(550) and PEGDMA(750) homopolymers were placed in de-ionized water as well as in 2-propanol to determine equilibrium swelling ratios in the two different liquids. The equilibrium swelling ratios of these pure PEGDMA polymers were slightly higher in water than in the

2-propanol (average values: $q_{\text{water}} = 1.4$, $q_{2\text{-propanol}} = 1.1$) because of the more hydrophilic nature of the PEGDMA material. However, these values are lower than the equilibrium swelling ratios of the network materials with low mole % crosslinking agent concentration in 2-propanol. This indicates that while some of the decrease in swelling capacity with increasing DEGDMA/PEGDMA content may be due to decreasing solvent-polymer compatibility, it is also due to an increasing crosslink density. This is also confirmed by the increase in E_R with crosslinking agent concentration, as will be discussed.

The T_g values of the studied network systems are dependent on both the crosslinking agent concentration as well as its MW (Fig. 3). This is similar to the trend previously reported for photopolymerized networks systems produced by the copolymerization of *n*-octyl methacrylate with DEGDMA and PEGDMA crosslinking agents.¹⁸ An increase in DEGDMA, the smallest crosslinker, leads to an increase in T_g , whereas an increase in the longer PEGDMA crosslinkers resulted in a decrease in T_g , with PEGDMA(750), the longest crosslinker, resulting in the lowest T_g values. When modifying the crosslink density of a system consisting of two chemically different monomers by compositional variations, there are two effects contributing to the resulting T_g values, commonly referred to as the "crosslinking effect" and the "copolymer effect."^{18,29-31}

The crosslinking effect is due to the addition of junctions between chains in the structure, which will affect the free volume³² and act to restrict molecular motion of the polymer chains.³⁰ The copolymer effect is due to the change in chemistry that occurs in the polymer as chemically different crosslinks are added to the base polymer/monomer. The crosslinking effect will act to increase T_g , while the copolymer effect can either increase or decrease T_g depending on the chemical and physical nature of the combined materials such as the inherent conformational rigidity of the backbones and the intermolecular interactions between the various chains. The DEGDMA crosslinking agent appears to act as more of a traditional crosslinker in terms of its effect on T_g . This is most likely due to the shorter crosslinks acting to decrease the free volume of the system as it pulls the main tBA chains together. This would effectively increase the temperature at which larger-scale molecular motions can occur. Additionally, the DEGDMA crosslinker does not introduce an appreciable fraction of the soft (low T_g) PEG units that are not bound-up close to a network junction. The longer PEGDMA crosslinkers result in a copolymer effect, lowering T_g by incorporating low- T_g molecules into the polymer network. The longer crosslinks might also increase the free volume of the system and thus decrease the temperature at which

molecular motion can occur. Thus the reduction in T_g due to the incorporation of low T_g PEG segments increases with the MW of this segment. However, the degree to which crosslinking restricts the networks decreases with increasing PEG MW, also acting to decrease T_g with increasing PEG MW. This reduction in the restriction of crosslinking with increasing PEG MW is also reflected in the mechanical properties of this system, with E_R and stress at failure decreasing with increasing PEG MW as the compositional limits are approached. Previous studies have evaluated the magnitude of the crosslinking and copolymer contributions to T_g in a number of crosslinked systems^{29–31}; however, no attempt was made to explicitly separate these effects in the present study.

Although the longer PEGDMA crosslinkers result in a copolymer effect with respect to T_g , the introduction of any of the three crosslinking agents still results in additional (permanent) junctions between chains that restrict molecular motion due to an applied load. This is evidenced by the increase in E_R with increasing crosslinking agent concentration for all three systems, confirming an increase in the degree of crosslinking. However, at low crosslinking agent concentrations, E_R for the two PEGDMA systems is dominated by the concentration of the crosslinking agent, and is less affected by the MW of the crosslinker. At higher crosslinking agent concentrations E_R is dominated by the MW of the crosslinking agent and is less sensitive to changes in the crosslinking agent concentration in that range. This results because at the high PEGDMA concentrations, the structure approaches that of the PEGDMA homopolymer and the crosslink density is limited by the MW of the PEGDMA crosslinker rather than by the added fraction of the agent. The shorter PEGDMA(550) chains produce a tighter network than that of the PEGDMA(750) system, resulting in additional crosslinking restrictions and thus higher modulus values at the compositional limits.

The DEGDMA crosslinking agent should provide the highest crosslink density of the three crosslinking agents because this monomer has the smallest chain length. However, modulus values of the DEGDMA system are smaller than those of the PEGDMA systems, indicating a lower effective crosslink density in this system (as reflected in larger calculated T/E_R values shown in Fig. 4). A similar response was previously reported by Kannurpatti et al.¹⁸ and attributed to the shorter DEGDMA molecules being more prone to cycle formation during polymerization than the larger PEGDMA molecules. This tendency has also been predicted by simulation studies done on free radical polymerizations of multifunctional monomers.^{14,33} The formation of primary cycles during polymerization (where a propagating radical on the main chain reacts with a pendant

double bond from the same chain) results in fewer effective crosslinks for a given molar crosslinking agent concentration than a monomer that does not form cycles. The less effective nature of DEGDMA crosslinking is also evident in its larger equilibrium swelling ratios (Fig. 1) and larger strains-to-failure (Fig. 6) than the PEGDMA systems for the same molar crosslinking agent concentration.

A trend toward the theoretical crosslinking limit (based on crosslinking agent MW) is, however, noticed as the DEGDMA concentration approaches 26 mole %. The properties of the DEGDMA-based system appear to transition from a material that is more lightly crosslinked than the PEGDMA-based materials (resulting in higher swelling and T/E_R ratios and strain-to-failure values as well as lower E_R values) to a material that is more tightly crosslinked than the PEGDMA-based materials (resulting in lower swelling and T/E_R ratios and strain-to-failure values as well as a higher E_R values).

Strain-to-failure has been shown to decrease with increasing concentration of crosslinking agent in rubbers.^{26,34} The same trend is demonstrated in the current study, where strain-to-failure is most significantly affected by the crosslinking agent concentration. This property is very sensitive to compositional changes at low crosslinking agent concentrations (up to ~ 10 mole %), whereby a small addition of crosslinking agent results in a significant decrease in the strain-to-failure, similar to trends reported for rubber.²⁶ Thus, small additions of permanent crosslinks hinder molecular motion enough to impede large-scale deformation. The general trend in strain-to-failure and T/E_R (\bar{M}_c) as a function of molar concentration of crosslinking agent appear very similar, suggesting a correlation between these two properties. This correlation is observed more directly in Figure 9 in which strain-to-failure is plotted as a

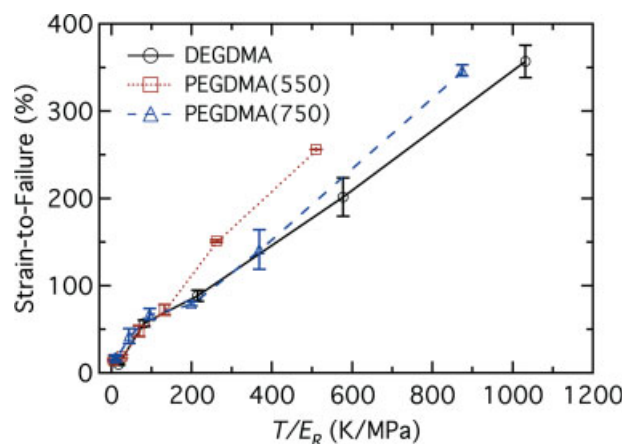


Figure 9 Strain-to-failure at T_g as a function of T/E_R for the three copolymer systems. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

function of the T/E_R ratio. The data demonstrate that there is a near linear relationship between strain-to-failure and \bar{M}_c , which has also been reported for peroxide-vulcanized rubbers (from work of Morell and Stern, in Treloar³⁵). At low T/E_R values (high crosslink densities) the strain-to-failure values are similar for the three crosslinkers. However, at larger T/E_R values (low crosslink densities) the responses of the three crosslinking systems deviate, with the PEGDMA(550) system resulting in the largest strains-to-failure and the DEGDMA system resulting in the smallest. Because this correlation considers crosslink density, as measured through rubbery modulus, rather than crosslinking agent concentration, it cannot be simply explained based on the effectiveness of the crosslinkers. The trend in strain-to-failure with crosslinker molecular weight at low crosslink densities is not fully understood; however, relative heterogeneity of the resulting network systems may be one factor contributing to this trend.

A reduction in strain-to-failure with increased crosslink density has also been reported for a number of network systems (beyond traditional rubbers and elastomers) with varying crosslink densities produced by modifying the crosslinking agent concentration prior to copolymerization, the crosslinker molecule size, or the prepolymerization solvent concentration.³⁶⁻³⁹ However, in contrast to such previous studies where mechanical testing was performed at room temperature, in the current study each polymer is tested at the determined T_g to ensure that each material is in a similar state. This ensures that the reported trends were mainly a result of the effective crosslink density in each system and not of relative shifts in T_g which can also have a first-order effect on deformation and strain-to-failure. For example, if testing on the current system was done at room-temperature, strain-to-failure could increase with addition of a PEGDMA crosslinker simply because the T_g is shifted toward the test temperature, providing a viscoelastic (not glassy) material for which failure strains would be naturally higher. Ensuring that each material is tested while in similar states allows a more direct correlation between the structure and resulting deformation behavior as well as determined mechanical properties, which is the main purpose of this study. Related work on strain-to-failure as a function of temperature in the glassy, viscoelastic, and rubbery regimes of photopolymerized polymer networks was recently reported.⁴⁰

The average stress at failure demonstrates a consistent initial decrease with increasing crosslinking agent concentration. This is also seen in Figure 5 by the loss of the upturn in the stress-strain response at large elongations as crosslinking agent concentration increases. This upturn in stress, commonly seen in rubber-like or elastomeric materials, has been attrib-

uted to limited chain extensibility and/or strain-induced crystallization.^{1,41} The stress at failure then increases again as the crosslink concentration increases and a more highly crosslinked structure forms. Failure stress is most affected by the mole % crosslinking agent at low crosslink agent concentrations, but then becomes additionally dependent on the MW of the crosslinking agent as the structure transitions to the PEGDMA-based network and again the increase in crosslink restrictions with decreasing PEG MW results in the shorter PEG system demonstrating higher stress at failure values at the compositional limits. The DEGDMA system evidences a second drop in failure stress at high crosslinking agent concentrations. This could be due to a more heterogeneous structure in the high DEGDMA material, which has been suggested as a cause of decreased ultimate properties in network systems due to a nonuniform stress distribution occurring in the network and weak interfaces between highly crosslinked (microgel) regions.^{26,38} Earlier studies (simulation and experimental) on networks formed from multifunctional monomers have concluded that short crosslinkers, such as DEGDMA, result in more heterogeneous structures than longer crosslinkers^{14,18} and that heterogeneity increases with increasing crosslinking agent concentration.^{14,15,18} An increased heterogeneity may also be indicated in the present system by the broader glass transition region of the 40 wt % DEGDMA system (compared with the high PEGDMA concentration systems), which has been suggested to correspond to a wider \bar{M}_c distribution and/or a general heterogeneity in the network structure.^{30,42}

When the stress at failure is analyzed as a function of T/E_R , a different trend is observed (Fig. 10), whereby the stress at failure decreases rapidly as the

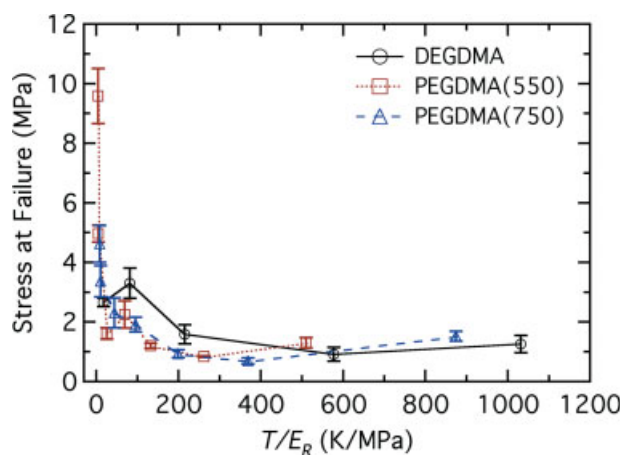


Figure 10 Stress at failure at T_g as a function of T/E_R for the three copolymer systems. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

distance between crosslinks is increased, and then plateaus or increases somewhat with a further increase in T/E_R . A number of different trends have been reported for the effect of crosslink density on the ultimate strength (or stress at failure) of rubber-like and elastomeric materials.^{35,41,43,44} One commonly reported trend for rubber-like materials is an increase in strength in the early stages of crosslinking followed by a reduction in strength as crosslinking is increased,^{34,35,45} typically attributed in part to the extent of chain orientation at high elongations, as a function of the degree of crosslinking. A more linear relationship between stress at rupture and crosslink density has been observed for polydimethylsiloxane (PDMS) networks,⁴³ which were reported as being resistant to strain-induced crystallization. In contrast, an exponential-like decrease in stress at failure with increasing \bar{M}_c for PDMS networks has also been reported.^{41,44} It has been suggested that the various trends reported could result from basic structural differences between the polymers tested.²⁶

Tensile toughness (as calculated from the area under the stress–strain curves) appears to be relatively unaffected by the concentration of crosslinking agent for the compositional ranges evaluated (Fig. 8). The PEGDMA(550) system appears to experience a slight increase in toughness as the composition approaches that of the PEGDMA(550) homopolymer due to the increase in stress at failure at high PEGDMA concentrations. The highest toughness values are observed in the most lightly crosslinked materials, because of their large elongations. If compositions with even smaller concentrations of crosslinking agent were studied, it is possible that a further increase in toughness would result due to an assumed increase in strain-to-failure and possible further increase in stress at failure (Figs. 6 and 7). Otherwise, additional means need to be employed (such as changes in deformation temperature and/or rate⁴⁰ or the chemical nature of the (meth)acrylates) to allow for “tailorability” of toughness.

Implications

The crosslinked tBA system is highly “tailorable” with respect to T_g , E_R , and strain-to-failure by simple modifications in crosslinking agent concentration and MW. The average T_g of these systems range from -22 to 124°C ; average E_R ranges from 0.4 to 70 MPa and average strain-to-failure ranges from <10 to 357% . Therefore, this system should enable property optimization for a number of applications. However, there are limitations on the degree of optimization for some properties. For example, there is a significant trade-off between E_R and strain-to-failure, so a stiff material with a large strain-to-failure

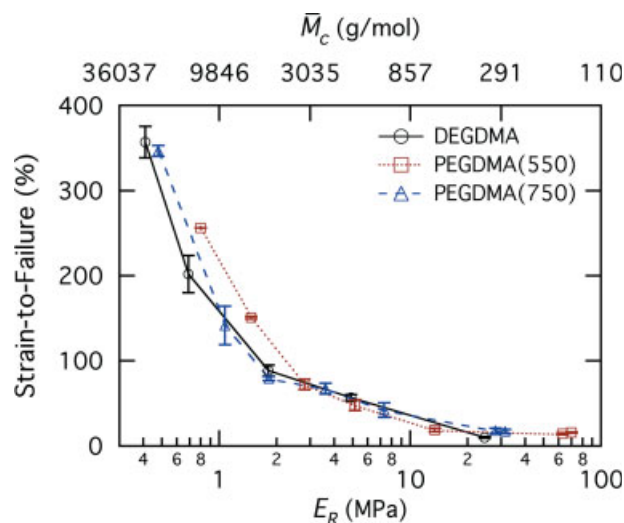


Figure 11 Strain-to-failure at T_g as a function of E_R and \bar{M}_c for the three copolymer systems. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

would be difficult to obtain. This is demonstrated in Figure 11 where strain-to-failure is plotted as a function of E_R as well as \bar{M}_c [calculated from the relationship given in eq. (2)]. Because of the dependency of the calculated value of \bar{M}_c on T (which is different for each composition), a fit between E_R and the calculated \bar{M}_c was determined for the combined data of all three systems. This fit was used to determine values of \bar{M}_c (for a given E_R) listed on the top x-axis in this figure. Deviation of the fit from calculated values of \bar{M}_c from specific data points increases as E_R increases, reaching a $\sim 25\%$ difference for the most highly crosslinked compositions of each of the three systems.

Figure 11 additionally demonstrates the diminishing sensitivity of strain-to-failure to E_R as E_R increases (and \bar{M}_c decreases). The strain-to-failure decreases as E_R begins to increase (and \bar{M}_c decreases), such that at low crosslinking levels a small increase in E_R generates a substantial decrease in strain-to-failure. As E_R continues to increase, strain-to-failure continues to decrease, however at a much smaller rate, with the PEGDMA(550) system reaching an apparent asymptotic value. Changes in monomer chemistry would need to be explored further to determine how additional properties such as strain-to-failure, toughness, and E_R could possibly be modified and further optimized. Nonetheless, this study quantifies the inherent trade-offs between major physical and mechanical properties of (meth)acrylate-based photopolymerizable systems.

The effect of crosslinker concentration and MW on a number of the studied properties “trade-off” as the crosslinking concentration is increased. For example,

at low crosslinking concentrations, a mixture of crosslinker of varying MW could be used to obtain a desired T_g , with E_R , q , and strain-to-failure being somewhat unaffected as long as the required crosslink concentration is maintained. However, additional drawbacks and benefits of the length of the crosslinking agent must be considered. For example, the longer crosslinkers could be considered superior to the shorter DEGDMA crosslinker in that they form a more homogeneous system, are less prone to form cycles during polymerization, and thus provide more effective crosslinking, as indicated via higher E_R values and larger achievable tensile strengths. Conversely, the possible values of T_g from systems using the longer PEGDMA crosslinks are all low and the shorter crosslinking agent (DEGDMA) would be needed if a higher T_g were required. Additionally, the primary cycles that form during the polymerization of the DEGDMA system result in larger strains-to-failure for a given molar concentration of the crosslinking agent, which could be a desired characteristic.

The results have considerable impact on the use of such networks for shape-memory behavior where, similar to elastomers, materials with varying and tailorable strain-to-failure and rubbery modulus values are highly desired. Similarly, the development of photocrosslinked hydrogels for tissue-engineering applications will benefit from the results because of varying requirements of stiffness and extensibility. In shape-memory polymers, low crosslink densities should result in large recoverable strains but low force generation under external constraint, and high crosslink densities in small recoverable strain levels but large recoverable forces under external constraint. Additionally, it is necessary to be able to tailor the recovery temperature and/or time of shape-memory polymers for specific applications, which can be accomplished by adjustment of T_g .

CONCLUSIONS

The studied systems are highly tailorable with respect to T_g (-22 to 124°C), E_R (0.4 to 70 MPa), and strain-to-failure at T_g (<10 to 357%) by simple modification of the fraction and MW (length) of the crosslinking agent added to the monoacrylate base monomer.

T_g is dependent on both the MW of the crosslinking agent and its concentration in the comonomer mixture. For the PEGDMA systems, at low concentrations of crosslinking agent, E_R is mainly driven by the crosslinking agent concentration. At higher crosslinking agent concentrations E_R is more dependent on the MW of the crosslinking agent. The same dependence on crosslinking agent concentration and MW are observed for the stress at failure of

these network systems. Strain-to-failure is more dependent on crosslinking agent concentration, as opposed to crosslinking agent MW. There is a significant trade-off between E_R and strain-to-failure for the three systems in the study.

DEGDMA is a less effective crosslinking agent than the longer PEGDMA molecules. This is most likely due to the greater propensity of the DEGDMA molecule for forming cycles during polymerization. This led to unexpected trends in various properties of the DEGDMA system, such as higher swelling capacities, lower E_R values, and higher strains-to-failure compared with those of the PEGDMA systems for a given molar concentration of crosslinking agent. A more heterogeneous structure in materials with a high DEGDMA concentration is a possible cause of apparently premature tensile failure, resulting in a reduced value of stress at failure.

Because of the use of compositional changes between a monoacrylate monomer and a dimethacrylate crosslinking agent as a means to control crosslinking density, the majority of the physical and mechanical properties of this system demonstrate a reduced sensitivity to compositional changes at higher crosslinking agent concentrations, because at this point the network system primarily consists of the crosslinking agent. A different trend in such properties will most likely occur if the crosslink density were to be controlled by other means such as the crosslinking of preexisting linear polymer chains.

With the wide range of physical and mechanical properties achievable in photopolymerizable systems such as those used in this study, a significant degree of property optimization can be achieved for a wide range of applications. This study demonstrates the ease with which a number of key physical and mechanical properties of photopolymerized network systems can be tailored by simple compositional modifications. Additionally, this work quantifies the trade-offs in the mechanical properties of such systems.

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