

On the Toughness of Photopolymerizable (Meth)Acrylate Networks for Biomedical Applications

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ABSTRACT: Photopolymerizable networks are being explored for a variety of biomedical applications because they can be formed *in situ*, rendering them useful in minimally invasive procedures. The purpose of this study was to establish fundamental relationships between toughness, network chemical structure, and testing temperature of photopolymerizable (meth)acrylate networks deformed in air and under hydrated conditions. Networks were formed by combining at least one monofunctional (meth)acrylate with a difunctional methacrylate, and weight ratios were adjusted to vary the degree of crosslinking, elastic modulus, and glass transition temperature (T_g). Stress-strain behavior and toughness were determined by performing tensile strain to failure tests at temperatures spanning the glassy and rubbery regimes of each network both in air

and phosphate-buffered saline. In air, all of the networks demonstrated a peak in toughness below the network's T_g . At an "equivalent" test temperature relative to T_g , crosslinking concentration and monomer chemistry influenced the toughness of each network. Apparent toughness is significantly altered in an aqueous environment, an effect driven by water absorption into the network causing the T_g to decrease. The results from this study provide the fundamental knowledge required to guide the development of tougher photopolymerizable networks for mechanically strenuous biomedical applications. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2711–2722, 2009

Key words: biomaterials; photopolymerization; thermal properties; thermosets; toughness

INTRODUCTION

Polymer networks formed through photopolymerization have emerged as candidate biomaterials for applications where it is advantageous to have *in situ* formation, fast synthesis rates, and simple processing into diverse geometries. These characteristics render these materials particularly useful in minimally invasive procedures.¹ They are currently used as adhesive resins in dental fillings,² but are also being explored as a scaffold material for tissue engineering applications or to deliver therapeutic molecules or cells *in vivo*.^{3,4} As a subset of photopolymers, (meth)acrylate-based networks are advantageous because their material properties can be easily tuned by control of chemistry and crosslinking density. The broad range of thermomechanical properties in these networks enables the development of various material

platforms ranging from hydrogels to shape memory polymers.^{5,6} For example, in the area of shape memory polymers, the glass transition temperature (T_g) can be tuned to body temperature so that the material can be thermally actuated into its functional form when implanted into the body. Moreover, by varying the crosslinking concentration of a system, the rubbery modulus can be tuned to control the force applied by the shape memory polymer during activation.^{5,7,8} A tunable rubbery modulus is also beneficial in hydrogel applications when designing a new tissue replacement that must mimic the stiffness of the host tissue.⁹ Additionally, the elastic modulus governs the deformation of the material and is critical in managing stress transfer to surrounding tissue.

Depending on the application, polymer networks must possess a certain range of mechanical properties. For instance, a polymer network used in a shape memory fixation device must possess a relatively high modulus (10–50 MPa) to allow for high-strength deployment into a stiff tissue such as bone⁸ while a soft-tissue replacement material must have a modulus that matches the native tissue that is replacing (0.1–100 MPa depending on the tissue).^{10,11}

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In applications involving cardiovascular stenting or implantation into readily deformable regions (i.e., intervertebral disk, tendon), a material that can sustain high-failure strains (greater than 100%) is often necessary.^{7,12} Despite the tailorability of many material properties, photopolymerizable (meth)acrylate networks sometimes lack the mechanical properties for implementation in high-loading environments or in applications where mechanical function must be maintained for long durations. Toughness broadly measures the capacity of a material to absorb strain energy and resist cracking under applied stress. Although it is relatively easy to tailor the stiffness of polymer networks to match that of host biological materials,^{13–15} maintaining toughness in line with biological tissues is elusive, especially in polymer networks.

To develop tougher, more durable photocurable (meth)acrylate networks, a fundamental understanding of the toughening mechanisms within such materials must be established. Several theoretical models have been developed to understand the structure–toughness relationship in linear polymers. For example, Wu¹⁶ predicts that toughness is dependent on the chemical composition and chain structure quantified through two interrelated variables in thermoplastic polymers, entanglement density (ν_e), and Flory's characteristic ratio (C_∞). Using the theory of Wu, the inherent toughness in polymers such as poly(ether ether ketone) (PEEK) and polycarbonate (PC), and the more brittle behavior of poly(methyl methacrylate) (PMMA) at room temperature can be better predicted and understood. In addition, these theoretical calculations have been validated with experimental observations.^{17–19} For example, one study has shown that incorporating phenyl rings into the backbone of photopolymerized thiolene-acrylates provides toughness beyond an effect dominated by the thermal transition behavior.²⁰ Although Wu's theory accounts for the relative toughness of linear polymers, because it pertains to the chemistry of the backbone, the models do not consider other distinct structural characteristics such as side-group chemistry and crosslinking density that are inherent in polymer networks.

Another reason many (meth)acrylate networks have limited toughness *in vivo* is the loss of “mechanical integrity” under aqueous conditions. For example, at room temperature, linear methacrylates such as PMMA will decrease in strength and begin to plasticize when soaked in water for long durations.²¹ When a polymer network is placed in water, a decrease in the T_g is observed resulting in a precipitous change in mechanical properties at a given test temperature.^{22,23} Previous studies using infrared spectroscopy have shown that hydrogen bonding is a large contributor to this water effect. On entering the network, water molecules will disengage the

hydrogen bonds present amongst the chains to form their own secondary bonds with hydrophilic groups such as amines, hydroxyl, or carbonyl groups.^{22,24,25} Developing tougher hydrogels for orthopedic applications has been particularly challenging since, by definition, hydrogels typically contain at least 50% of their weight in water. Several groups are currently working on developing mechanically enhanced hydrogels by changing network structure or type of crosslinking.^{26,27}

To date, there has been minimal work focusing on the toughness of biomedical grade (meth)acrylate networks. Specifically, the relationship between toughness and environmental testing conditions has not been fully characterized. The objective of this study is to build an understanding of how intrinsic and extrinsic factors influence network toughness in photopolymerizable (meth)acrylate networks. The approach consists of performing stress–strain measurements on a series of “benchmark” tough polymers and several model (meth)acrylate networks to understand how chemistry and polymer structure influence toughness. To further understand how the thermal transition behavior influences network toughness, we consider the stress–strain response at multiple temperatures spanning the glassy to rubbery regime. Finally, this study also aims to identify how the relationships between toughness, chemical structure, and temperature are influenced by immersion in phosphate-buffered saline (PBS). The results from this study provide a base knowledge required to guide the development and implementation of tough photopolymerizable polymers for load-bearing biomedical applications.

MATERIALS AND METHODS

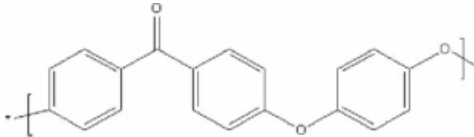
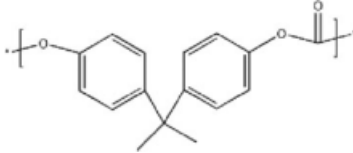
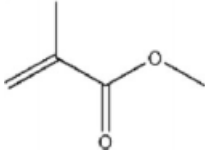
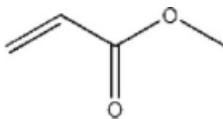
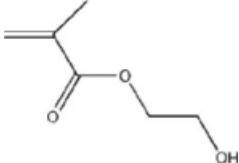
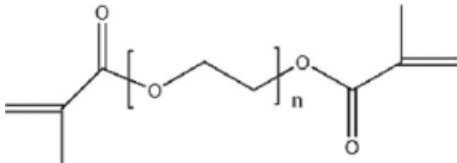
Materials

PMMA, PC, and PEEK were obtained from McMaster-Carr Inc. as sheets of thickness 1.6, 1.0, and 0.2 mm, respectively, and used as reference materials due to their well-studied mechanical behavior and common use as biomedical materials. Methyl methacrylate (MMA), methyl acrylate (MA), and 2-hydroxyethyl methacrylate (2HEMA) monomers, and a poly(ethylene glycol) dimethacrylate (PEGDMA) crosslinker with a molecular weight of $M_n = 750$ were chosen as the photopolymerizable acrylates. The monomer solutions and photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, were purchased from Sigma-Aldrich and used as received.

Network synthesis

Monomer solutions were formulated by combining a monofunctional (meth)acrylate (linear chain builder)

TABLE I
Selected Thermoplastic Polymers and (Meth)Acrylate Monomers and their Chemical Structures

Name	Abbreviation	Chemical Structure
Poly(ether ether) ketone	PEEK	
Polycarbonate	PC	
Methyl methacrylate	MMA	
Methyl acrylate	MA	
2-Hydroxyethyl methacrylate	2HEMA	
Poly(ethylene glycol) dimethacrylate	PEGDMA	

and a difunctional methacrylate (crosslinker) in a ratio determined by weight and 0.5 wt % photoinitiator. Table I shows the monomer components and their chemical structures. The weight ratios of the

monomers in each copolymer network are displayed in Table II. Each of the networks was carefully designed to screen for various chemical and structural effects. The 2HEMA-*co*-2%PEGDMA is a lightly

TABLE II
Networks Created Using a Monofunctional (Meth)Acrylate and Crosslinker (PEGDMA)

Name	Monomer Ratio Wt %	T_g (°C)	E (MPa)	q
MMA- <i>co</i> -45%PEGDMA	55% MMA 45% PEGDMA	66.8 ± 2.2	12.4 ± 0.3	1.14 ± 0.01
2HEMA- <i>co</i> -2%PEGDMA	98% 2HEMA 2% PEGDMA	111.7 ± 1.3	1.43 ± 0.2	1.58 ± 0.05
MA- <i>co</i> -MMA- <i>co</i> -2%PEGDMA	52% MA 46% MMA 2% PEGDMA	57.1 ± 1.2	0.270 ± 0.2	1.02 ± 0.01
100%PEGDMA	100% PEGDMA	-20.3 ± 0.3	30.9 ± 0.6	1.46 ± 0.02

The names and weight ratios of components used in each network are listed as well as their T_g s, rubbery moduli values (E) and swelling ratios (q) ($n=4$).

crosslinked, hydrophilic hydrogel network, similar to that used in soft contact lens applications. The MMA-co-45%PEGDMA is a moderately crosslinked material that demonstrates excellent shape memory properties in high-force applications⁸ and is moderately hydrophilic. The MA-co-MMA-co-2%PEGDMA is a lightly crosslinked, relatively hydrophobic shape memory polymer that would operate best in large deformation, low-stress biomedical applications.

Each solution was mixed manually in a glass vial and injected in between two glass slides using a glass pipette. The glass slides were separated with two 1 mm glass spacers and coated with Rain-X to enhance release. The samples were then placed under a 365 nm UV lamp (Blak Ray Model B 100AP) for 10 to 30 min depending on the network.

Dynamic mechanical analysis

Thermomechanical properties were determined using a dynamic mechanical analyzer (DMA) (TA Instruments DMA Q800). All copolymers were cut into $20 \times 5 \text{ mm}^2$ rectangular samples, and the edges were sanded to remove any microdefects. Samples were cooled to -75°C , equilibrated at -75°C for 2 min, and subsequently heated to 200°C at a constant rate of $5^\circ\text{C}/\text{min}$. Tests were performed in tension mode at a frequency of 1 Hz with a 0.1 kN preload force, 0.2% strain rate, and 150% force track. The glass transition temperature (T_g) was defined as the peak of the $\tan \delta$ (ratio of loss modulus to storage modulus) curve produced by plotting $\tan \delta$ versus temperature.²⁸ The Universal Analysis software package was used to determine the exact temperature corresponding to the maxima on the curve. The rubbery modulus (E_r) was determined as the value of the storage modulus above T_g where the $\tan \delta$ does not change. DMA was repeated once for each composition. T_g and E_r values for each composition were averaged and standard deviation was calculated.

Tensile strain to failure testing

Tensile strain to failure tests were performed on a universal testing machine (MTS Systems, Insight 2) using a 2-kN load cell and a crosshead speed of 1 mm/min. Dogbone samples were laser-cut according to dimensions specified in ASTM D 638-03 Type IV or V (see below). The edges were sanded to remove any defects from the laser and the width and thickness in the gauge section were measured using digital calipers. Samples were loaded into tensile grips, heated in a thermal chamber, and held at the testing temperature for 10 min to allow for thermal equilibration. Each polymer system was tested in tension at temperatures below and above its T_g .

Only samples that broke in their gauge length were used for further calculations. Elastic modulus was denoted as the slope of the initial linear region of the stress-strain curve while toughness was calculated as the area under the stress-strain curve in units of MJ/m^3 . The failure strain and consequently, toughness of PMMA and PEEK could not be captured for temperatures near their T_g (120 and 140°C , respectively) due to the height limits of the thermal chamber that prevented the samples from stretching to strains past 500%. However, since samples of both PMMA and PEEK were able to break at all other temperatures, it was assumed that the peak failure strain and toughness would occur at that temperature closest to their individual T_g .

For all polymers except MA-co-MMA-co-2%PEGDMA, the Type IV specimen geometry was adopted with a 20-mm gauge length and 2.8-mm gauge width. Because the characteristic ability of MA-co-MMA-co-2%PEGDMA to sustain large deformations, a specimen geometry (ASTM D 638 Type V) with a smaller gauge length was used for this material. During initial testing, a large amount of deformation was observed outside the Type IV designated gauge length (7.62 mm) in the MA-co-MMA-co-2%PEGDMA specimens. To account for this large deformation, an effective gauge length at each temperature was determined by placing laser tape at the ends of the prescribed gauge section and using a laser extensometer to measure the displacement. Although these networks stretched outside the region distinguishable by the laser, the initial strains recorded from the laser and the grip-to-grip displacement measured from the crosshead were used to calculate the effective gauge length at each temperature. This average gauge length (25 mm) was used to calculate the engineering strains sustained by the MA-co-MMA-co-2%PEGDMA samples.

Network toughness under aqueous conditions was assessed by performing the same tensile strain to failure tests in a heated PBS bath. PBS was formulated by mixing one PBS tablet (Sigma-Aldrich; #P4417) with 200 mL of distilled water until dissolved. Before soaking, the mass and sample dimensions (gauge length, width, and thickness) were measured. Each sample was soaked for 24 h in PBS and remeasured. Swelling ratio was calculated according to the formula²⁹:

$$q = W_s/W_i$$

where W_s is the wet mass of the sample and W_i is the initial preswelling mass ($n = 4$). Samples were immediately loaded on the MTS Insight 2 and allowed to equilibrate in a heated PBS bath for 10 min. Because of the limitations of the PBS freezing

near 0°C and boiling near 100°C, tests were only performed at temperatures between 20 and 80°C.

Given the large number of temperatures and materials, tests under each condition were repeated only once ($n = 2$). In these instances, the stress-strain curves after two tests visually demonstrated clear repeatability in behavior as indicated by the magnitudes of the elastic modulus, ultimate stresses, and failure strains as well as the repeated presence of other observable behaviors (i.e., yielding or strain hardening). For the MA-co-MMA-co-2%PEGDMA networks, this defined repeatability in stress-strain behavior at certain temperatures was not observed after two tests, mostly because of large variability in failure strain, at certain temperatures (20 and 30°C). As will be highlighted in the Results and Discussion sections, at these temperatures the network is entering its viscoelastic state where it is beginning to transition from glassy to rubbery. Thus within this region, it is expected for there to be large sample to sample variability in certain properties (i.e., failure strain). Therefore, for MA-co-MMA-co-2%PEGDMA tested at 20 and 30°C in air, a sample size of 4 was used to better identify the characteristic stress-strain behavior under those testing conditions. All toughness and failure strain values for each testing condition were averaged and presented as means \pm standard deviation in the results. Although one cannot reliably use these data to perform an extensive statistical analysis for comparing values at one temperature to the next, the trends with increasing or decreasing temperature are very clear, as will be discussed below.

RESULTS

Dynamic mechanical analysis

Representative plots of storage modulus as a function of temperature for each material is shown in Figure 1. The glass transition region was identified as the range of temperatures where the storage modulus drops several orders of magnitude. As shown in Figure 1(a), PEEK, PMMA, and PC have T_g s between 130 and 150°C, but possess different behaviors past their glass transition region. A complete loss of modulus in PC after the glass transition indicates thermoplastic flow. The modulus of PMMA reaches a temporary plateau with a more gradual flow behavior while the modulus of PEEK significantly increases above T_g marking thermally induced crystallization. By design, the photopolymerized acrylate systems exhibit a wide range of T_g s and rubbery moduli [Fig. 1(b)] ranging from -230 to 110°C and 0.1 to 30 MPa, respectively (Table II). The transition behavior of the designed (meth)acrylate systems most closely resemble PMMA, with exception to the

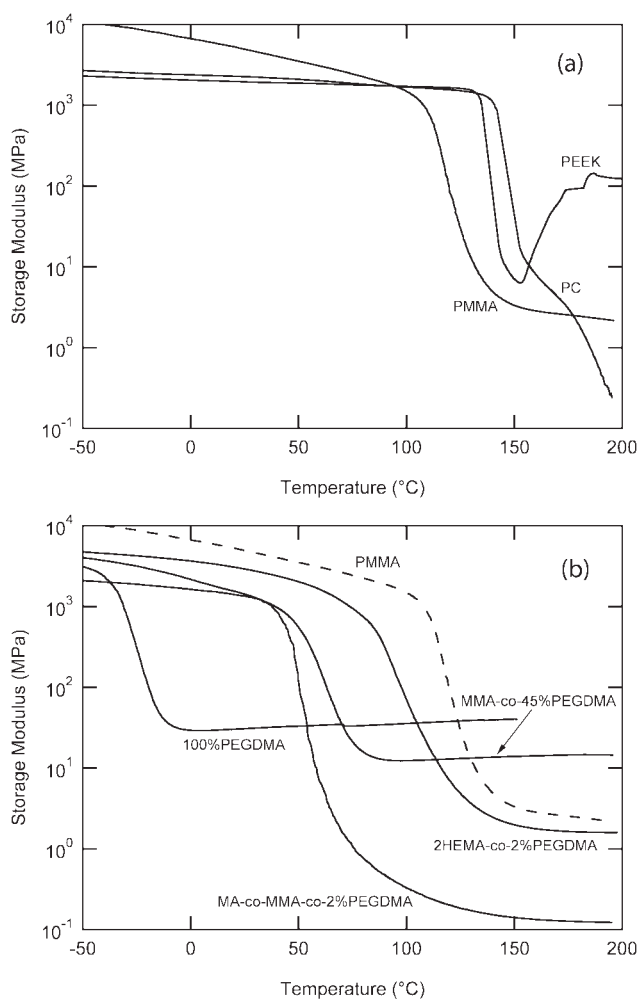


Figure 1 Representative DMA plots of the storage modulus versus temperature for (a) some common thermoplastic polymers and (b) the photopolymerized (meth)acrylate networks. The glass transition region can be identified as the temperature region where the storage modulus decreases by several orders of magnitude.

distinct rubbery plateau in the more heavily cross-linked (meth)acrylate networks.

Stress-strain behavior

The influence of polymer chemistry and testing temperature on stress-strain behavior was examined by performing tensile strain to failure tests at different temperatures. Representative stress-strain curves at selected temperatures are displayed in Figure 2. At temperatures below 80°C, PMMA [Fig. 2(a)] exhibits brittle behavior reaching high stresses around 55 MPa and failing without any noticeable yielding. As the temperature increases toward the T_g , PMMA begins to yield and plasticize exhibiting more rubber-like behavior at and above the T_g . On the other hand, PEEK [Fig. 2(a)] exhibits a ductile deformation response throughout the range of testing

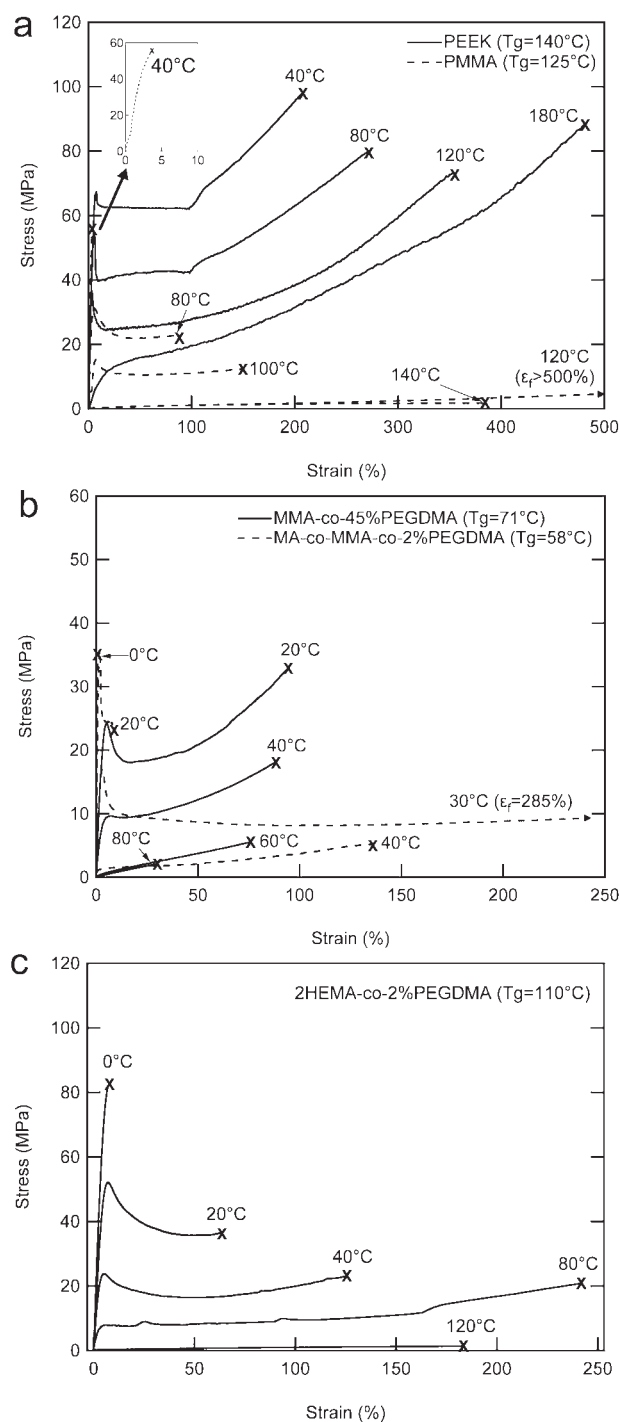


Figure 2 Representative stress vs. strain behavior for (a) PMMA and PEEK, (b) MMA-co-45%PEGDMA and MA-co-MMA-co-2%PEGDMA, and (c) 2HEMA-co-2%PEGDMA at selected temperatures illustrating each polymer changing from its glassy to rubbery state as testing temperature is increased.

temperatures and maintains both high stresses (>60 MPa) and high strains (>500%) as the testing temperature approaches and surpasses T_g . An increase in strength around 100% strain is observed in PEEK at testing temperatures below its T_g . PC is not included in Figure 2 for clarity, but its stress-strain

behavior demonstrated a similar trend with temperature as PMMA.

The (meth)acrylate networks, 2HEMA-co-2%PEGDMA, MA-co-MMA-co-2%PEGDMA, and MMA-co-45%PEGDMA, follow very similar trends with temperature as PMMA [Fig. 2(b,c)]. A drop in modulus and increase in failure strain is observed as the testing temperature approaches the material's T_g . Above T_g , the networks show a drop in failure strain and plateau in modulus (a slight increase is seen with increasing temperature as would be expected based on the theory of rubbery elasticity). The addition of a significant amount of crosslinker (PEGDMA) to MMA results in a decrease in extensibility of the system but an increase in modulus and strain hardening [Fig. 2(b vs. a), PMMA]. The (meth)acrylates with lower crosslinker concentration, MA-co-MMA-co-2%PEGDMA [Fig. 2(b)] and 2HEMA-co-2%PEGDMA [Fig. 2(c)] reach higher failure strains with little strain hardening. When comparing the stress-strain behavior between the networks and thermoplastics near body temperature (40°C), the elastic modulus falls within the same range for all the polymers, but the failure strain and yield behavior vary considerably from material to material.

Toughness in relation to temperature

Using the stress-strain curves in Figure 2, failure strains and toughness as a function of temperature were averaged for each material and superimposed with representative temperature-dependent $\tan \delta$ curves obtained from DMA to identify any significant correlations with the thermal transition behavior (Fig. 3). The $\tan \delta$ curve reaches a maximum at a material's T_g and is an indicator of increased dampening and energy loss, key components of suppressing material damage and enhancing material toughness. Both PMMA [Fig. 3(a)] and PEEK [Fig. 3(b)] experience maximum failure strains near their T_g . PMMA peaks in toughness slightly below its T_g and maintains relatively low toughness at all other testing temperatures above and below T_g . This peak in toughness is significant, as the peak value is typically an order of magnitude higher than toughness values at other temperatures for all of the networks considered. Conversely, in PEEK, the failure strain continues to increase as temperature increases while toughness remains relatively constant and is nearly an order of magnitude higher or more than PMMA at all temperatures.

For the crosslinked (meth)acrylate networks, peaks in both toughness and failure strain also occur below their T_g . However, the distance between the toughness and $\tan \delta$ peaks as well as the breadth of each peak differs significantly between each system. Before further examining the results, it is important

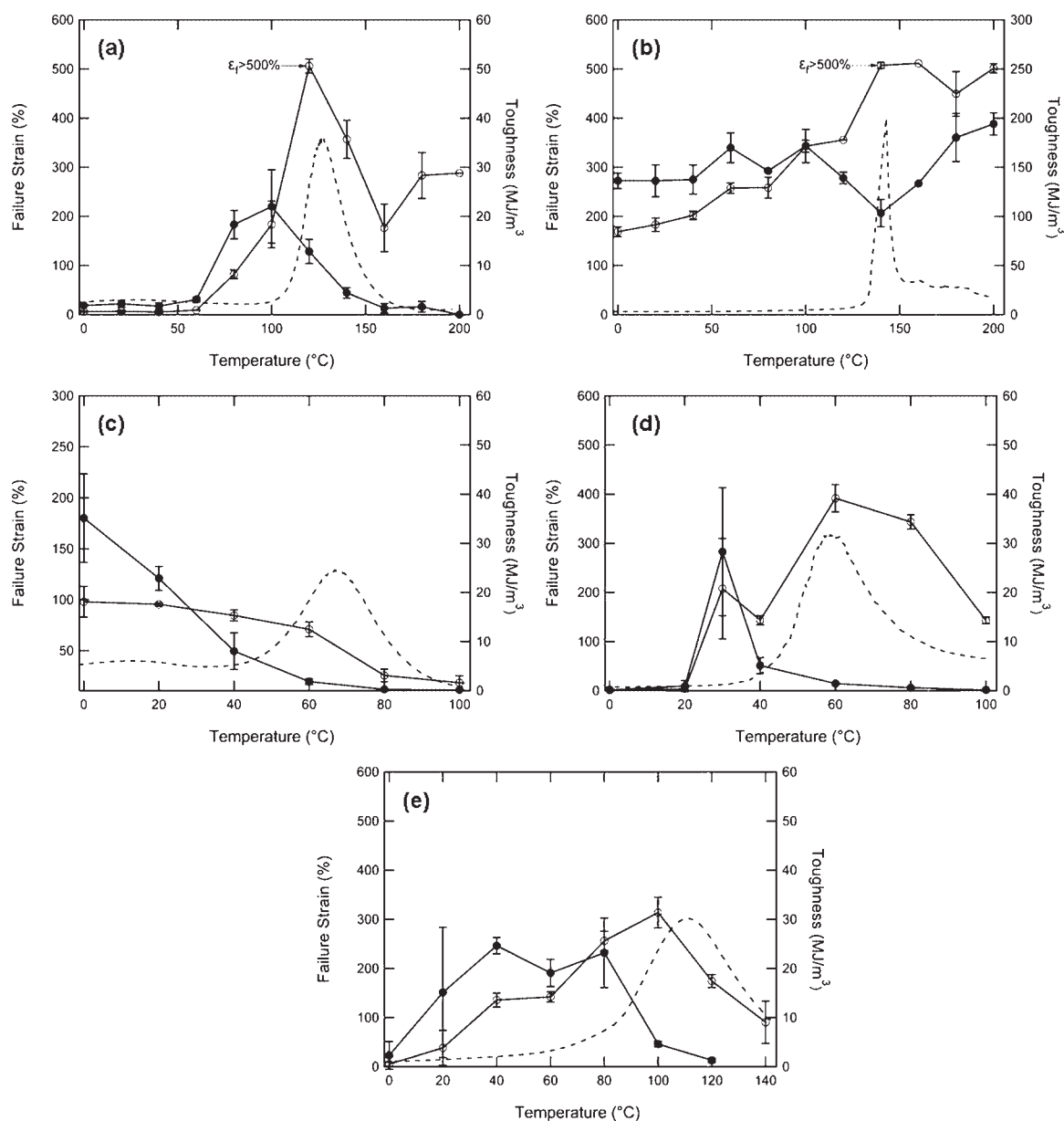


Figure 3 The influence of temperature on the failure strain (open circles) and toughness (closed circles) of (a) PMMA, (b) PEEK, (c) MMA-co-45%PEGDMA, (d) MA-co-MMA-co-2%PEGDMA, and (e) 2HEMA-co-2%PEGDMA. Dotted line denotes the $\tan \delta$ curve obtained from DMA. Each point is the mean of two tests while error bars denote standard deviation.

to note that the location of both the toughness and $\tan \delta$ peak will vary with applied strain rate, a variable held constant here. The width of both the $\tan \delta$ and toughness peaks of MMA-co-45%PEGDMA are very broad (50°C and at least 40°C temperature spans, respectively) with about 70°C separation between the peak of the $\tan \delta$ and maximal toughness peak [Fig. 3(c)]. In addition, another smaller $\tan \delta$ peak occurs at 10°C above the toughness peak. Thus, both the $\tan \delta$ peak around T_g and this smaller peak could contribute to the enhanced toughness of MMA-co-45%PEGDMA at lower temperatures. From Figure 3(e), 2HEMA-co-2%PEGDMA shows a similar trend as MMA-co-45%PEGDMA with broad $\tan \delta$

and toughness peaks (60°C temperature spans each) with the two peaks occurring 60°C apart. Conversely, for MA-co-MMA-co-2%PEGDMA, the $\tan \delta$ and toughness peaks cover a much narrower temperature range compared with the other networks (20 and 10°C) and occur 30°C apart from each other [Fig. 3(d)].

Toughness in PBS

Figure 4 highlights the change in stress-strain behavior in the presence of PBS for the (meth)acrylate networks. The stress-strain curves shown represent one test of two performed at each testing

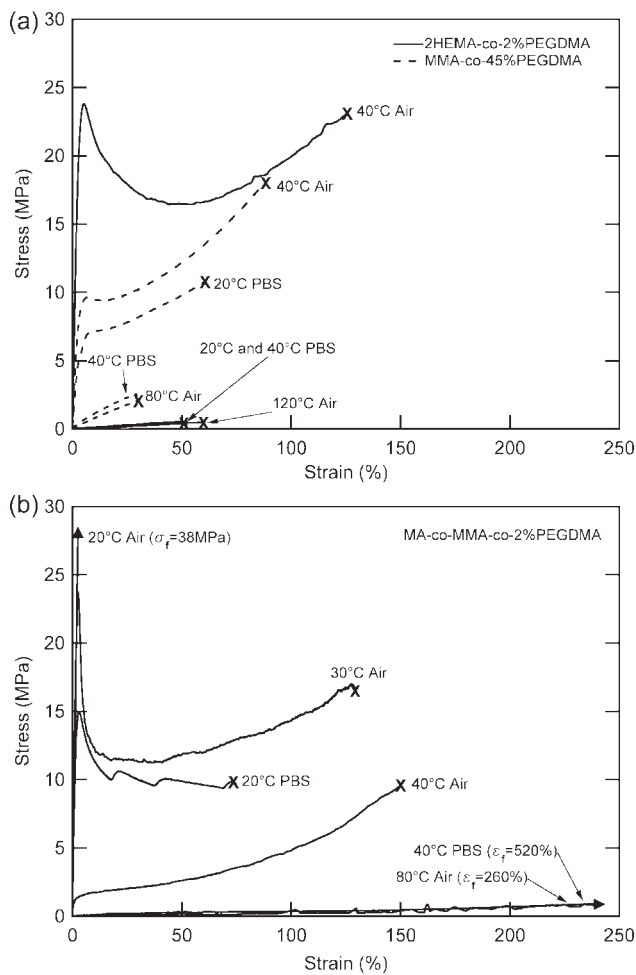


Figure 4 Representative stress vs. strain curves for (a) 2HEMA-co-2%PEGDMA and MMA-co-45%PEGDMA and (b) MA-co-MMA-co-2%PEGDMA at different temperatures tested in air and PBS.

condition. For MMA-co-45%PEGDMA and 2HEMA-co-2%PEGDMA, the stress-strain behavior in PBS below T_g matches the behavior of the same system tested at temperatures above the T_g in air. Thus at 40°C in PBS, the (meth)acrylate systems are effectively above their glass transition and are acting in their rubbery state in terms of failure strain and toughness [Fig. 4(a)]. When tested at 20°C, MA-co-MMA-co-2%PEGDMA experiences a large increase in failure strains with soaking, which is also consistent with the network deformed in the dry state at slightly elevated temperatures [Fig. 4(b)]. In addition, failure strains still remain greater than 200% at temperatures above 40°C while at lower temperatures ($\sim 20^\circ\text{C}$), yielding behavior still occurs. It is important to highlight that depending on the system and testing temperature the toughness can seem to increase (MA-co-MMA-co-2%PEGDMA, $T = 20^\circ\text{C}$) or decrease (2HEMA-co-2%PEGDMA, $T = 40^\circ\text{C}$) with exposure to PBS. This difference is related to the relative position of the testing temperature on the

toughness peak in temperature space and will be further explored in the Discussion section.

Toughness versus elastic modulus

When designing synthetic biomaterials that must function under rigorous loading environments, two key properties to consider are the elastic modulus and toughness of the material. In Figure 5, average toughness values are plotted against average elastic modulus values for all (meth)acrylate networks tested in air and PBS at 40°C and compared with several common biomedical grade polymers studied in the literature.^{24,30,31} For the sake of clarity in the figure, error bars have been removed and thus the indicated points can be considered a range of toughness and modulus values indicative of that composition. Looking at this plot, several important trends can be identified. First, both (meth)acrylate networks and linear polymers with similar moduli at 40°C show a broad range of toughness values ranging three orders of magnitude from over 100 MJ/m^3 to approximately 0.1 MJ/m^3 . Second, the photopolymerized (meth)acrylate networks possess less toughness than other polymers such as PC, PEEK, ultra-high molecular weight polyethylene, and segmented polyurethane. Finally, PBS decreases the modulus and toughness of the networks significantly with exception to MA-co-MMA-co-2%PEGDMA. The decrease in modulus and toughness of the 2HEMA-co-2%PEGDMA polymer is extreme, dropping three orders of magnitude in both quantities while MMA-

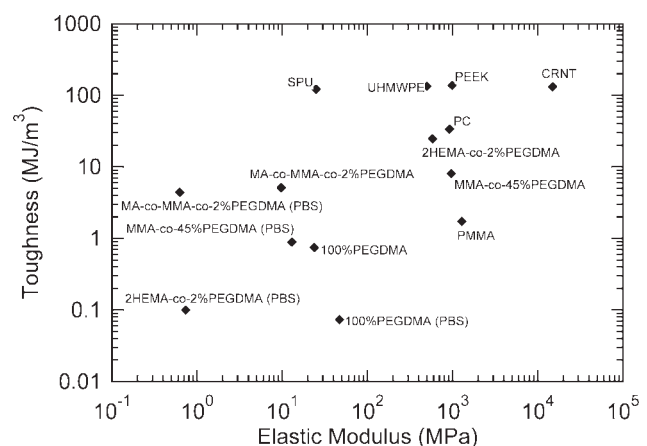


Figure 5 Average toughness plotted as a function of elastic modulus for acrylate networks and the thermoplastic polymers tested in this study at 40°C at a strain rate of 5%/min as well as some other common biomedical polymers. Toughness values of CRNT, UHMWPE, and SPU were calculated as the area under the stress-strain curves found in the literature.^{24,30,31} The elastic modulus values were provided in the literature. CRNT, carbon reinforced nanotubes; UHMWPE, ultra-high molecular weight polyethylene; SPU, segmented polyurethane.

co-45%PEGDMA only decreases about one order of magnitude for both properties.

DISCUSSION

Toughness of a material dictates the ultimate stress and strain the material can withstand and is an important mechanical consideration when designing biomaterials for long-term implantation. For example, a tougher contact lens would prevent frequent tearing and ripping from daily insertion and removal. A tough cardiovascular stent would enable implantation in remote locations in the leg where large bending forces are exerted on the blood vessel wall. Additionally, a tough replacement disk for spinal applications would improve the longevity of the device and allow it to sustain the rigorous loading regime imparted on the spine. The purpose of this study was to characterize toughness in photopolymerized (meth)acrylate networks by performing uniaxial tension experiments under various environmental conditions. Although many factors are known to influence the mechanical properties of polymer systems, especially thermoplastics, this is the first comprehensive study on the toughness of photopolymerized (meth)acrylate networks. In the remainder of the discussion, various toughening mechanisms in photopolymerized (meth)acrylate networks will be explored focusing on the relevance toward designing potential biomaterial platforms.

The temperature dependence of network toughness is strongly dependent on the T_g as revealed in earlier work on thermoplastics³² and rubber networks.^{13–15} Similar to previous studies involving linear polymers,^{14,32–34} the (meth)acrylate networks demonstrate a transition from brittle to ductile to rubbery behavior as temperature is increased, correlating with peaks in both toughness and failure strain at temperatures slightly below the T_g . This temperature-dependent toughness maximum can be attributed to the viscoelastic nature of the chains that occurs at the onset of the glass transition.^{13–15} Within this temperature region, molecular vibrations are beginning to increase allowing the chains to cooperatively disentangle and stretch without substantial loss in load carrying capacity.³² Thus, one way to enhance toughness within a particular (meth)acrylate network could involve tailoring the T_g of the system to create a toughness peak at a particular temperature (i.e., body temperature). The drawback with this monolithic (single material) approach is that the elastic modulus of the material is fixed in the viscoelastic regime and will be extremely rate dependent.

Another method to enhance network toughness involves altering the crosslinking density. In this study, slightly higher toughness values are observed

in the lightly crosslinked networks (MMA-co-MA-co-2%PEGDMA) compared with the highly crosslinked network (MMA-co-45%PEGDMA) [Fig. 3(e vs. c) and Fig. 5]. In general, toughness remains constant in a network despite changing crosslinker concentrations,³⁵ with exception of lightly crosslinked networks,³⁴ which can show enhanced toughness. Unfortunately, there are several inherent trade-offs with adjusting the crosslinking density^{36,37} or molecular weight³⁸ to control network toughness. A high-crosslink density inhibits global chain movement during deformation, thus increasing strength (higher yield strength), limiting strains (lower strain to failure), and increasing stresses at equivalent deformation levels (higher rubbery modulus).^{32,34} Another drawback of maximizing toughness through network crosslinking density is that other important material features such as swelling capacity and rubbery modulus also depend strongly on crosslinking density.

Aside from toughening with temperature-dependent viscous effects and network crosslinking, enhancement of toughness through monomer chemistry is another possibility. The influence of the network chemistry can be observed by comparing the toughness of uncrosslinked polymers such as PMMA, PC, and PEEK (Fig. 3 and 5), which all have similar T_g s, but contain unique chemical features. From Figures 2 and 3, the vast difference in the stress–strain behaviors of these polymers at similar testing temperatures indicates that polymer chemistry can greatly impact the toughness of polymers. The high levels of toughness of PEEK and PC can be explained by the phenyl ring-oxygen bonds located in the backbone of the polymer chains. Phenyl rings consist of tight chemical bonds that provide rigidity and strengthen a chain while their intermittent bonding with oxygen atoms along the backbone allow them to flip rapidly and rotate around the backbone, thus adding flexibility during deformation.³⁹ The significantly larger toughness values of PEEK compared with PC suggest that there is another toughening mechanism driven by polymer structure. In the case of PEEK, this mechanism is the semicrystalline nature of the polymer induced by strain hardening increasing the energy required to break.^{17,32} Thus, provided the chemistries are biocompatible, the incorporation of unique chemical structures, such as phenyl rings, into the backbone to provide enhanced toughness in photopolymerizable (meth)acrylates is an important avenue for future research.

When comparing toughness in thermoplastics with the (meth)acrylate networks at 40°C, 2HEMA-co-2%PEGDMA and MA-co-MMA-co-2%PEGDMA (under dry conditions) exhibit toughness levels in the same range as some common tough polymers

such as PC (Fig. 5) near body temperature. The chemical structures of the individual monomers would suggest that these backbones would have limited toughness based on the theory of Wu,¹⁶ but the macromolecular structure of the crosslinked network and the interactions between side groups imparts toughness beyond predictions based on chain backbone flexibility. For example, hydrogen bonding between hydroxyl side groups can be a contributing factor to the toughness of the 2HEMA-based network. Therefore, network chemistry can not only influence the toughness of individual polymer chains, but can also enhance the macromolecular toughness through the formation of intermolecular bonds.

An overarching concern in developing new polymer biomaterials, especially hydrogels and shape memory polymers with T_g s close to body temperature, is the toughness in the presence of water or saline. A material that cannot maintain toughness in solution may be unable to function properly in the body potentially leading to device failure or injury to the surrounding tissue. The results of this study demonstrate that the toughness mechanisms discussed thus far in (meth)acrylate networks are significantly altered when the polymer is soaked in solution. The drop in network elastic modulus observed in this study corresponds to findings of previous studies and is attributed to water “plasticizing” the T_g of the polymer.^{22,23} Comparing the stress–strain behavior in air and PBS, no obvious trend in toughness occurs among the networks. 2HEMA-*co*-2%PEGDMA and MMA-*co*-45%PEGDMA have decreased toughness in PBS at all temperatures while the toughness of MA-*co*-MMA-*co*-2%PEGDMA actually improves at 20°C in PBS compared with air conditions [Fig. 5(b)].

This apparent anomaly of both decreasing and increasing toughness with water uptake is explained if one considers a shift in the toughness–temperature peak with hydration. The interrelationship between toughness, temperature, and capacity to absorb water is illustrated in Figure 6. Water absorption changes the effective location of the toughness peak by lowering the T_g . Depending on where the testing temperature intersects the original toughness peak and how far the peak shifts by the amount of water, toughness could increase or decrease under aqueous conditions. Specifically, if the test temperature is to the left of the toughness peak in air, moderate water uptake may increase toughness [Fig. 6(a)]. An example of this would be the MA-*co*-MMA-*co*-2%PEGDMA system where 20°C is to the left of the air toughness peak [Fig. 3(d)], and water exposure increases toughness at 20°C due to a moderate shift of the toughness peak toward a lower temperature [Fig. 4(b)]. On the other hand, if the testing tempera-

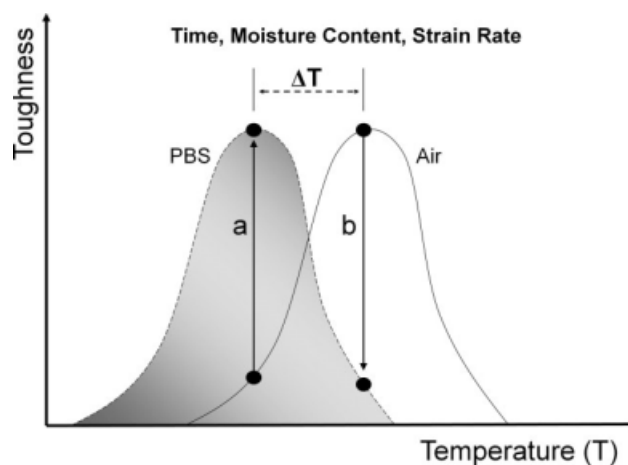


Figure 6 Schematic illustrating how the temperature-dependent toughness maxima shifts to lower temperatures in PBS. The temperature difference between the toughness peak in air and PBS (ΔT) is governed by several factors including soak time, strain rate, and swellability of the network. As discussed, “a” and “b” represent two scenarios explaining how the toughness of acrylate networks can either increase or decrease in PBS.

ture is located at the toughness peak or to the right of the peak in air, water exposure can decrease toughness [Fig. 6(b)]. An example of this would be the 2HEMA-*co*-2%PEGDMA network that sits at the middle of its toughness “peak” in air at 40°C [Fig. 3(e)]; however, a large leftward shift of this peak with water uptake leaves the material with low toughness at 40°C [Fig. 4(a)]. Based on this paradigm, one way to control a polymer’s toughness under aqueous conditions is to tailor the monomer components so that the T_g and consequently, the maximal toughness of the polymer system will occur around body temperature in the presence of water. This approach would require knowledge on the shift in toughness with temperature (strain rate) and water absorption (time) to assure that the toughness peak in water was at equilibrium.

As mentioned earlier, the degree of the toughness shift in PBS is partially dictated by the swellability of the network components. When comparing the toughness loss in PBS, 2HEMA-*co*-2%PEGDMA exhibits a larger change in toughness compared with MMA-*co*-45%PEGDMA and MA-*co*-MMA-*co*-2%PEGDMA. Because of the hydroxyl groups located in the pendant group, the 2HEMA network will contain large water-chain interactions that drive increased water absorption as indicated by the swelling ratio ($q = 1.58$). It is interesting to note that if the high toughness of the 2HEMA system was partially driven by chain interactions caused by hydrogen bonding, the PBS effectively eliminates this toughening mechanism by forming new bonds with

the hydroxyl side groups. Although MMA-*co*-45%PEGDMA and MA-*co*-MMA-*co*-2%PEGDMA have low swelling ratios, their change in mechanical properties in PBS indicates that the PBS still alters the network structure, mostly by interacting with the glycol groups in the PEGDMA crosslinker. Even in the absence of PEGDMA, pure PMMA,^{21,40} thiolene acrylates,²³ and polyurethane acrylates^{22,23,25} have previously exhibited this water effect over much longer time scales. Based on these observations between toughness and swelling, it can be suggested that the more water the network can absorb, the more water molecules are present to interact with the polymer chains, and the larger the shift the toughness peak with exposure to water. However, further work would be necessary to explicitly prove this hypothesis and to understand if the magnitude of the toughness-temperature peak changes or if it only experiences a shift to lower temperatures.

CONCLUSIONS

The results presented in this study provide several key mechanisms of the toughness-structure relationships exhibited within photopolymerizable (meth)acrylate networks. Specifically, the study demonstrates that toughness in photopolymerizable networks is controlled by

- (1) *Test temperature relative to T_g .* All of the networks demonstrate a peak in toughness at a temperature below the glass transition temperature. The location and breadth of the toughness peak depends strongly on the nature of the glass transition in the network (i.e., breadth, number of peaks).
- (2) *Network structure, in particular crosslinking density.* At "equivalent" test temperatures relative to T_g , networks with different crosslink densities demonstrate varying toughness, with low crosslink concentration offering better toughness relative to highly crosslinked systems, even though less crosslinking results in lower rubbery moduli values.
- (3) *Network chemistry.* For equivalent T_g and crosslink density, the presence of certain chemical groups is shown to impact toughness.
- (4) *Water content.* Since water lowers the glass transition temperature of polymers, apparent toughness is significantly altered in water driven by changes in the test temperature relative to the glass transition temperature discussed in item (1).

Optimizing toughness in (meth)acrylate networks can only be achieved by considering these relation-

ships between mechanical properties, chemical structure, and environmental conditions. By selecting "toughening" chemical components and using the appropriate amount of crosslinker, the ability to tune the toughness of these systems under physiological conditions will render them useful in the design of implant materials or tissue engineering constructs for applications involving mechanically strenuous environments.

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