

Combinatorial investigation of the structure-properties characterization of photopolymerized dimethacrylate networks

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Abstract

The effects of co-monomer composition and irradiation time in a model two-component dimethacrylate dental resin blend were evaluated using combinatorial methods to determine the degree of methacrylate conversion and resulting mechanical properties. 2-Dimensional gradient samples varying in monomer composition and light exposure time were fabricated. The conversion was measured using near infrared spectroscopy (NIR) and the mechanical properties (i.e., hardness and elastic modulus) were determined using nanoindentation via the continuous stiffness method. An excellent correlation was observed between the reaction conversion and mechanical properties for the cross-linked networks. The methacrylate conversion ranged from 40% to 85% and the mechanical properties increased over two orders of magnitude over this conversion range. The ultimate reaction conversion and mechanical properties depended on both the co-monomer composition and cure time.

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1. Introduction

Dental restorative composites are complex systems with a large number of material and processing parameters that influence their properties [1]. For example, dental resins are generally comprised of a binary or ternary resin mixture in which the material processability and properties can be easily adjusted by compositional changes. However, there is a lack of understanding of the effects of monomer structure and resin composition on the development of cross-linked polymers. In the most complete studies involving reaction kinetics, conversion, and network physical/mechanical properties, only a single co-monomer composition was considered. This is understandable since a complete study of how monomer chemical structure and composition affect the processability and properties is time consuming and laborious.

High throughput and combinatorial methods have become increasingly popular in material discovery, characterization, and optimization. Combinatorial methods have several advantages over traditional techniques, including faster data acquisition, more thorough examination of experimental variables, equal processing conditions for a given specimen, and lower experimental error [2]. In a typical combinatorial measurement, an array specimen varying in two material parameters (variables) is first fabricated. The material properties as a function of the defined parameters are then characterized and analyzed. The knowledge generated using combinatorial and high-throughput approaches could drive the design of future experiments and facilitate process and application optimization.

With increasing demand for high throughput and combinatorial methods, the need to develop gradient fabrication and characterization tools for rapid measurement and analysis is surging. For studying the mechanical properties, instrumented indentation testing (IIT) or nanoindentation has recently emerged as a useful tool for

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the measurement of the mechanical properties of materials [3]. Rooted in elastic contact mechanics first developed by Hertz [4,5], nanoindentation can determine the hardness and elastic modulus of a wide variety of materials. Similar in concept to hardness testing [6], nanoindentation consists of pushing an axisymmetric indenter into contact with the test material until reaching a specified load or displacement. IIT instruments provide load, displacement, and contact area throughout the experiment and this information is used to calculate the hardness and elastic modulus from contact mechanics solutions [7]. The small contact dimensions of nanoindentation enable the measurement of mechanical properties over length scales that are many orders of magnitude smaller than can be examined with conventional mechanical characterization instrumentation, thus making this technique well suited for combinatorial methods where a single sample may contain a multitude of parameter space.

The use of nanoindentation as a polymeric material characterization tool has been successfully demonstrated through the use of depth sensing indentation (DSI), which continuously measures the stiffness of the indenter/sample interaction as the indenter travels into the material. This is accomplished by imposing a high frequency (45–75 Hz) small amplitude oscillation (< 50 nm) on top of the loading portion of the indentation experiment. By modeling the instrument as a damped harmonic oscillator, a continuous value of stiffness (S) and modulus is calculated throughout the loading curve. Moreover, the transient mechanical properties of polymers, such as creep compliance or stress relaxation moduli, can be measured with nanoindentation [8,9]. Additional details about nanoindentation can be found elsewhere [7,10,11]. Other small volume or localized techniques for characterizing the mechanical properties include laser induced surface acoustic wave spectroscopy and Brillouin light scattering, both of which determine the elastic modulus under high frequencies and are non-destructive, and a buckling-based test for determining the elastic modulus for thin films [12].

Nanoindentation has gained wide acceptance in various material science disciplines including biomedical applications [13]. In dental research, nanoindentation has been used to characterize the mechanical anisotropy of enamels, their chemical composition and location dependence [14–16] and to examine how the mechanical properties vary with the demineralization/remineralization cycle [17]. Nanoindentation has also been used to compare the mechanical properties of various types of dental restoratives [18] and in assessing the effect of ceramic whisker filler content on the mechanical properties [19]. Because nanoindentation measures localized small volume properties, it is also ideal for examining the mechanical properties across an interface, as demonstrated in one study which involved the mechanical characterization at the interphase between cementum and dentin [20].

In restorative dental materials, continuing questions exist with regard to how the monomer composition affects the

reaction kinetics and conversion and how the conversion affects a host of properties. High-throughput and combinatorial approaches are natural for elucidating properties over a large parameter space. Two recent studies have used high-throughput analysis to determine the reaction kinetics [21] and reactivity ratios [22] of free radical copolymerizations. In the current study, we examine the relationships between chemical composition, conversion, and properties of two-component dimethacrylate networks via combinatorial approaches. Two-dimensional gradient samples varying in two parameters (i.e., resin composition and irradiation time) along orthogonal axes were prepared and characterized. The resin mixtures were comprised of an ethoxylated Bis-GMA (EBPDMA) base monomer blended with the diluent monomer triethylene glycol dimethacrylate (TEGDMA) at different compositions. Upon photo-activation and subsequent photopolymerization, three-dimensional cross-linked networks were formed. The effects of composition and irradiation time on the conversion and mechanical properties (i.e., hardness and elastic modulus) were determined. The gradient test specimens were standardized to accommodate multiple measurement techniques, thus allowing various characterizations on a single specimen and direct data correlation.

2. Experimental

2.1. Materials¹

Ethoxylated bisphenol-A dimethacrylate (EBPDMA, degree of ethoxylation = 6), and the diluent monomer triethylene glycol dimethacrylate (TEGDMA) were obtained from Esstech Inc. Camphorquinone (CQ) and ethyl 4-*N*, *N*-dimethylaminobenzoate (4E) were purchased from Aldrich Corp. All reagents were used as received.

2.2. Methods

2.2.1. Fabrication of gradient samples

EBPDMA and TEGDMA were mixed to obtain the following compositions: 100:0, 90:10, 80:20, 70:30, and 60:40 mass ratios. The resin mixtures were activated for blue light photopolymerization with 0.2% CQ and 0.8% 4E (by mass fraction) and stored in the dark until use.

The two-dimensional libraries examined in the current study consisted of a discrete gradient in monomer composition along one axis with an orthogonal gradient in methacrylate conversion, which was varied in a continuous fashion. The gradient specimen was prepared as follows. A sandwich mold consisting of a standard microscope glass slide, PET release film, poly(dimethylsiloxane) spacer (thickness ≈ 1.5 mm) with 5 channels stamped out, and another glass slide was assembled. Resin mixtures of different compositions were syringed into the separate channels, thus keeping the monomer composition discrete. The assembly was then placed on a translation stage that was mostly covered by a light shield leaving approximately 15 mm of the sample strip exposed (Fig. 1). The stage was programmed to hold in place for a desired amount of time, then gradually move the sample away from the light shield creating a gradient in light exposure time, hence a methacrylate conversion gradient.

¹Certain commercial materials and equipment are identified in this work for adequate definition of the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology that the material and the equipment identified is necessarily the best available for the purpose.

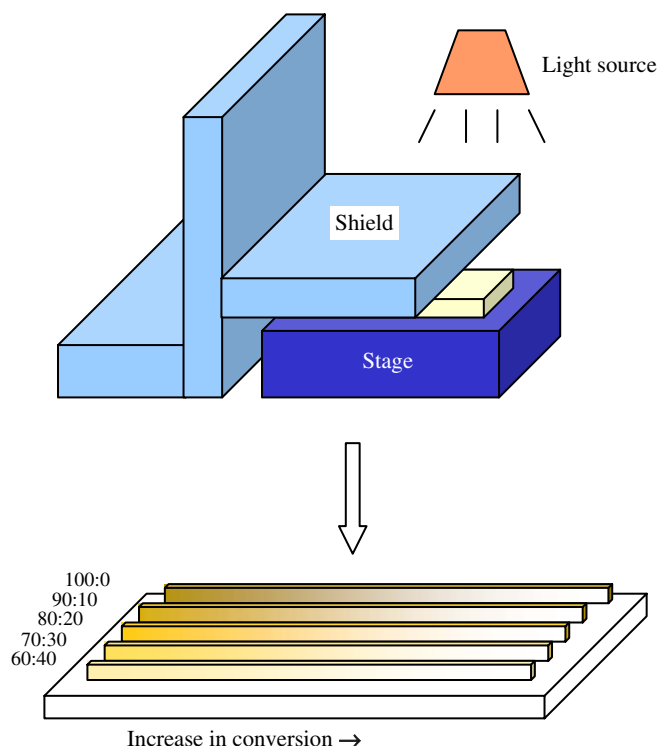


Fig. 1. 2-Dimensional gradient sample preparation. Each strip correspond to a discrete dimethacrylate composition, and the degree of conversion is varied orthogonal to the composition gradient.

The light source was a Dentsply Triad 2000 replacement Tungsten halogen light bulb (250 W, 120 V) installed 10 cm above the stage. The EBPADMA-TEGDMA samples were held in the light for 1 min, and then the stage was moved at 2 mm/s for 25 s until the sample was fully exposed to the light source. To ensure uniform cure throughout the sample, this cure protocol was repeated on the other side of the glass slide. As a result of the photopolymerization process, conversion gradients were generated onto a single glass slide (gradient sample shown in Fig. 1). It should be noted that although the light source used in the current experiments is a halogen light that produces a slight intensity variation with respect to the sample distance, the sample array was designed to be smaller than the illuminated area of the light source and placed in close proximity to the light source. The variations in light intensity due to distance are thus assumed to be negligible. It should also be noted that irradiation does lead to heating of the gradient specimen. It is difficult to decouple reaction due to irradiation and heating because the temperature increase in a specimen is non-uniform due to variations in exposure time and localized radiation heating likely transfers to the adjacent masked area. Nevertheless, polymerization due to irradiation and heat under the current cure profile lead to control methacrylate conversion gradients. In addition, the high conversion end of the specimen was irradiated for a significantly longer period of time so that the ultimate reaction conversion had been reached.

All measurements were carried out at least 24 h after light exposure to ensure that the conversion no longer changed with post-cure time. A notch was made across the composition gradient at the high conversion end and was defined as the zero position for subsequent conversion measurements and mechanical testing. Data were collected and reported over 50 mm at 5 mm intervals beginning at the zero position for each composition.

2.2.2. Near infrared spectroscopy (NIR)

The degree of conversion for the resins was determined using transmission NIR spectroscopy. The NIR spectrum of the uncured and cured resin (approximately 1 mm in thickness) between the glass slides was

obtained with a Nicolet Magna 550 FT-IR spectrometer (Madison, WI) configured with a white light source, a CaF_2 beam splitter, and an InSb detector. The NIR spectrum in the region of $7000\text{--}4000\text{ cm}^{-1}$ was acquired from 64 co-added scans at 2 wavenumber resolution. The NIR spectrum of the gradient sample was collected using the same procedure. The glass slide containing the gradient sample was clamped to a card with a wide opening for the NIR beam. The glass slide was shifted vertically or horizontally so that the appropriate sample spot could be analyzed. The relative uncertainty associated with the NIR measurements is 5%.

2.2.3. Nanoindentation

Nanoindentation measurements were performed using an MTS Nanoindenters NanoXP instrument (Oak Ridge, TN) equipped with a $10\text{ }\mu\text{m}$ radius, 90° diamond cone indenter. The continuous stiffness method, using 45 Hz, 5 nm dynamic oscillations, was used to determine the elastic modulus continuously throughout the loading portion of the experiment. With the area function of the indenter tip determined from calibration procedures in a known standard, Eq. (1) was used to calculate the effective elastic modulus ($E_{\text{effective}}$). The sample modulus (E_{sample}) was then calculated with knowledge of the sample's Poisson's ratio (ν_{sample}), indenter elastic modulus (E_{indenter}), and indenter Poisson's ratio (ν_{indenter}) (Eq. (2)):

$$E_{\text{effective}} = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}}, \quad (1)$$

$$\frac{1}{E_{\text{effective}}} = \frac{(1 - \nu_{\text{sample}}^2)}{E_{\text{sample}}} + \frac{(1 - \nu_{\text{indenter}}^2)}{E_{\text{indenter}}}. \quad (2)$$

The reported values of modulus are the average of the moduli obtained over a depth range from 1000 to 4000 nm. All indentation experiments were conducted using a strain rate of 0.05 s^{-1} . The value of Poisson's ratio was assumed to be 0.30, a reasonable assumption for glassy polymers. At this depth the hardness was nearly constant with respect to loading depth indicating the measurement is a proper measure of the maximum stress required for yielding. The relative uncertainty associated with the nanoindentation measurements is 3%.

2.2.4. Dynamic mechanical analysis

The glass transition temperature (T_g) of a fully cured sample at various compositions was determined using a TA Instruments RSA III dynamic mechanical analyzer (DMA) in the three-point bend geometry (span = 10 mm). The storage and loss Young's moduli (E' and E'' , respectively) were measured at 45 Hz, same as nanoindentation measurements, from 30 to 120°C at $3^\circ\text{C}/\text{min}$. The T_g is defined as the peak of the $\tan \delta$ (E''/E') curve. The relative uncertainty associated with the DMA measurements is 5%.

3. Results and discussion

The fabrication technique described within yields two-dimensional gradient samples varying the monomer composition in a discrete fashion and the irradiation time in a continuous fashion orthogonally. Each composition strip is approximately 1.5 mm in width and 55 mm in length. The advantage of keeping the compositions discrete is that there are no ambiguities in the network chemical composition and this allows for a straightforward data analysis. The current process is also amenable for high viscosity monomer mixtures and eliminates non-uniform (laminar) flow as typically observed when co-syringing monomer mixtures with a large disparity in viscosity. In addition, the sample geometry (width) is large enough for quantitative NIR characterization and allows for multiple

nanoindentation data to be collected at a specific reaction conversion.

The degree of conversion along the exposure gradient was determined using NIR spectroscopy, a technique that can be used in transmission mode for measuring the bulk conversion properties of thick dimethacrylate samples [23]. Fig. 2 shows the NIR spectra of the 90:10 composition photopolymerized to various degrees. The top spectrum corresponds to the high conversion end measured at 0 mm position. Subsequent NIR spectra were obtained at 5 mm intervals along the conversion gradient. The characteristic absorption bands located at 4743 and 6165 cm^{-1} represent the methacrylate $=\text{C}-\text{H}$ stretch and these peaks diminish in height and area as the methacrylate reacts. As shown in Fig. 2, the peak height (and area) at both wavenumbers is the lowest for the top few NIR spectra, corresponding to the high conversion end. The peak height (and area) decreases with decreased irradiation time, indicating that the degree of methacrylate conversion is reduced.

The insets of Fig. 2 show overlapped methacrylate $\text{C}=\text{C}-\text{H}$ absorption at 6165 cm^{-1} and aromatic $\text{C}-\text{H}$ absorption at 4623 cm^{-1} taken along the conversion gradient. The methacrylate $=\text{C}-\text{H}$ peak increased as the conversion gradient distance increased, indicating that the methacrylate conversion decreased. Similar NIR spectra were obtained for the all monomer compositions.

One approach for quantitatively determining the methacrylate conversion is by comparing the area of the methacrylate $\text{C}=\text{C}-\text{H}$ absorption band normalized to the aromatic $\text{C}-\text{H}$ absorption band as compared to the unreacted resin. The methacrylate $\text{C}=\text{C}-\text{H}$ absorption at 6165 cm^{-1} is well resolved, whereas the 4743 cm^{-1} overlaps with other peaks; therefore, the 6165 cm^{-1} peak is used for all methacrylate conversion calculations. The EBPADMA aromatic $\text{C}-\text{H}$ absorption at 4623 cm^{-1} is used as an internal standard to normalize the monomer and polymer spectra. Since the aromatic absorption overlaps with neighboring absorption bands that change upon photopolymerization, the minima are not stable such that peak areas calculated by drawing a direct baseline between the two minima are not reliable as an internal standard. This is consistent with previous findings that such data reduction produced anomalous conversion values for some resin compositions [23]. In the present study, the peaks in the region of 4550–4800 cm^{-1} wavenumbers are baseline corrected and deconvoluted, then the area under the aromatic $\text{C}-\text{H}$ peak is integrated. Fig. 3 illustrates the observed absorption peaks, four deconvoluted peaks, and the generated curve, which matches closely with the observed curve. The integration for peak 2 is used as the internal standard. An alternative method for calculating the conversion is by monitoring the methacrylate

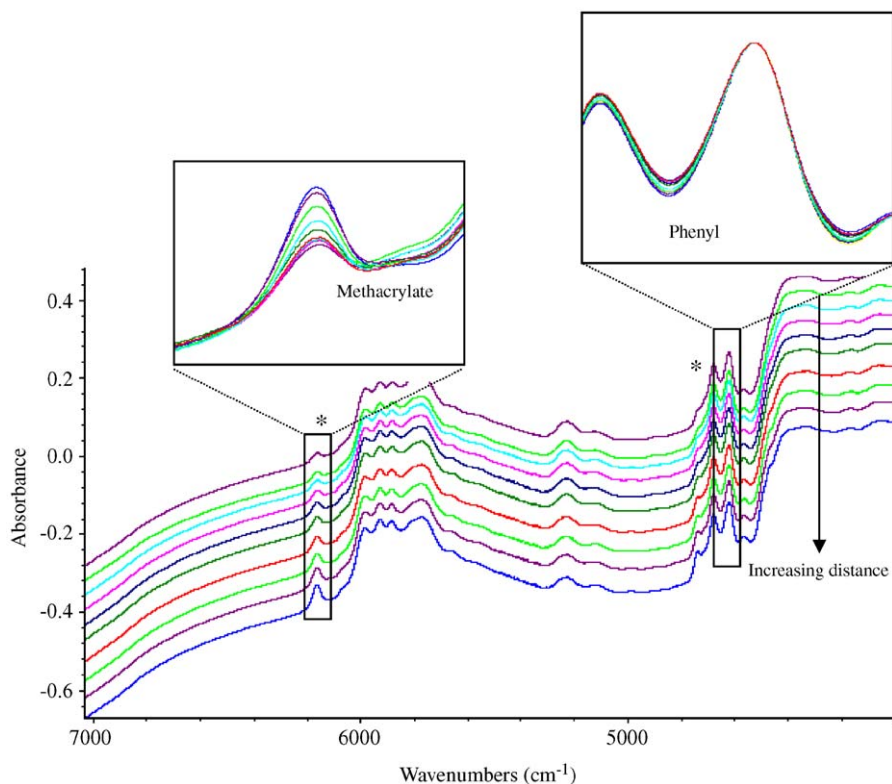


Fig. 2. NIR spectroscopy for the 90:10 composition. From the top, zero position, and increasing at 5 mm intervals. Data are offset for clarity. The peaks at 4743 and 6165 cm^{-1} , labeled with (*), are due to methacrylate $=\text{C}-\text{H}$. The inset shows the overlaps of the methacrylate $=\text{C}-\text{H}$ and aromatic $\text{C}-\text{H}$ absorption.

absorption directly with corrected sample thickness [23], but this method did not produce satisfactory results for the current system. The conversion values at the longer exposure end had reached the maximum, and were therefore defined as the ultimate conversion. In general, the gradients exhibited conversions ranging from approximately 40% to approximately 85% spanning a large cross-linked conversion range.

The corresponding mechanical properties (i.e., hardness and elastic modulus) are characterized using nanoindentation, a powerful technique for probing the mechanical properties in small volumes. The methacrylate conversion

and elastic modulus for all compositions along the exposure gradient are summarized in Fig. 4. The reaction conversions are nearly identical for distances 0 to 10 mm as a result of the fabrication process used in the current study and this is manifested in the corresponding elastic moduli, which are also comparable at these irradiation distances. It is apparent that the ultimate reaction conversion depends on the chemical structure of the co-monomers. For the EBPADMA-TEGDMA system, ultimate conversions for all compositions ranged between 82% and 88% with the 100:0 composition showing the lowest ultimate conversion and the 80:20 showing the highest ultimate conversion. While the difference between the highest and the lowest conversion are statistically different, the conversion differences among other compositions are not statistically significant.

The effect of co-monomer composition on the elastic modulus was also evaluated. The 60:40 composition exhibited the highest modulus and the elastic modulus decreased as the TEGDMA content decreased. In BisGMA-TEGDMA networks, another commonly used dental matrix, the flexible lower molecular mass TEGDMA is considered a reactive diluent and thus reduces the mechanical properties. However, co-monomer compositions containing higher TEGDMA contents also have a higher number of methacrylates per volume. At comparable reaction conversions, it is reasonable to conclude that the crosslink density for systems containing higher TEGDMA contents is higher. In the current system, the ability of TEGDMA to increase the network crosslink density dominates its diluent effects and this is observed in the increased elastic modulus as the TEGDMA content increased. Moreover, the 80:20 composition exhibits the

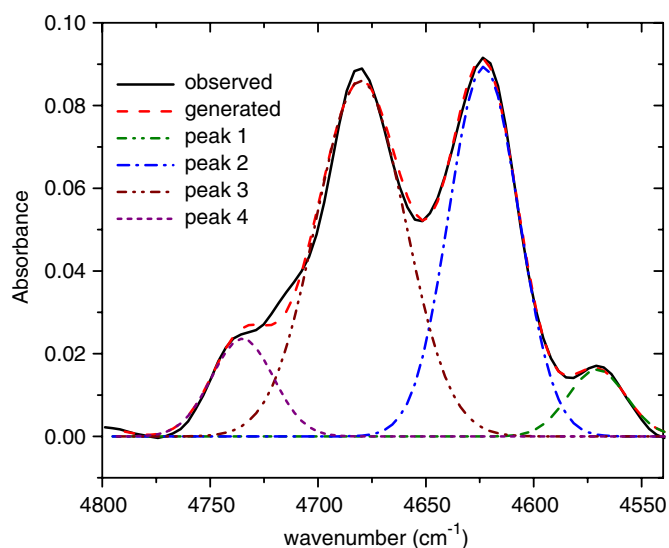


Fig. 3. Schematic showing the peak deconvolution in the 4550 to 4800 cm^{-1} region. Peak 2 at 4623 cm^{-1} is the aromatic C–H absorption.

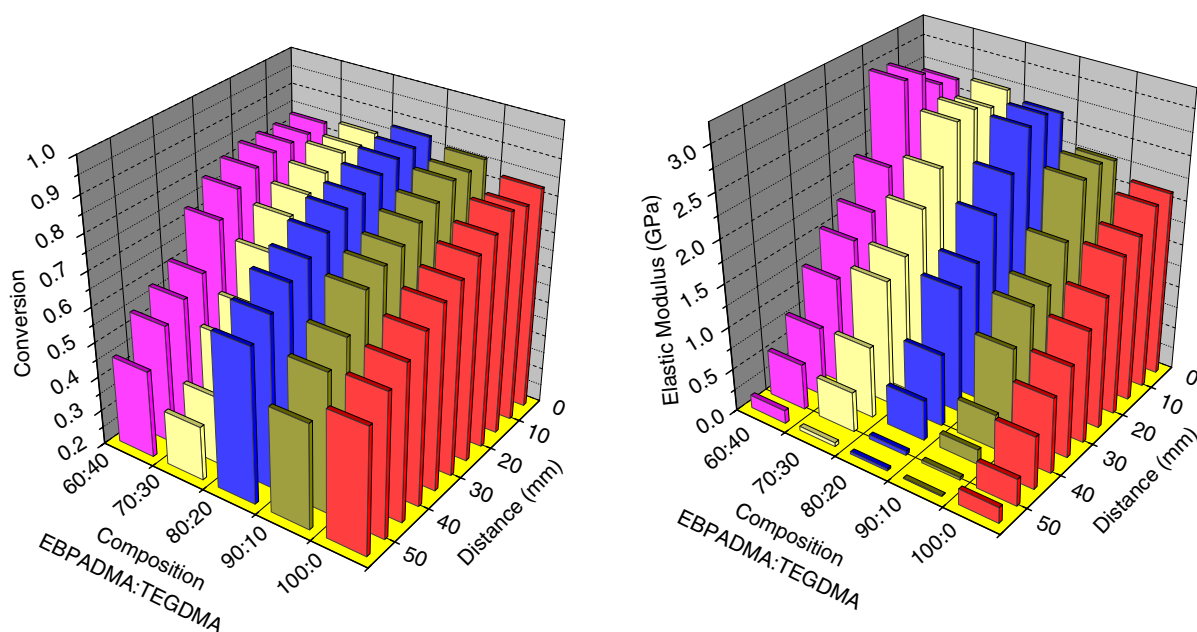


Fig. 4. The methacrylate conversion (left) and elastic modulus (right) for EBPADMA:TEGDMA blends of different compositions and photopolymerized by different irradiation time.

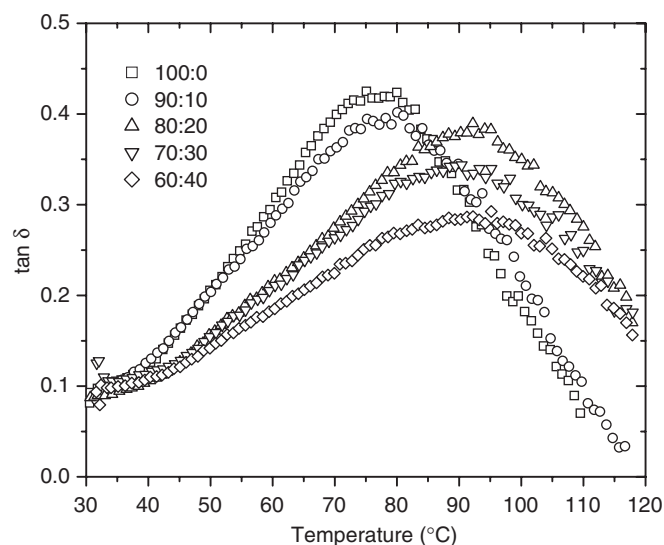


Fig. 5. $\tan \delta$ curves of EPBADA-TEGDMA networks of different compositions measured at the ultimate reaction conversion. The peak of the $\tan \delta$ corresponds to the glass transition temperature.

highest methacrylate conversion but not the highest modulus. The 60:40 composition exhibits the highest modulus while showing a lower ultimate reaction conversion. This further indicates that the role of the TEGDMA diluent monomer is complex in affecting the conversion and properties.

The glass transition temperature (T_g), defined as the peak of the $\tan \delta$ curve, for the EPBADA-TEGDMA networks was determined using DMA. Fig. 5 shows that the T_g increased from 76 to 94 °C as the TEGDMA content increased from 0% to 40%. T_g generally is inversely related to the molecular mass between cross-links. For these chemically and structurally similar materials at a comparable reaction conversion, the molecular mass between cross-links decreases and the cross-link density increases as the TEGDMA content is increased, thus giving rise to an increase in T_g . These observations are consistent with the increased elastic modulus measured by nanoindentation. In addition to a shift in the peak position, the breadth of the $\tan \delta$ curve increases as the TEGDMA content increases. This suggests that the networks are becoming more heterogeneous in nature as the amount of TEGDMA increases. In other words, the cooperative motion of the network is broad and reflects a distribution of relaxation times due to heterogeneity in the network structure (i.e. distribution of molecular weight between cross-links, differences in relaxation times due to chemical constituents, etc.). These factors should also affect the mechanical properties of the networks.

The relationship between reaction conversion and network mechanical properties is examined in detail. As an example, the effect of methacrylate conversion on the elastic modulus and hardness for the 90:10 composition is plotted in Fig. 6. The inset of Fig. 6 shows the harmonic contact stiffness (S) versus displacement curve. As de-

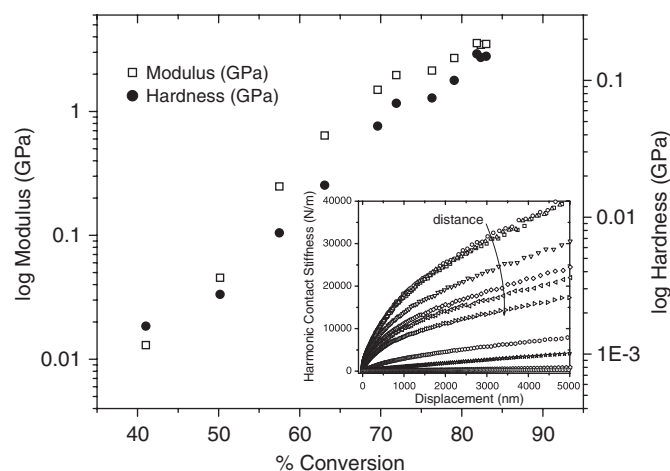


Fig. 6. Elastic modulus and hardness measured as function of % conversion for the 90:10 composition. The standard uncertainty associated with the nanoindentation measurements is smaller than the size of the symbol. Inset shows the harmonic contact stiffness versus displacement curves for the 90:10 composition measured as a function of conversion gradient distance.

scribed earlier, the contact stiffness is used for determining both the elastic modulus and hardness. As expected, the contact stiffness increases as the methacrylate conversion is decreased (i.e., increased conversion gradient distance). Similar data are obtained for all monomer compositions. Excellent agreement is observed between the conversion and modulus as an increase in methacrylate conversion corresponds to a dramatic increase in the modulus. The modulus increased over 2 orders of magnitudes (from approximately 0.01 to 3.5 GPa) as the conversion increased from approximately 50–86%. It is well understood that the mechanical properties change rapidly with conversion at the low conversion range. These results show appreciable changes in modulus as the conversion increased at the high conversion range. This is due to changes in the network crosslink density at the high conversion range and clearly illustrates the importance of obtaining high reaction conversion in the dental restorative composites. Equally important is the evolution of the hardness (H) with conversion, also shown in Fig. 6 for the 90:10 composition. The hardness (H) increased with increased conversion as expected. High reaction conversion is important to increase the hardness (or approximate yield stress) of the network, which is another important material property of dental restorative composites. With an increase in conversion from 70% to 85% the elastic modulus only modestly increased from ≈ 1.5 to ≈ 3 GPa. Over this same conversion range the hardness of the network increased by nearly a factor of 6. Similar trends were also observed in the other compositions.

4. Conclusions

Two-dimensional gradient samples of EPBADA-TEGDMA networks were fabricated. The methacrylate

conversion was adjusted by the time of light exposure controlled by a programmable stage. A broad conversion range was obtained for all monomer compositions. The conversions were measured using near IR spectroscopy and the mechanical properties (elastic modulus and hardness) were determined using nanoindentation with the continuous stiffness method. Excellent correlation was observed between the reaction conversion and mechanical properties of the cross-linked networks. Relationships between the chemical composition, reaction conversion, and mechanical properties were also evaluated. The addition of the TEGDMA diluent monomer increased the network modulus by increasing the cross-link density, while no clear trends were observed for the ultimate reaction conversion as the TEGDMA content was varied. The present technique allows several properties to be investigated on the same sample platform. Data obtained using these types of combinatorial/high-throughput approaches are useful in providing fundamental information in the structure properties characterization of materials.

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