

# Combinatorial Methods for the Characterization of Dental Materials

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## INTRODUCTION

Dental restorative composites are complex systems with a large number of material and processing parameters that influence their properties.<sup>1</sup> 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 appreciation for 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 is considered. This is understandable since a complete study of how monomer chemical structure and composition affect the processability and all properties is time consuming and laborious.

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.<sup>2,3</sup> In the current study, 2dimensional 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 networks were formed. The effects of composition and irradiation time on the conversion and mechanical properties (i.e., 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.

## EXPERIMENTAL

**Materials.**<sup>†</sup> 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 4N,N-dimethylaminobenzoate (4E)

were purchased from Aldrich Corp. All reagents were used as received.

**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: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 gradient samples examined in the current study varied in monomer composition in a discrete fashion, and orthogonal to it, varied in methacrylate conversion in a continuous fashion. The gradient specimen was prepared as follows. A sandwich mold consisting of a standard microscope glass slide, release film, poly(dimethylsiloxane) spacer 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 translate stage that was mostly covered by a light shield leaving approximately 15 mm of the sample strip exposed (Figure 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. The light source was a Dentsply Triad 2000 replacement halogen light bulb installed above the stage. The EBPADMA-TEGDMA samples were held 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 Figure 1). 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 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.

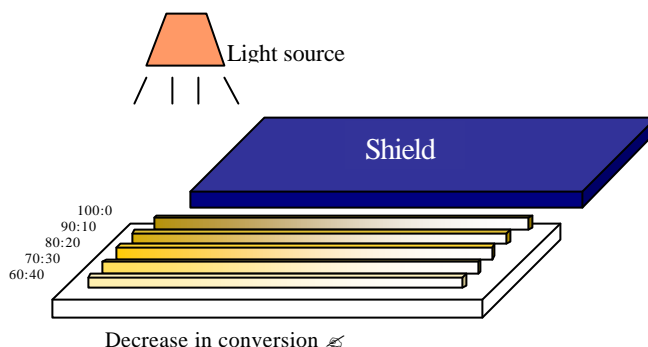


Figure 1. 2-Dimensional gradient sample

**Near Infrared Spectroscopy (NIR).** The degree of conversion for the resins was determined using NIR. The NIR spectrum of the uncured and cured resin (approximately 1 mm in thickness) between glass slides was obtained with a Nicolet Magna 550 FT-IR (Madison, WI) configured with a white light source, a CaF<sub>2</sub> beam splitter and an InSb detector. The NIR spectra in the region of 7000 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> was acquired from 64 co-added scans at 2 wavenumber resolution.

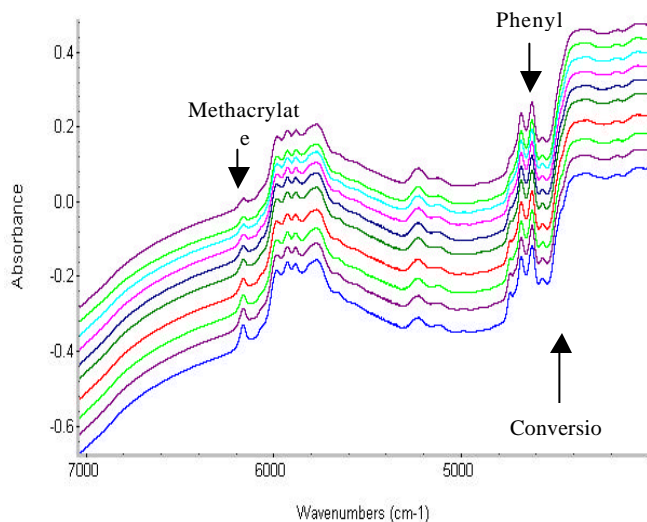
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<sup>†</sup> Certain commercial materials and equipment are identified in this work for adequate definition of the experimental procedures. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards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

**Nanoindentation.** Nanoindentation measurements were performed using a MTS Nanoindenters NanoXP instrument (Oak Ridge, TN) equipped with a 10  $\mu$ 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. The reported values of modulus are the average modulus obtained over a depth range from 1000 nm to 4000 nm. All indentation experiments were conducted using a strain rate of 0.05 s<sup>-1</sup>. The value of Poisson's ratio was assumed to be 0.30 for all measurements.

## RESULTS AND DISCUSSION

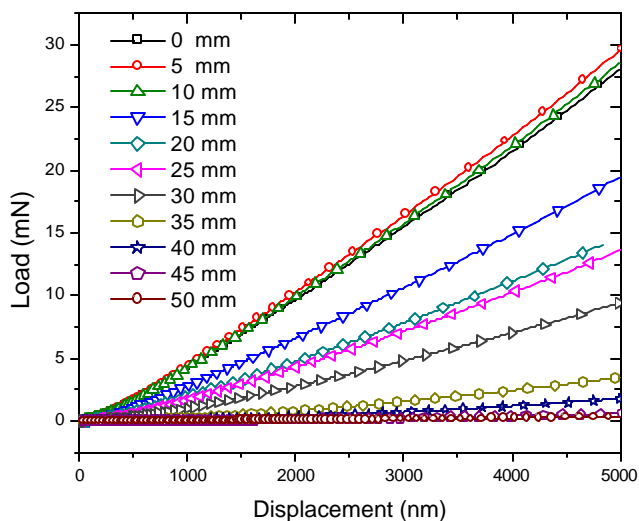
The conversion gradient was confirmed using near infrared spectroscopy, a technique shown to be valid for thick dental resin specimens.<sup>4</sup> Figure 2 shows the NIR spectra of the 90:10 composition along the conversion gradient. The top spectrum corresponds to the high conversion end measured at 0 mm position. Subsequent NIR spectra were obtained at 5 mm intervals. The methacrylate C=C-H peak increased as the conversion gradient distance increased, indicating that the methacrylate conversion decreased.



**Figure 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 standard uncertainty is 3 %.

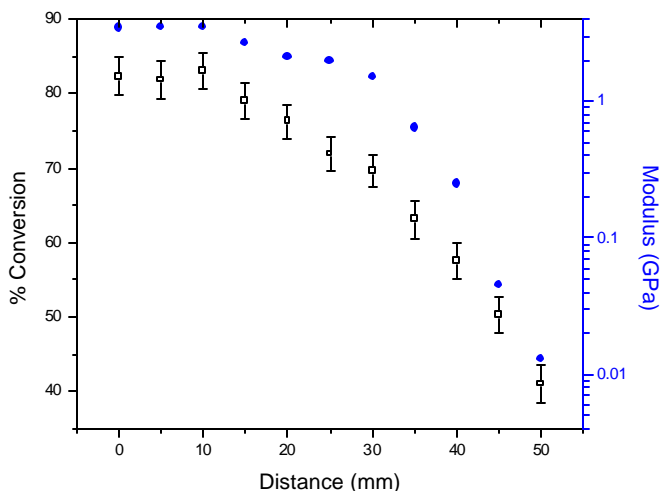
Similar NIR spectra were obtained for the other monomer compositions. The methacrylate conversion at each defined distance was calculated as the reduction in the C=C-H absorption at 6164 cm<sup>-1</sup> normalized to the aromatic absorption at 4623 cm<sup>-1</sup> as compared to the unreacted resin. The conversion values at the longer exposure end had reached the maximum, and were therefore defined as the ultimate conversion. For these tetra-functional monomers, the critical branching coefficient ( $\rho_c = 1/(f-1)$ , where  $f$  is the functionality) is 1/3 or 33.3 %. In general, the gradients exhibited conversions ranging from approximately 40 % to approximately 80 % spanning most of the cross-linked conversion range.

The corresponding load versus displacement curves for the 90:10 composition obtained using nanoindentation are shown in Figure 3. As expected, the slope for the curves (indicative of the elastic modulus) decreased as the conversion gradient distance increased (i.e., decreased methacrylate conversion). Similar data were obtained for the other monomer compositions.



**Figure 3.** Load versus displacement curves for the 90:10 composition measured as a function of conversion gradient distance. The standard uncertainty is 5 %.

The results for the 90:10 composition are summarized in Figure 4, which shows both the methacrylate conversion and network modulus as a function of the conversion gradient distance. Excellent agreement was observed between the conversion and modulus as an increase in methacrylate conversion corresponded to a dramatic increase in the modulus. The modulus increased over 2 orders of magnitude as the conversion increased from approximately 40 % to 82 %. These results clearly illustrate the importance of obtaining high reaction conversion in the dental restorative composites.



**Figure 4.** Percent methacrylate conversion ( $\square$ ) and network modulus ( $\bullet$ ) as a function of the conversion gradient distance for the 90:10 composition. The standard uncertainty associated with the nanoindentation measurements is smaller than the size of the symbol.

The effect of composition on the ultimate reaction conversion and modulus was also evaluated. While this will not be discussed in detail, it is interesting to note that the 90:10 composition exhibited the highest methacrylate conversion, but the 70:30 exhibited the highest modulus while showing a significantly lower ultimate reaction

conversion. The role of TEGDMA diluent monomer is complex in affecting the conversion and properties. It is likely that the TEGDMA also affects the reaction kinetics. These issues will be addressed in detail.

In summary, 2-dimensional monomer composition and conversion gradients were fabricated. The methacrylate conversion was adjusted by the amount of light exposure controlled by a programmable stage. The conversions were measured using NIR and the mechanical properties were determined using nanoindentation. Excellent agreement was observed between the reaction conversion and mechanical properties of the cross-linked network.

#### ACKNOWLEDGEMENTS

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