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Network structure of Bis-GMA- and UDMA-based resin systems

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ABSTRACT

Objectives. The commonly used dental base monomers 2,2-bis[*p*-(2'-hydroxy-3'-methacryloxypropoxy)phenylene]propane (Bis-GMA) and 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA) require the use of a diluent monomer, such as triethylene glycol dimethacrylate (TEGDMA). The aim of this study was to measure double bond conversion of UDMA/TEGDMA and Bis-GMA/TEGDMA polymeric systems, determine the leachable portion, and analyze network formation by evaluating crosslinking and pendant double bonds.

Methods. UDMA or Bis-GMA was combined with TEGDMA in systematic increments and irradiated to form light cured polymers. Fourier transform infrared spectroscopy in the near-infrared region was used to measure double bond conversion. The leachable sol fraction was analyzed by ^1H NMR. Resin composites were formulated. Flexural strength was measured by three-point bending and volumetric shrinkage was determined with a mercury dilatometer.

Results. The amount of base monomer greatly influenced double bond conversion, sol fraction, and crosslinking. Increasing base monomer concentration decreased double bond conversion, increased the leachable fraction, and decreased crosslinking and network formation. At mole fractions higher than 0.125, the UDMA polymers had significantly higher conversion than the Bis-GMA polymers. Bis-GMA polymers had higher leachable amounts of unreacted monomer, while UDMA mixtures had more crosslinking than the Bis-GMA mixtures. In regards to the physical properties of resin composites, increasing the base monomer improved flexural strength and decreased volumetric shrinkage.

Significance. This systematic study for the evaluation of conversion, leachability, crosslinking, and network structure along with physical properties, like volumetric shrinkage and flexural strength, are required for the optimization of competing desirable properties for the development of durable materials.

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1. Introduction

2,2-Bis[*p*-(2'-hydroxy-3'-methacryloxypropoxy)phenylene]propane (Bis-GMA) and 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA) are commonly

used as dental base monomers in composite formulations, but their high viscosity and multiple functional groups require the use of a low viscosity diluent monomer, such as triethylene glycol dimethacrylate (TEGDMA). The structures of the monomers are shown in Fig. 1. When cured, these systems often have incomplete double bond conversion after

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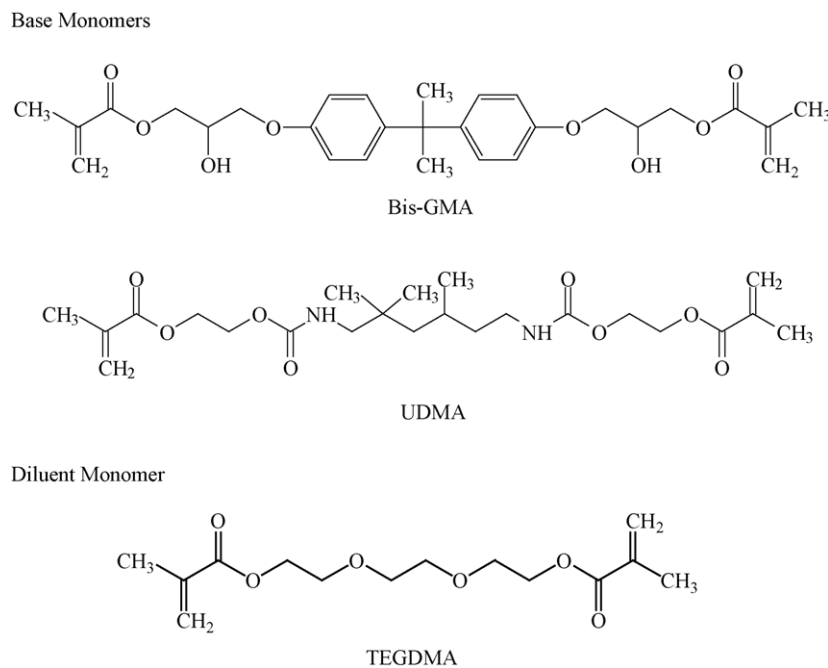


Fig. 1 – Structures of monomers used. For acronyms see Section 1.

polymerization [1–4]. As the polymerization progresses, the network formation decreases the mobility of monomers and oligomeric molecules resulting in pendant methacrylate groups and unreacted monomer trapped in the material. Low levels of conversion affect physical properties of the polymer, decreasing its strength [5].

It has been a common practice to measure the reduction in double bonds due to the polymerization process via infrared (IR) spectroscopy on thin films [6] and in bulk [7,8]. In crosslinking systems, residual double bonds in the polymer do not necessarily indicate free monomer, but may also result from pendant double bonds that are tied into the polymer network. Crosslinking is important for good network formation and physical properties. The extent of crosslinking, pendant double bonds, and leachable components have been analyzed by extraction of methyl methacrylate and crosslinking dimethacrylates from denture base polymers [9]. Also, crosslink density has been indirectly assessed by softening of polymers after exposure to ethanol [10,11].

If unreacted free monomer is left in the polymer matrix, the unbound components are able to diffuse out of the polymer system [12–17]. When this free monomer leaches out of the polymer, it may damage or irritate the surrounding tissue [18,19]. Pulpal cellular components can also be affected by the other components of the system, such as initiators or radicals [20]. The amount leached out of the polymer may vary with the type of monomers in the system and the degree of cure [21]. The toxicity of dental monomers also varies depending on the type and quantity of monomer [18,19,22,23]. Some monomers have been found to encourage bacteria growth [24]. Estrogenicity or allergic reactions have been reported [25,26], however, the estrogenic reaction may have come from impurities or degradation products.

To better understand the dependence of double bond conversion on monomer structure and reactivity of the monomer molecules in the forming network, these parameters were evaluated in a previous study [1] by photo-differential scanning calorimetry (DSC) using resin mixtures of TEGDMA with Bis-GMA or UDMA as base monomers. When compared at similar diluent concentrations, UDMA resins were significantly more reactive than Bis-GMA resins. Optimum reactivities in the UDMA resin system was obtained with the addition of relatively small amounts of TEGDMA, whereas the Bis-GMA/TEGDMA resin system required near-equivalent mole ratios for highest reactivity. Synergistic effects of base and diluent monomer on the polymerization rate and the final conversion were found for both Bis-GMA and UDMA base resins. The structures of the individual monomers, and consequently, the resin viscosities of the comonomer mixtures strongly influence both the rate and the extent of conversion of the photo-polymerization process.

This paper focuses on the network formation in bulk resin specimens of the same monomers, analyzing the leachable monomer fractions, and determining polymer crosslinking and pendant double bonds.

2. Materials and methods

The monomers Bis-GMA, TEGDMA, and UDMA (Esstech, Essington, PA), the photo- and cointiators camphorquinone (CQ) and ethyl-4-dimethylaminobenzoate (4-EDMAB), inhibitor 2,6-di-*tert*-butyl-4-methylphenol (BHT, Aldrich Chemical Co., Milwaukee, WI) and solvents dichloromethane and cyclohexane (J.T. Baker, Phillipsburg, NJ) were used as received.

TEGDMA was mixed with Bis-GMA or UDMA in mole fraction increments of 0.125, creating the series B1 (all TEGDMA) to B9 (all Bis-GMA) and U1 (all TEGDMA) to U9 (all UDMA). The resins were activated with fixed concentrations of the initiators by incorporating a mole fraction of 0.6% CQ and a mole fraction of 2.0% 4-EDMAB. Polymer disks, 20 mm × 0.5 mm, were made by irradiating the resin mixtures, clamped in metal molds between mylar sheets and glass slides, for 1 min from one side in a TRIAD curing unit (Dentsply, York, PA). Three disks were made for each formulation. Initial Fourier transform infrared spectra (Nicolet Magna 550, Nicolet Inc., Madison, WI) in the near-infrared (NIR) region were collected with 128 scans at 4 cm⁻¹ resolution to measure bulk polymer cure (C=CH₂ peak at 6164 cm⁻¹) [8] using an area baseline technique with peak areas being normalized to the polymer thickness. The disks were dried over calcium sulfate. After 2 weeks of drying, NIR spectra were again collected to determine the extent of post-cure. The disks were left over calcium sulfate until they reached a constant mass (±0.00003 g), which took approximately 3 weeks.

The dried polymer disks were extracted into a series of organic solvents containing a mass fraction of 0.01% BHT. The BHT serves to inhibit monomer polymerization upon extraction. For the extraction cycles, the disks were first immersed in 15 mL dichloromethane/BHT. After 72 h, the solvent was changed to 15 mL fresh dichloromethane/BHT. After another 72 h, the solvent was changed to 15 mL cyclohexane/BHT. Three extraction cycles and two organic solvents were used to insure complete removal of any extractable portion [21]. At the end of the cyclohexane extraction, the solvent was removed and the disks were redried in a vacuum oven at 90 °C for at least 3 days. After cooling, the disks were reweighed to measure total mass loss. The combined extracts were filtered to remove any polymer particles and the solvent was evaporated.

The residual solvent-free extract was analyzed in CDCl₃ by ¹H NMR (GSX 270, JEOL USA Inc., Peabody, MA). NMR calibration curves using the unique peaks for each component were calculated relative to BHT, δ 7.0 ppm, which was used as an internal standard. For the Bis-GMA series, the chemical shifts of the protons used for the calibration, correlation coefficients, and standard error of the estimate as a measure of uncertainty were Bis-GMA, 6.8 ppm, R=0.998, 1.62 × 10⁻⁵; TEGDMA, 3.7 ppm, R=0.997, 5.40 × 10⁻⁵; 4-EDMAB, 3.0 ppm, R=0.998, 2.64 × 10⁻⁶. The chemical shifts, correlation coefficients, and standard error of the estimate as a measure of uncertainty for the UDMA series were UDMA, 0.9 ppm, R=0.997, 2.40 × 10⁻⁵; TEGDMA, 3.7 ppm, R=0.999, 2.68 × 10⁻⁵; 4-EDMAB, 3.0 ppm, R=0.997, 2.49 × 10⁻⁶.

Crosslinking was calculated using the starting double bonds, extracted double bonds, and conversion values resulting in the %crosslink and the pendant double bonds.

Resin composites were made by mixing silanated, milled, barium oxide containing glass filler (Dentsply Caulk, Milford, DE) 3:1 with the monomer mixture. Flexural strength samples, 25 mm × 2 mm × 2 mm, were made by filling the composite resins in metal molds, clamping them between mylar and glass slides and light curing them for 1 min per side. The edges were lightly polished and the samples stored in water at 37 °C. Samples (n=6) were broken in three-point bending, at a crosshead speed of 0.5 mm/min, on a universal testing

machine (Instron Corp., Canton, MA). Volumetric shrinkage of the composites was determined with a computer controlled mercury dilatometer with 60 s curing time (n=3; ADAF, Gaithersburg, MD).

Microsoft Excel was used for the NMR regression analysis and Sigma Stat (SPSS Inc., Chicago, IL) for the Pearson correlation, analysis of variance (ANOVA) and post hoc Tukey tests (α=0.05). Standard deviations were calculated as a measure of the standard uncertainty.

3. Results

Generally, the double bond conversion, measured by the decrease of the normalized C=CH₂ peak area at 6164 cm⁻¹, showed an increase in conversion with a decrease in base monomer. The exception was pure TEGDMA, which had the lowest conversion around 42% (Fig. 2a). For the Bis-GMA containing polymers, the conversion ranged from 54% to 85%. The UDMA containing polymers conversion ranged from 76% to 87%. The UDMA rich mixtures had significantly higher conversion than the Bis-GMA polymers at mole fractions greater than 0.125 (Fig. 2a). The free, leachable monomer, also called sol fraction, which was quantitatively determined by measuring the extracted polymer disk weight loss, accordingly increased with increasing base monomer, with Bis-GMA polymers having higher leachable amounts (Fig. 2b) than UDMA-based polymers. Consequently, the extent of crosslinking decreased with increasing base monomer, with UDMA polymers having more crosslinking than the Bis-GMA polymers (Fig. 2c). While increasing the diluent monomer had a positive effect on the cure efficiency and network structure of the polymer systems, pure TEGDMA polymers had low conversion, 42%, a high extractable sol fraction, ≈50%, and low crosslinking.

The sol fraction, analyzed quantitatively by ¹H NMR, showed that the main components of the extracts were the leachable monomers in the system. Other components, e.g., the coinitiator 4-EDMAB, were also identified. No CQ was detected in the extracts. The amount of monomer leached from the polymer matrix was inversely correlated to the amount of TEGDMA in the system and positively correlated to the base monomer concentration (Fig. 2b). The proportions of the two monomers in the sol fraction were not the same as in the starting mixtures (Fig. 3). Volumetric shrinkage decreased with increasing base monomer (Pearson Product Moment Correlation, R=0.943, p<0.01), with the UDMA-rich composites having higher shrinkage than the Bis-GMA materials at and above 0.50 mol fraction, p<0.05 (Fig. 4a). Flexural strength did not differ between base monomers, although there was an upward trend with increasing base monomer concentration (Fig. 4b, Pearson Product Moment Correlation, R=0.588, p<0.01).

4. Discussion

Measuring the conversion of double bonds in a given resin system has generally been considered a good indicator for the prospective physical properties of such systems. The conver-

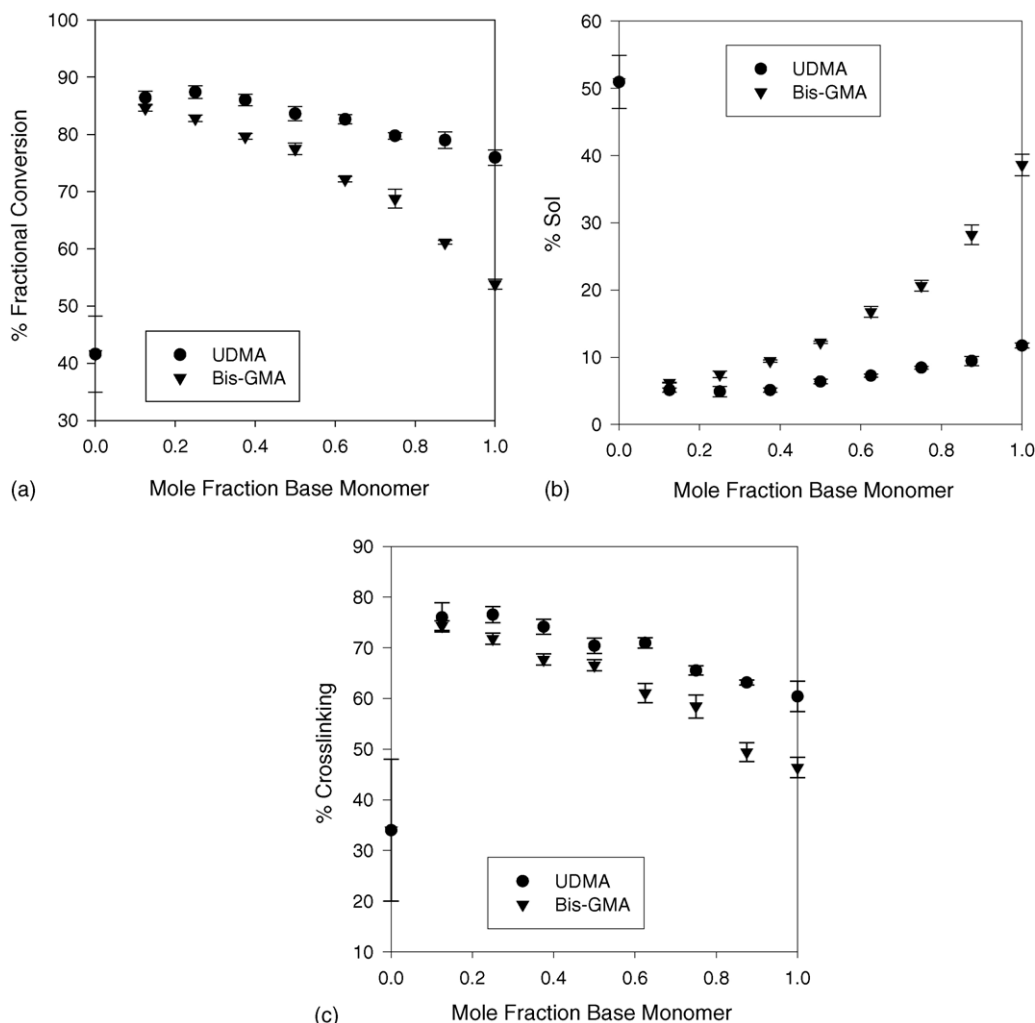


Fig. 2 – (a) Double bond fractional conversion, measured by NIR, of the UDMA/TEGDMA and Bis-GMA/TEGDMA polymer formulations. (b) Leachable sol fraction of the UDMA/TEGDMA and Bis-GMA/TEGDMA polymers. (c) Polymer crosslinking in UDMA/TEGDMA and Bis-GMA/TEGDMA systems. The vertical bars indicate the standard deviations as a measure of the standard uncertainty. Separate TEGDMA experiments (no base monomer) were run for each experimental group. Student's t-tests showed that the results for the separate TEGDMA experiments were not statistically different ($p > 0.1$). The larger than normal scatter of the TEGDMA specimens is attributed to the difficulty of sample preparation with the low viscosity monomer.

sion data reported here were measured by NIR spectroscopy. In a previous study on the same comonomer series, where photo-differential scanning calorimetry was used for more basic analyses of the relationship of diluent and base monomer [1], the same trends of double bond conversion with respect to the resin composition were found. However, the conversion measured by NIR spectroscopy on bulk specimens resulted in considerably higher conversion numbers. These differences can be explained through differences in the power density and heat developed during curing. NIR bulk samples were cured at approximately 120 mW/cm^2 for 1 min, while DSC thin layer samples were cured at 0.100 mW/cm^2 for 12 min. The light unit used to cure bulk samples also heated the resin during polymerization. Yet, while there was a difference in the final conversion data, a strong correlation was found between the two methods (Fig. 5, $R = 0.964$).

As reported in the previous investigation [1], it was found that optimum conversion in the Bis-GMA and UDMA resin systems were obtained at high TEGDMA concentrations. With decreasing TEGDMA (increasing base monomer) content the conversion decreased dramatically owing to the increased viscosity of the resin mixture. A similar pattern was observed in this study where the conversion, leachability and crosslink density worsened with increasing amounts of the base monomers. Both base monomers UDMA and Bis-GMA are relatively large molecular structures compared to the flexible TEGDMA structure and undergo hydrogen bonding. In addition, Bis-GMA with its isopropylidene-diphenoxy center core is a stiff molecule, which may have hampered the mobility even more.

However, while the conversion is highest for the diluent-rich mixtures, other physical properties, which are also

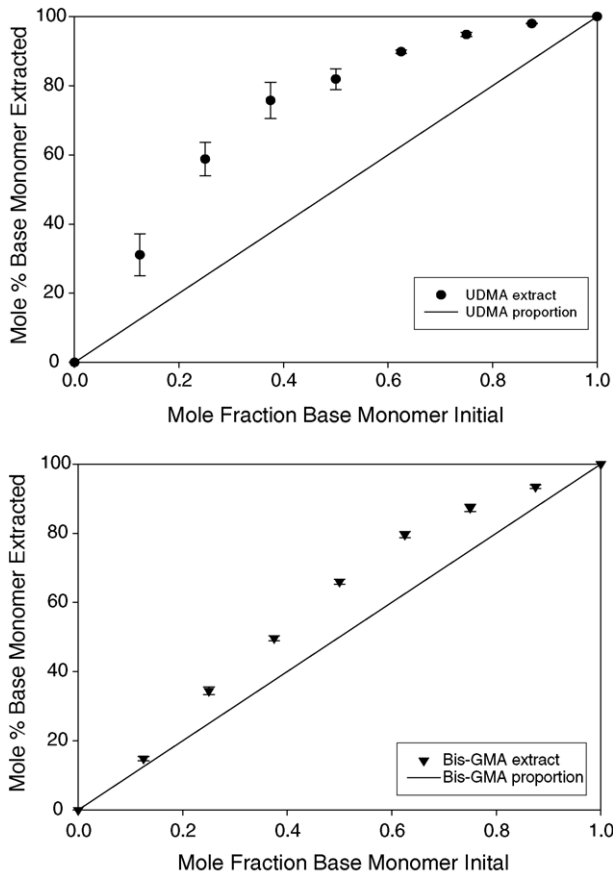


Fig. 3 – Composition of UDMA/TEGDMA and Bis-GMA/TEGDMA monomer formulations and polymer leachable fractions. Compositional drift is reflected by the amount of base monomer in the extracts not being proportional to the initial mixtures. The vertical bars indicate the standard deviations as a measure of the standard uncertainty.

affected by the crosslink density, e.g., the flexural strength and volumetric shrinkage, are compromised at lower base monomer concentrations. Low strength of TEGDMA-rich resin mixtures could also be caused by TEGDMA cyclization. TEGDMA, being a small, flexible molecule, has been found to cyclize in addition to forming crosslinks [27]. The pendant double bonds react to form primary cycles, which increase conversion, but do not contribute to network formation. This may lead to inhomogeneous polymer formation, with varying composition throughout the bulk polymer. Heterogeneous polymer formation has been shown in network formation studies [3]. Another problem with increasing TEGDMA content is that the high conversion of the relatively small TEGDMA molecule results in high polymerization shrinkage as shown in Fig. 4a. This dilemma between high conversion and low leachability on the one hand, and high polymerization shrinkage with the potential of gap formation within the cavity on the other, has long worried the dental community. Without the (still future) development of fast curing, truly expanding monomers, compromises will have to be made by choosing the resin combination that is optimized with respect to as many

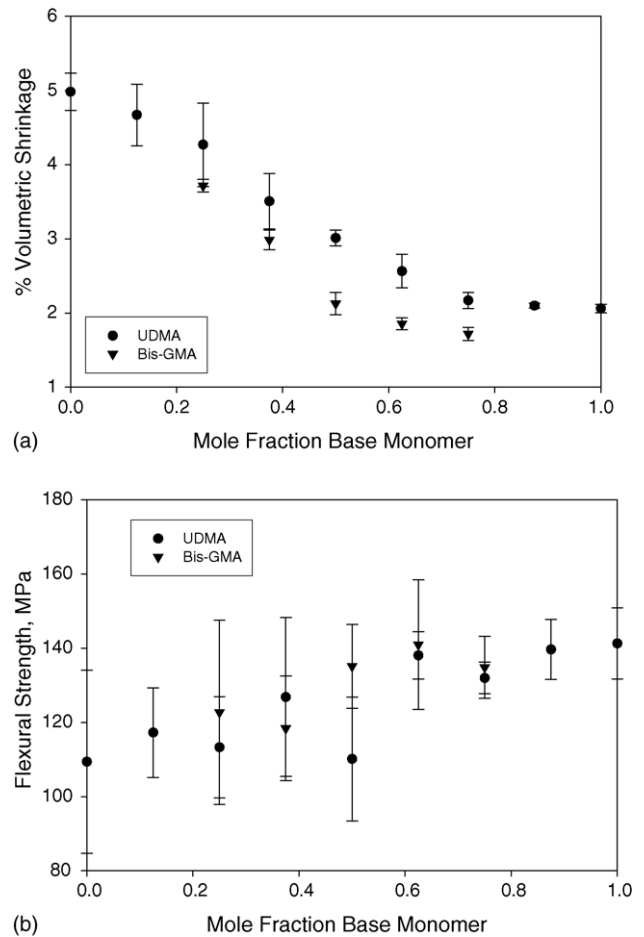


Fig. 4 – Volumetric shrinkage (a) and flexural strength (b) of resin composites formulated with UDMA/TEGDMA and Bis-GMA/TEGDMA blends. (Only resins 3–7 were used for the Bis-GMA composites.) The vertical bars indicate the standard deviations as a measure of the standard uncertainty.

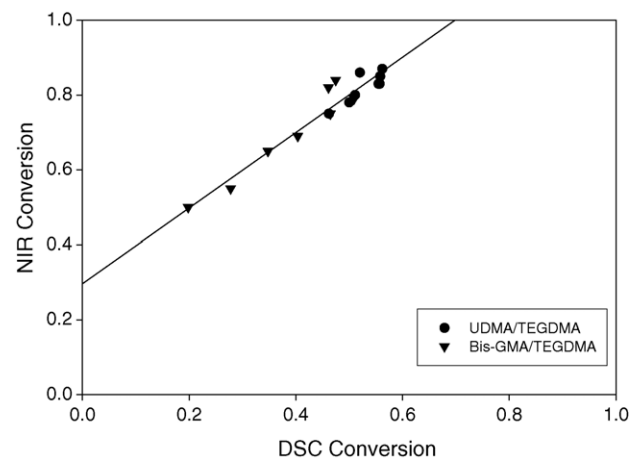


Fig. 5 – Comparison of polymer double bond conversion data obtained from NIR on bulk samples and photo-DSC of thin layer samples, $R = 0.964$. The error of the estimate of the linear regression line is 0.0305.

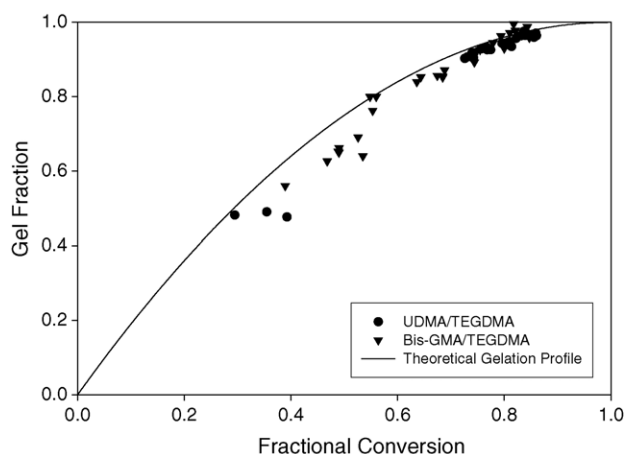


Fig. 6 – Theoretical curve produced from gel theory compared to experimental values. Deviation from theory is shown at lower conversion.

essential properties as possible. For example, with respect to conversion and leachability, flexural strength and shrinkage, there appears to be a small window of compositions (mole fractions of base monomers 0.375–0.625) that will allow such compromises (Figs. 2 and 4). This range has very similar properties with the exception of conversion and leaching. If lower leaching is desired, higher filler loading could be utilized to reduce shrinkage.

As shown in Fig. 3, the composition of the extracts was not proportional to the initial mixtures. Similar compositional drifts have also been reported by other authors [21,28]. Here, we found that the base monomer was leached at a higher proportion than found in the starting mixture. Since the extract was rich in either Bis-GMA or UDMA, the final polymer product was also affected, resulting in a compositional drift and the polymer having a higher TEGDMA concentration. The drift can be attributed to the higher mobility and reactivity of the diluent monomer, allowing it to be better tied into the polymer network [21]. In corroboration, the amount of monomer leached from the polymer matrix is inversely correlated to the amount of TEGDMA in the system and positively correlated to base monomer concentration. Increasing diluent monomer concentration increases double bond conversion, decreases the leachable fraction, and increases crosslinking and network formation. In order to fully examine the polymer network, all unreacted monomers had to be removed, which was accomplished by using the organic solvent extraction. This is in contrast to the clinical situation where the hydrophilic TEGDMA would be favored to leach into the aqueous oral environment.

Analysis of the polymer network can also be done using gel theory, presenting the gel fraction as a function of conversion [29]. The Bis-GMA/TEGDMA and UDMA/TEGDMA data are shown together with the theoretical curve (Fig. 6). Only the samples with lower conversion, like the pure TEGDMA samples, deviate from the curve. Since some of the TEGDMA may cyclize during polymerization [27], a small part of the leachable portion may be low molecular weight cycles or oligomers. These TEGDMA cycles would contribute to the degree of conversion, but would leave the gel fraction and leach as sol. Cook

[30] also showed a deviation from gel theory for low conversion of less than 50%, which was attributed to non-random polymerization.

As stated above, the conversion of double bonds in a given cured resin system has generally served as a material property indicative for the prospective performance of these materials in use. While such data may be misleading if considered in isolation, they do serve, especially in combination with leachability, to evaluate the network structure. However, other properties, e.g., strength and volumetric shrinkage, need to be considered and are of similar importance for the development of durable materials.

Disclaimer

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

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