Influence of the Base and Diluent Methacrylate Monomers on the Polymerization Stress and Its Determinants

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ABSTRACT: The aim of this study was to evaluate the effect of the association between bisphenol-A diglycidyl dimethacrylate (BisGMA) or its ethoxylated version (BisEMA) with diluents derived from the ethylene glycol dimethacrylate (EGDMA), with increasing number of ethylene glycol units (1: EGDMA, 2: DEGDMA, 3: TEGDMA, or 4: TETGDMA), or trimethylol propane trimethacrylate (TMPTMA) or 1,10-decanediol dimethacrylate (D_3MA) on polymerization stress, volumetric shrinkage, degree of conversion, maximum rate of polymerization (Rp_{max}), and elastic modulus of experimental composites. BisGMA containing formulations presented lower shrinkage and stress but higher modulus and Rp_{max} than those containing BisEMA. TMPTMA presented the lowest stress among all diluents, as a result of lower conversion. EGDMA, DEGDMA, TEGDMA, and TETGDMA presented similar polymerization stress which was higher than the stress presented by D_3MA and TMPTMA. D_3MA presented similar conversion when copolymerized with both base monomers. The other diluents presented higher conversion when associated with BisEMA. EGDMA showed similar shrinkage compared with DEGDMA and higher than the other diluents. The lower conversion achieved by TMPTMA did not jeopardize its elastic modulus, similar to the other diluents. Despite the similar conversion presented by D_3MA in comparison with EGDMA and DEGDMA, its lower elastic modulus may limit its use. Rather than proposing new materials, this study provides a systematic evaluation of off the shelf monomers and their effects on stress development, as highlighted by the analysis of conversion, shrinkage and modulus, to aid the optimization of commercially available materials. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2985–2991, 2012

Key words: dimethacrylates; infrared spectroscopy; modulus; polymerization stress; volumetric shrinkage

INTRODUCTION

High conversion during polymerization in dental composites is associated with high elastic modulus and volumetric shrinkage, both of which are intimately related to polymerization stress.[1] Such stresses contribute to failure at the bonded interface and microleakage, increasing the chance of restoration early loss,[2] as well as leading to strain in the remaining dental structure.[3] High conversion is nevertheless highly desirable to provide the necessary mechanical strength for the restoration to withstand masticatory loading[4] and chemical degradation in the oral environment.[5] Therefore, the development of materials with a combination of high conversion and low polymerization stress remains a challenge.

Many combinations of base and diluent monomers have been investigated. The most commonly used base monomer in dental composites is still Bisphenol-A diglycidyl dimethacrylate (Bis-GMA), synthesized by Bowen in the early sixties.[6] Due to its high viscosity at room temperature ($\sim$ 1200 Pa s),[7] BisGMA is usually combined with diluent monomers (with lower viscosity and generally lower molecular weight) to allow not only for inorganic filler incorporation (that ensure adequate mechanical properties) but also to improve medium mobility during the polymerization reaction, ultimately increasing conversion.[8] The higher conversion, allied to the augmented reactive group concentration, leads to increased volumetric shrinkage[9,10] (which is clearly a disadvantage), but also contributes to denser, more crosslinked networks, less prone to degradation.[11,12] This is even more evident for diluent monomers with functionalities greater than two.[13,14]

Ethyl and triethylene glycol (EGDMA, $M_w = 198$ g/mol and TEGDMA, $M_w = 286$ g/mol) have been

extensively investigated as diluents. Other ethylene-glycol derivatives such as di- and tetra-ethyleneglycol dimethacrylate (DEGDMA and TETGDMA, M_w 242 and 330 g/mol, respectively) have not been used as extensively but may be potential alternatives. The hompolymer of DEGDMA presents slightly lower rate of polymerization compared with TEGDMA,[11] which could extend the opportunity for viscous flow before gelation, thus contributing to stress relaxation. In turn, the use of larger molecules such as TETGDMA, D₃MA (1,10-decanediol dimethacrylate; M_w = 310 g/mol) and TMPTMA (trimethylol propane trimethacrylate; M_w = 338 g/mol) would afford lower volumetric shrinkage. Due to its flexibility, D₃MA renders a polymer with low elastic modulus,[12,15] also contributing less stress. Obviously, reductions in stress due to lower shrinkage or lower modulus should not come at the expense of conversion, or long term longevity of restorations will likely be reduced.

Because the high viscosity of BisGMA often requires the addition of as much as 20–30% of diluents by weight[16] (with the disadvantages already mentioned), some of the new synthesis efforts have concentrated on the development of analogs of BisGMA (M_w = 512 g/mol) as high molecular weight.[17,18] Despite the many molecules available, in commercial formulations of dental restoratives, the most largely used BisGMA analog is its ethoxylated version (BisEMA, M_w = 540 g/mol), which lacks pendant hydroxyl groups.[8,19] The different hydrogen bonding potential reflects in a monomeric glass transition temperature (T_g) 40°C lower in BisEMA compared with BisGMA, as well as lower viscosity, both contributing to greater reactivity.[8] The lower T_g and reactivity lead to higher conversion, partially compensating for the fact that the less hindered BisEMA presents intrinsically lower modulus than BisGMA,[20] all these playing major roles in stress development.

In commercial materials, base and diluent monomer ratios are optimized to address conversion, mechanical properties, handling characteristics, and ultimate clinical performance. Polymerization stress, which is a function of conversion, shrinkage, and modulus development, has been correlated with secondary decay, with restoration replacement being a significant public health issue. Rather than synthesizing new monomers or proposing monomer blends, the objective of this study was to systematically evaluate polymerization stress and its determinants (conversion, shrinkage, and modulus), as a function of base and diluent monomers at a fixed weight ratio. The criteria for monomer selection here were the prompt availability from commercial sources and, specifically for the base monomers, the fact that they are currently being used in dental composite commercial formulations.
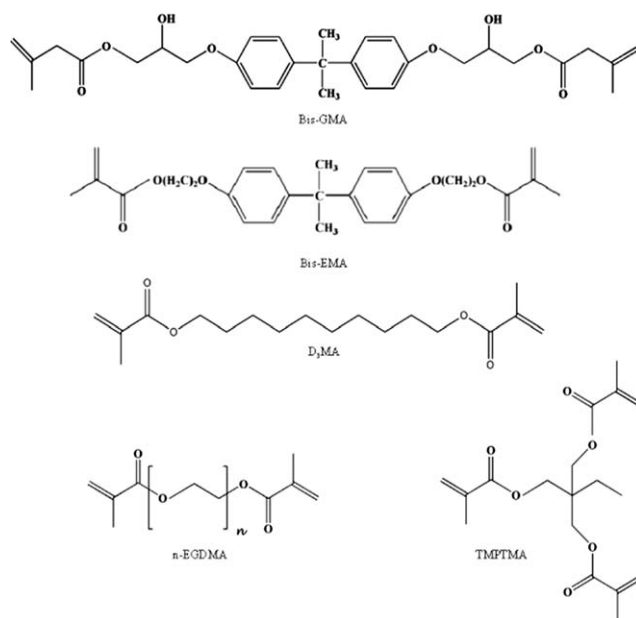

Figure 1 Molecular structures of the monomers used in this study.

MATERIALS AND METHODS

Materials

Twelve experimental materials were formulated containing either Bis-GMA (Bisphenol A diglycidyl dimethacrylate, Evonik Industries, Essen, Germany) or Bis-EMA (Ethoxylated bisphenol A dimethacrylate, Esstech, Essington, PA, USA) as base monomers and one of the following diluents, at 3 : 1 by weight: ethyleneglcol dimethacrylate (EGDMA), diethyleneglycol dimethacrylate (DEGDMA), triethyleneglycol dimethacrylate (TEGDMA), trimethylol propane dimethacrylate (TMPTMA), 1,10-decanediol dimethacrylate (D₃MA) (all from Cognis Performance Chemicals, Southampton Hampshire, United Kingdom), and tetraethyleneglycol dimethacrylate (TETGDMA) (Evonik Industries, Essen, Germany). Monomers were used as received, and the structures are shown in Figure 1. Composites were prepared by incorporating 71 wt % of alumino silicate barium glass (average particle size = 0.7 μm, Schott AG, Mainz, Germany), treated with 3-methacryloxypropyltrimethoxy silane (Evonik Industries, Essen, Germany). Materials were rendered photopolymerizable by the addition of 0.5 wt % of camphorquinone (Esstech, Essington, PA, USA) and 1 wt % dimethylamineethyl methacrylate (DMAEMA, Sigma-Aldrich, Steinheim, Germany).

Polymerization stress test

The polymerization stress method used in this study has been described in detail elsewhere.[21] Briefly, opposing surfaces of acrylic rods (polymethyl methacrylate) 6 mm in diameter and 13 or 28 mm in
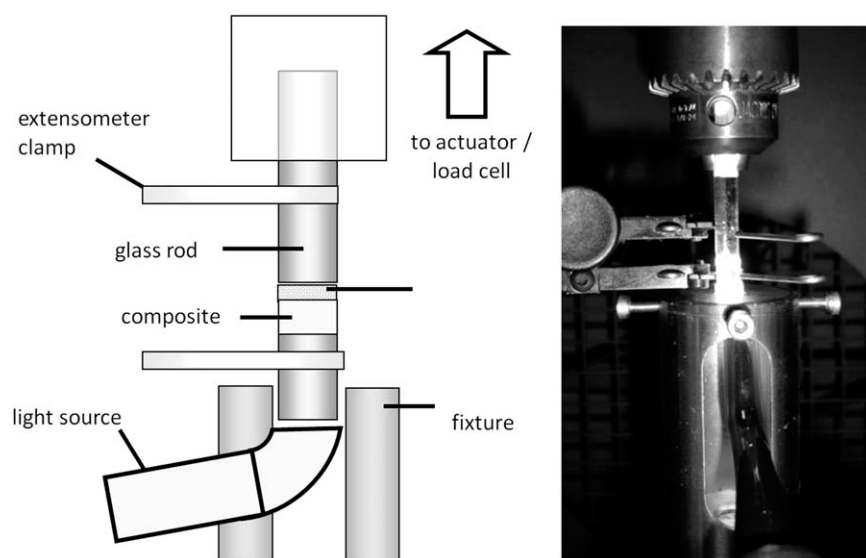
Figure 2 Polymerization stress test set up (picture and diagram).

height were used as the bonding substrate (Fig. 2). The longer rod was attached to the upper chuck of a universal testing machine (model 5565, Instron, Canton, MA) and the shorter rod was attached to a customized grip, so that the ends of the two rods opposed each other, and were separated by a 1 mm gap (where the composites were eventually inserted). The surfaces of the rods were prepared for bonding as follows: the surfaces were roughened with grit #180 sandpaper and by sandblasting with 250 μm aluminum oxide; then, a coat of methyl methacrylate (JET Acrílico Auto-polimerizante, Artigos Odontológicos Clássico, São Paulo, Brazil) was applied, followed by a coat of an adhesive system (Scotchbond Multipurpose Plus bottle 3, 3M ESPE, St. Paul, MN), photoactivated for 40 s at 300 mW/cm^2. As the material was polymerized *in situ*, the 13 mm rod had the surface opposing the one used for bonding polished to allow for light transmission through the rod, which worked as a light guide.

The experimental composite was placed in between the two rods, forming a cylindrical specimen with the same diameter of the rods (6 mm). The configuration factor of this set up was calculated to be 3.0,[22] and the volume was 28.3 mm^3. Composites were photoactivated for 40 s at 600 mW/cm^2 (irradiance leaving the tip of the light curing unit—VIP Junior, Bisco, Schaumburg, IL). The irradiance effectively reaching the specimen (through the rod) was determined to be 400 mW/cm^2, totaling a radiant exposure of 16 J/cm^2. Irradiance was checked before starting each series of experiments daily with the built-in radiometer and with Model 100 Optilux Radiometer (SDS Kerr, Danbury, CT). The specimen height was kept constant throughout the experiment with the aid of an extensometer with a 0.1 μm reso-

lution (model 2630-101, Instron). As the material polymerizes and shrinks (i.e., produces strain), the load cell recorded the resulting load, for a period of 10 min. Nominal stress was calculated by dividing the force recorded in real time by the specimen cross-sectional area. Final stress values are reported (maximum load at 10 min divided by the cross-sectional area of the rod). Five repetitions were performed for each material.

Degree of conversion and kinetic parameters

Degree of conversion and maximum rate of polymerization were determined by real-time near infrared spectroscopy using a Nicolet Magna 670 FTIR (Madison, WI), equipped with white light source, extended KBr beamsplitter and MCT/A detector. Specimens (3 repetitions) were placed in silicone rubber molds (1.0 mm thick and 5 mm in diameter), sandwiched between glass slides and photoactivated with 400 mW/cm^2 for 40 s (VIP Junior, Bisco), totaling 16 J/cm^2. Near-IR spectra were collected in the interval between 6099 and 6199 cm^{-1} (2 scans/spectrum, 4 cm^{-1}) at a temporal resolution of 2 scans/s, for 10 min. The reduction in the area of the methacrylate vinyl first overtone absorbance band centered at 6165 cm^{-1} was used to follow the polymerization reaction.[23] The first 30 s of the run corresponded to the period before the light source was turned on, and those spectra were averaged to provide the baseline area in the monomeric state. Then, after light turn on, at every 0.5 s, the areas corresponding to the polymeric state were rationed against the area in the monomeric state, giving 2 conversion data points per second. The polymerization rate was calculated as the first derivative of the conversion × time curve.

TABLE I
Mean and Standard Deviations for Polymerization Stress, Volumetric Shrinkage, Degree of Conversion, and Elastic Modulus as a Function of Base and Diluent Monomer

Formulation		Polymerization stress (MPa)	Degree of conversion (%)	Maximum rate of polymerization (%.s^{-1})	Volumetric shrinkage (%)	Elastic modulus (GPa)
Base monomer	Diluent					
BisGMA	EGDMA	4.4 ± 0.4^{abc}	50.3 ± 0.6^{d}	4.8 ± 0.1^{ab}	4.2± 1.2^{ab}	5.4 ± 0.4^{ab}
	DEGDMA	4.4 ± 0.3^{abc}	53.3 ± 0.6^{c}	5.4 ± 0.1^{ab}	3.6 ± 0.1^{ab}	5.8 ± 0.5^{a}
	TEGDMA	4.2 ± 0.2^{abc}	54.7 ± 0.6^{bc}	6.0 ± 0.9^{a}	3.0 ± 0.3^{b}	5.5 ± 0.4^{ab}
	TETGDMA	4.1 ± 0.3^{bc}	55.3 ± 1.2^{bc}	5.9 ± 0.1^{a}	3.2 ± 0.5^{b}	5.3 ± 0.6^{ab}
	D$_3$MA	3.9 ± 0.4^{c}	53.3 ± 0.6^{c}	5.7 ± 1.4^{ab}	3.0 ± 0.2^{b}	4.8 ± 0.6^{b}
	TMPTMA	3.0 ±0.4^{d}	37.0 ± 0.0^{f}	4.1 ± 0.6^{ab}	2.7 ± 0.4^{b}	5.2 ± 0.6^{ab}
BisEMA	EGDMA	5.0 ± 0.6^{a}	55.0 ± 1.0^{bc}	4.1 ± 0.8^{ab}	4.8 ± 0.9^{a}	5.3 ± 0.5^{ab}
	DEGDMA	5.0 ± 0.3^{a}	56.3 ± 0.6^{b}	3.7 ± 0.3^{b}	3.8 ± 0.2^{ab}	5.3 ± 0.6^{ab}
	TEGDMA	4.9 ± 0.4^{ab}	59.7 ± 0.6^{a}	3.7 ± 0.0^{b}	3.6 ± 0.2^{ab}	5.1 ± 0.5^{ab}
	TETGDMA	4.7 ± 0.2^{abc}	61.2 ± 0.6^{a}	4.4 ± 0.6^{ab}	3.8 ± 0.1^{ab}	5.1 ± 0.7^{ab}
	D$_3$MA	4.5 ± 0.3^{abc}	55.3 ± 0.6^{bc}	3.6 ± 1.1^{b}	3.5 ± 0.1^{ab}	3.7 ± 0.3^{c}
	TMPTMA	4.2 ± 0.4^{bc}	47.0 ± 1.0^{e}	3.7 ± 0.9^{b}	3.2 ± 0.7^{b}	4.7 ± 0.5^{b}

Values followed by the same superscript on the same column are not statistically different ($\alpha = 5\%$).

Polymerization shrinkage

Volumetric shrinkage was followed for 10 min in real-time using a linometer (3 repetitions, ACTA, Netherlands). The material was inserted between the isolated surfaces of an aluminum disc and a glass slide, positioned on top of a noncontact displacement probe (LVDT-linear variable displacement transducer). Specimens were photoactivated with 400 mW/cm^2, for 40 s (VIP Junior, Bisco). Volumetric shrinkage was calculated from the linear displacement as a function of specimen's final thickness.[24]

Elastic modulus

This test was performed according to ISO 4049.[25] Bar-shaped specimens were produced in stainless-steel split molds (1 × 2 × 10 mm; 10 repetitions), sandwiched between mylar strips and glass slides. Excess material was extruded with manual pressure. Photoactivation (400 mW/cm^2, 40 s, VIP Junior) was performed through the mylar strip only. Specimens were stored in distilled water at 37°C for 24 h. Before being subjected to 3-point bending test in a universal testing machine (Instron, span between supports = 8 mm, crosshead speed = 0.5 mm/min), specimens dimensions were determined with a digital caliper (Digimatic Caliper CD-6"OS, Mitutoyo, Japan), to the 0.01 mm.

Elastic modulus was calculated as the slope of the strain × strain curve in the linear portion, using the following equation:

$$E = \frac{L_1 \times D^3 \times 10^{-3}}{4 \times B \times H^3 \times d}$$

where E: elastic modulus (GPa), L_1: load (N), D: span (mm), B: width (mm), H: height (mm), d: displacement (mm).

Statistical analysis

Data passed the tests for normality and homocedasticity, and therefore were analyzed with two-way analysis of variance (base and diluent monomers being the factors) and Tukey's test, at a global level of significance of 95%. Regression analysis having polymerization stress as the dependent variable were also performed.

RESULTS

Results are summarized in Table I. For polymerization stress, both factors (base × diluent monomer) were statistically significant ($P < 0.001$) but the interaction between the factors was not ($P = 0.517$). Formulations containing Bis-EMA (4.7 ± 0.5 MPa^a) showed higher stress than the ones containing Bis-GMA (4.0 ± 0.6 MPa^b). EGDMA (4.7 ± 0.6 MPa^a) and DEGDMA (4.7 ± 0.4 MPa^a) presented mean stress values similar to TEGDMA (4.5 ± 0.4 MPa^{ab}) and TETGDMA (4.4 ± 0.4 MPa^{ab}) and higher than D$_3$MA (4.2 ± 0.5 MPa^b) and TMPTMA (3.6 ± 0.7 MPa^c).

The interaction between base and diluent monomer was statistically significant for degree of conversion ($P < 0.001$). In general, formulations containing Bis-EMA presented higher conversion than Bis-GMA within the same diluent, with the exception of D$_3$MA mixtures, which demonstrated similar values regardless of the base monomer. TMPTMA showed lower conversion for both base monomers, with values statistically lower when associated with BisGMA. When copolymerized with Bis-EMA, TEGDMA and TETGDMA led to higher conversion than the other diluents. When associated with BisGMA, diluents TEGDMA and TETGDMA
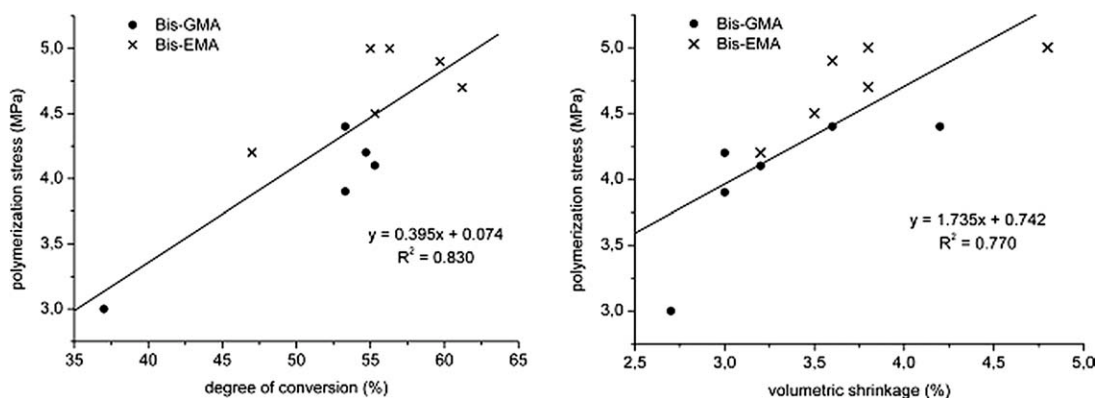
Figure 3 Regression analysis having polymerization stress as the dependent variable.

showed similar conversion to DEGDMA and D_3MA, but higher conversion than EGDMA. For the maximum rate of polymerization, the interaction between the factors ($P = 0.201$) and the factor "diluent" ($P = 0.113$) were not significant. The base monomer was significant ($P < 0.001$). Formulations containing Bis-GMA presented higher Rp_{max} than Bis-EMA (5.3 $\pm$ 0.9 e 3.9 $\pm$ 0.7%/s, respectively).

As for the volumetric shrinkage, the interaction was not significant ($P = 0.961$). The factors base monomer ($P < 0.05$) and diluent ($P < 0.01$) were significant. The formulation containing Bis-EMA presented greater polymerization shrinkage than the ones with BisGMA (3.8 $\pm$ 0.7% and 3.3 $\pm$ 0.7%, respectively). The diluent EGDMA (4.5 $\pm$ 1.0%[a]) presented similar shrinkage compared with DEGDMA (3.7 $\pm$ 0.2% [ab]) and higher than the other diluents, which showed similar average values (TEGDMA: 3.3 $\pm$ 0.4%[b]; TETGDMA: 3.5 $\pm$ 0.5%[b]; D_3MA: 3.3 $\pm$ 0.3%[b]; TMPTMA: 2.9 $\pm$ 0.6%[b]).

For elastic modulus, the interaction was not significant ($P = 0.07$), while both factors were significant ($P < 0.001$). Formulations containing BisGMA presented higher modulus than the ones with BisEMA (5.3 $\pm$ 0.6 GPa and 4.9 $\pm$ 0.8 GPa, respectively). The diluents deriving from ethyleneglycol showed similar moduli, in average (EGDMA: 5.4 $\pm$ 0.5 GPa[ab]; DEGDMA: 5.6 $\pm$ 0.6 GPa[a]; TEGDMA: 5.3 $\pm$ 0.5 GPa[ab]; TETGDMA: 5.2 $\pm$ 0.6 GPa[ab]). TMPTMA (4.9 $\pm$ 0.6 GPa[b]) showed statistically lower modulus compared with DEGDMA and higher than D_3MA (4.2 $\pm$ 0.7 GPa[c]).

The regression analysis between stress and its determinants are shown in Figure 3. The highest regression coefficients were observed between stress and conversion ($R^2 = 0.830$, left) and between stress and shrinkage ($R^2 = 0.770$; right). No correlation was found between stress and modulus or Rp_{max}.

DISCUSSION

The proposed formulations were obtained by combining one of two base monomers (Bis-GMA or Bis-EMA) to one diluent (EGDMA, DEGDMA, TEGDMA, TETGDMA, D_3MA, or TMPTMA) and were evaluated with regards to polymerization stress and its determinants. To highlight the polymer matrix contribution, base : diluent ratio, filler loading, and initiator system were kept constant for all formulations. As the range of initial viscosities of all diluents was very narrow, from 18×10^{-3} to 40×10^{-3} Pa s (data not shown), the base to diluent monomer ratio was kept at 3 : 1 by weight, regardless of the individual molecular weights to keep the initial viscosity at a similar level, a practical consideration in commercial materials. In mixtures where a diluent with higher M_w was used, the relative concentration of methacrylate groups was lower, as follows: for every 3 mols of base monomer, there were approximately 0.9 mols of EGDMA; 0.7 of DEGDMA; 0.6 of TEGDMA; 0.5 of TETGDMA; 0.5 of D_3MA; or 0.5 of TMPTMA. The ratios by weight, therefore, highlighted the influence of initial viscosity on network and stress development.

BisGMA formulations rendered lower degree of conversion, due to the monomer's reduced mobility compared with BisEMA, given not only by its backbone rigidity but also due to strong intermolecular hydrogen bonding,[26] which translates into high viscosity and monomeric Tg.[8] BisEMA, in turn, facilitates small molecule diffusion, and, therefore, leads to more conversion before gelation, as well as increased overall conversion.[27] Regarding the diluents, TEGDMA and TETGDMA showed higher conversion than EGDMA, probably due to the increased reactivity that accompanies a greater number of ethylene glycol units between methacrylate groups.[28] TMPTMA presented the lowest conversion compared with TEGDMA, TETGDMA, and D_3MA, all with similar M_w. This can be explained both by TMPTMA higher viscosity, which may have impaired mobility to some extent, but also by the fact that in tri-functional molecules, once one or more vinyls are engaged in the network formation, a substantial decrease is observed on the reactivity of the remaining functional groups, that are then pendant on the network.[27]

The higher polymerization rate observed for BisGMA based mixtures relates to its greater viscosity, which restricts initial medium mobility and leads to diffusion-controlled reaction at earlier stages in conversion.[29] As methacrylates terminate predominantly by disproportionation,[27] macroradical diffusion becomes limited and autoacceleration (until Rp_{max}) is observed due to small molecule diffusion, favoring propagation.[30] As network formation progresses, propagation also becomes diffusion-limited (autodeceleration). Therefore, the lower final conversion obtained for BisGMA is explained by autoacceleration/autodeceleration taking place at earlier in the polymerization reaction. The diluent monomer did not seem to influence rates of polymerization in this study, probably due to their similar viscosities and also due to the relatively low concentration at which they were used (25 wt %).

Volumetric shrinkage was greater for BisEMA materials, due to the higher conversion in comparison to BisGMA, as previously demonstrated in a study using BisGMA or BisEMA individually as base monomers.[1] As expected, shrinkage increased as the molecular weight decreases,[31] more so in the case of this study where the lower M_w diluents were also associated with greater vinyl group concentration, as previously mentioned. EGDMA presented similar shrinkage to DEGDMA, higher than all the other groups. In addition, denser networks were probably formed with the monomer presenting shorter spacers between functional groups, ultimately translating into shorter crosslinks.[32] The shrinkage values registered for EGDMA copolymerized with BisGMA was 31 to 40% higher than TEGDMA and TETGDMA and 33 to 26% higher when copolymerized with BisEMA. The fact that EGDMA presented around 10% lower conversion than TEGDMA and TETGDMA minimized the effect of molecular weight on volumetric shrinkage and polymerization stress.

Apart from the well-demonstrated effect of conversion on the elastic modulus of polymers,[33] the strength of secondary intermolecular interactions is also important in determining mechanical properties. In this study, hydrogen bonding interactions in the BisGMA molecule explain why materials formulated with this base monomer presented higher modulus despite the lower conversion obtained compared with BisEMA based formulations.[26] The same can be said about the diluents, in which molecules lacking hydrogen bonding acceptor sites (such as the glycol linkages) presented lower modulus, as was the case with D_3MA.[15] However, in the case of TMPTMA, even with lower conversion and lower hydrogen bonding capacity, the modulus was comparable with the one obtained by the ethylene glycol derivatives, probably due to extended opportunity for crosslinking formation given by its triple functionality.

Polymerization stress showed a strong direct correlation with conversion and shrinkage. The elastic modulus did not show correlation with stress in this study, as would be expected based on previous investigations.[1] This can be explained by the narrow range of modulus values observed (between 4.7 and 5.8 GPa), in turn influenced by molecular structure, as already mentioned. The rate of polymerization was already shown to have little influence on stress development, especially in the relatively narrow distribution observed in this study, as previously demonstrated,[1,34] highlighting in this case the influence of volumetric shrinkage. Ethylene glycol derived diluents showed statistically similar polymerization stress. This can be explained by two factors: in one hand, lower M_w monomers (EGDMA and DEGDMA) presented higher shrinkage values, while TEGDMA and TETGDMA achieved higher conversion. In turn, the lower stress values observed with TMPTMA, especially when copolymerized with BisGMA, stems from the lower conversion achieved with this diluent (and also possibly due to lower shrinkage, although this was not statistically significant). Still regarding TMPTMA, it was expected that it would lead to greater shrinkage compared with TETGDMA and D_3MA materials because, for the same molar monomer concentration, the vinyl group concentration is higher for TMPTMA.[31] However, TMPTMA presented similar shrinkage to TETGDMA and D_3MA. This is explained by the fact that in multifunctional monomers, more so for tri than for difunctional species, once one or more functionalities react and the molecule becomes a part of the network, the reactivity decreases for the remainder vinyls, leading to unreacted pendant double bonds,[35] which was also evidenced by the conversion results discussed previously. TEGDMA, TETGDMA, and D_3MA presented intermediate and statistically similar polymerization stress, probably due to the similar shrinkage. At least for D_3MA, similar shrinkage values compared to TEGDMA in copolymerizations with the same base monomer had already been reported, despite the 15% lower conversion achieved by D_3MA.[36] The same was true in this study for BisEMA copolymerizations only and can be explained by D_3MAs lower flexibility.

CONCLUSION

This study provides a systematic evaluation of methacrylate combinations commonly used in dental materials applications, in terms of stresses generated at the bonded interfaces and the factors determining its magnitude. BisGMA copolymers led to lower stress, related to the lower conversion and shrinkage, without compromising the elastic modulus. For BisEMA, on the other hand, the greater stress was a

function of higher conversion and shrinkage, despite the lower modulus. For these reasons, BisEMA is not recommended for use as the single base monomer in commercial formulations. Copolymers containing ethylene glycol dimethacrylate derived diluents all presented similar shrinkage and modulus, explaining their similar stress development. As far as stress is concerned, D$_3$MA showed a better compromise than EGDMA or DEGDMA, although the modulus was lower. TMPTMA presented the lowest polymerization stress, accomplished at the expense of conversion, but that did not seem to influence the elastic modulus. This information is relevant not only to dental applications but also spans a broad range of biomaterials that use dimethacrylates in their compositions.

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