Evaluation of two Bis-GMA analogues as potential monomer diluents to improve the mechanical properties of light-cured composite resins

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KEYWORDS
Composite resin; Mechanical properties; Bis-GMA; TEGDMA; Monomer diluents

Summary  Objectives. The aim of this study was to investigate the influence of new diluent agents, diluent ratio and filler content, on relevant mechanical properties of several novel composite resins containing Bis-GMA as resin matrices, and to compare these with the properties of composites based on TEGDMA, a conventionally used diluent.

Methods. Two Bis-GMA analogues were synthesized and 20 experimental composite resins were prepared combining three monomer mixtures (Bis-GMA/TEGDMA, Bis-GMA/\textsubscript{CH}{3}\textsubscript{bis}-GMA and Bis-GMA/CF\textsubscript{3} Bis-GMA), at three dilution rates (85/15, 10/90, 0/100) and three levels of hybrid filler content (barium aluminosilicate glass): 0, 10 and 35%. Flexural strength (FS), modulus of elasticity (ME) and microhardness (VHN) of the composites were evaluated. Five specimens of each material were prepared for each mechanical test, light-cured over 120 s and stored in water at 37 \degree C for 1 week. Three-point bending test was used for FS measurement and VHN was quantified by using a Vickers microindentor. Data were analyzed by ANOVA and Student-Newman-Keuls tests ($P<0.05$).

Results. Materials with CH\textsubscript{3} Bis-GMA showed an enhanced VHN. Mean FS was higher for matrices containing TEGDMA. Overall, dilution favored FS and VHN but not ME. Filler loading specially improved ME and VHN.

Significance. Results correlate with an increase in the extent of polymerization due to the higher flexibility of the less viscous comonomer starting system and the hydrophobic character of the Bis-GMA analogues.

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Introduction

Restorative dental materials are desired to have mechanical properties comparable to those of enamel and dentin [1]. Composite resins currently
used contain three components: a cross-linked polymeric matrix, a high volume fraction of particulate filler and a coupling agent to ensure matrix-filler adhesion. Increases in filler concentration generally lead to improved mechanical properties, while reducing polymerization shrinkage. The influence of the filler morphology in filler loading and of these two parameters in flexural strength and flexural modulus of some contemporary composites has been studied and it was found that composites with the highest filler content (about 80 wt%) exhibited the highest flexural strength, flexural modulus and hardness, and that both the filler loading and the filler morphology influenced all the properties [2]. However, the maximum filler loading is limited by the viscosity of the ensuing pastes [3].

Most of the composite resins widely used in restorative dentistry contain the highly viscous monomer 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (Bis-GMA) and low-viscosity monomers, used as diluents, in order to achieve high filler loading. In particular, triethylene-neglycoldimethacrylate (TEGDMA) has been extensively used for such purpose. When the effect of dilution with TEGDMA on the kinetics of Bis-GMA polymerization and on the degree of conversion (DC) has been evaluated using DSC and 13C NMR spectroscopy, systems with lower viscosity and lower glass transition temperature ($T_g$) of the monomer mixture exhibited higher DC [4]. Taking into account that $T_g$ is the temperature at which monomer characteristics change from that of a glass to that of rubber; below the glass transition temperature, the available polymer motions are limited, but above the glass transition, a motion that starts with one atom can pass through the chain and creates an effect.

The dilution effect was found to be predominant rather than the presence of intermolecular hydrogen bonding [4]. In order to get monomers with low-viscosity, that could replace TEGDMA in Bis-GMA/diluent mixtures, several dimethacrylate monomers of propoxylated-diphenols were synthesized: 2,2-bis[4-(2-methacryloxyprop-1-oxy)phenyl]propane, CH$_3$ Bis-GMA, 1,1,1,3,3,3-hexafluoro-2,2-bis[4-(2-methacryloxyprop-1-oxy)phenyl]propane and CF$_3$ Bis-GMA [5,6] (Fig. 1). It was previously stated that the replacement of the hydroxyl group, or its substitution by silylation greatly reduced Bis-GMA viscosity [7,8]. Consequent improvement of DC, polymerization shrinkage (PS) and handling properties were attained [9,10]. The photopolymerization of CH$_3$ Bis-GMA, CF$_3$ Bis-GMA and TEGDMA was followed by 1H Stray-Field MRI and the extent of spatially resolved polymerization was found to correlate well with flexibility (lower $T_g$ and lower viscosity) of the monomeric precursors [11].

![Figure 1](image-url)
The influence of filler content in the composite paste plasticity of binary monomer mixtures of Bis-GMA with TEGDMA or with Bis-GMA analogues were also investigated and it was concluded that the use of hydrophobic low-viscosity CH₃ Bis-GMA comonomer significantly improved DC and PS properties, as compared with TEGDMA [3,9].

As monomer chemical composition, monomer viscosity, Tₔ, and DC are expected to be related with mechanical properties of polymeric materials, the objective of this study was to ascertain if probed physico-chemical and polymerization improvements, previously obtained [12], would also lead to an improvement in final mechanical properties of the novel materials, and to evaluate the effect of different percentages of filler content on these properties. The null hypothesis to be tested was that differences do not exist between the mechanical properties of the different proposed resin matrices and filler contents.

Materials and methods

Materials

Bis-GMA (Polysciences, Inc., Warrington, PA), TEGDMA (Aldrich Chemical Co., Milwaukee, WI) and N,N-dimethyl-p-toluidine (DMPT, Aldrich Chemical Co., Milwaukee, WI) were used as received. Camphorquinone (CQ, Aldrich Chemical Co., Milwaukee, WI) was sublimed at 140 °C under reduced pressure before using. Bis-GMA analogues, CH₃ Bis-GMA and CF₃ Bis-GMA, were synthesized, purified and stored according to the earlier described method [5,6].

Monomer mixtures of Bis-GMA/TEGDMA and Bis-GMA with either CH₃ Bis-GMA or CF₃ Bis-GMA were prepared in the proportions 85/15 and 10/90 (wt%./wt%). Bis-GMA/TEGDMA mixtures were used as controls. Samples of pure Bis-GMA analogues were also prepared. CQ (1 mol%) and DMPT (1 mol%) were added to the different samples, as a photosensitizer and a reducing agent initiator, respectively, necessary to induce photopolymerization. Table 1 shows viscosity, Tₔ, DC and PS values of the different monomers. The two comonomers are more viscous than TEGDMA, but much less than Bis-GMA [13].

Resins were loaded with a silanated submicron hybrid filler of barium aluminosilicate glass and pyrogenic silica, with an average particle size of 0.7 μm (A-174 Herculite, Kerr, CA), to a content of 10 or 35 (wt%). All the samples were homogeneously mixed in an ultra sound bath for 1 min.

Table 1  Viscosity, glass transition temperature of monomeric state (Tₔ), degree of conversion (DC) and volumetric polymerization shrinkage (PS) of some dimethacrylate comonomer systems, as reported in the literature.

<table>
<thead>
<tr>
<th>Monomer system</th>
<th>Viscosity (Pa s)</th>
<th>Tₔ (°C)</th>
<th>DC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA/CF₃</td>
<td>750.0 [14]</td>
<td>-10.0 [14]</td>
<td>30 [14]</td>
</tr>
<tr>
<td>Bis-GMA/TEGDMA</td>
<td>40.0 [14]</td>
<td>-22.0 [14]</td>
<td>46 [14]</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>-80.2 [14]</td>
<td>83 [14]</td>
</tr>
<tr>
<td></td>
<td>0.01 [5]</td>
<td>-81.7 [14]</td>
<td>-</td>
</tr>
</tbody>
</table>

Specimen preparation

Five samples of each of the 20 different composite resins described in Table 2, were prepared for each measurement. Unpolymerized material was applied to molds, which were covered on both sides with a clear matrix strip and glass plate of 0.14 mm thickness. Specimens were subsequently irradiated over 120 s using a visible light source unit (=470 nm, Optilux 401, Demetron/Kerr, Danbury, CT) with a light-intensity of about 500 mW/cm².

The final dimensions of the specimens to be tested were measured after wet grinding using silicon carbide paper (up to 4000 grit) in order to eliminate the poorly polymerized layer, and then placed in distilled water at 37 °C for 1 week. The samples were analysed upon removing excess water.
Methods

Flexural strength
Rectangular shaped specimens were molded (25 x 2 x 2 mm; \( n = 5 \)). The flexural properties were quantified by a three-point bending test in a universal machine (Model 4411, Instron Corp., Canton, MA) with a cross-head speed of 1.0 mm/min. Flexural strength (MPa) was obtained by measuring the load at fracture and the elasticity or Young’s modulus (GPa) was calculated from the recorded load–deflection curves, as specified in Arcis et al. [15].

Microhardness
Disc shape specimens were molded (diameter = 8.0 mm, height = 2.0 mm; \( n = 5 \)). Microhardness was quantified by applying 300 g load during 30 s, with a pyramidal diamond microindentor (Indenter V-testor 402; Instron Ltd). Five square indentations were produced in each composite resin tested. The dimensions of each indentation produced were measured as the lengths of the diagonals of the indentation mark at a microscopic level and each measurement was repeated five times; the corresponding average was used to determine the Vickers hardness number (VHN), according to the usual procedure [16].

Statistical analysis
Mean and SD were calculated for each group of specimens. ANOVA tests were performed for each dependent variable (flexural strength, Young’s modulus and microhardness), considering as main effects: diluent agent, Bis-GMA/diluent ratio and filler content. Interactions were also included in the analysis. Student-Newman-Keuls tests were used for multiple comparisons and statistical significance was considered at the 95% confidence level.

Results
Mean values and SDs of flexural strength (MPa), modulus of elasticity (GPa) and microhardness (VHN) are shown in Table 2.

Flexural strength
The three main effects influence flexural strength in the following order of decreasing importance: diluent concentration, type of diluent and filler content (Table 3). For modulus of elasticity an inverse order of importance was found and the reliability obtained for both models was high: 91 and 86%, respectively. Table 2 shows that

<table>
<thead>
<tr>
<th>Matrix composition (wt%)</th>
<th>Filler content (wt%)</th>
<th>Flexural strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Microhardness (VHN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA/TEGDMA</td>
<td>0</td>
<td>85.5 (3.9)</td>
<td>4.8 (0.7)</td>
<td>16.62 (0.16)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>94.4 (5.4)</td>
<td>6.1 (0.9)</td>
<td>19.42 (0.61)</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>84.2 (7.3)</td>
<td>9.3 (1.6)</td>
<td>19.77 (0.75)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>89.6 (3.2)</td>
<td>5.0 (1.1)</td>
<td>10.78 (0.96)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>103.2 (4.0)</td>
<td>7.3 (0.8)</td>
<td>11.79 (0.39)</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>95.3 (3.8)</td>
<td>10.1 (1.4)</td>
<td>16.56 (0.28)</td>
</tr>
<tr>
<td>Bis-GMA/CH₃ Bismuth</td>
<td>0</td>
<td>67.2 (3.3)</td>
<td>2.1 (0.2)</td>
<td>13.76 (0.34)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>69.5 (5.4)</td>
<td>2.8 (0.3)</td>
<td>17.40 (0.21)</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>63.7 (7.1)</td>
<td>4.0 (0.4)</td>
<td>18.12 (0.16)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>84.0 (1.8)</td>
<td>1.5 (0.6)</td>
<td>17.00 (0.07)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>85.7 (3.6)</td>
<td>3.2 (0.5)</td>
<td>21.58 (0.13)</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>90.1 (3.0)</td>
<td>1.0 (0.2)</td>
<td>18.50 (0.22)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>92.0 (3.9)</td>
<td>2.9 (0.4)</td>
<td>22.97 (0.52)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>62.0 (2.2)</td>
<td>1.8 (0.3)</td>
<td>10.32 (0.31)</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>64.6 (5.5)</td>
<td>2.7 (0.7)</td>
<td>11.17 (0.16)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>59.7 (7.1)</td>
<td>3.9 (0.8)</td>
<td>14.14 (0.23)</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>80.7 (3.0)</td>
<td>1.0 (0.4)</td>
<td>16.76 (0.48)</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>82.2 (4.3)</td>
<td>3.3 (0.6)</td>
<td>19.56 (0.32)</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>84.5 (3.6)</td>
<td>0.6 (0.2)</td>
<td>16.80 (0.26)</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>88.0 (4.7)</td>
<td>2.6 (0.5)</td>
<td>22.09 (0.19)</td>
</tr>
</tbody>
</table>

Within each column, identical letters were assigned to results not significantly different at \( P > 0.05 \).
the flexural strength of all resins increased with the increase of comonomer concentration except when TEGDMA was used as diluent; the highest flexural strength was obtained when using TEGDMA or CH₃ Bis-GMA as diluents. Within the used range of filler content (0–35%), the effect of filler loading on flexural strength is very low and non-linear (Table 2). Resins containing CH₃ Bis-GMA at 10/90 or 0/100 dilution rate, independent of the filler loading, present flexural strength similar to that of the Bis-GMA/TEGDMA system. A decrease in modulus of elasticity with dilution was obtained for resins containing Bis-GMA analogues, while for TEGDMA resins a clear trend was not found.

Microhardness measurements

According to ANOVA test results (Table 3), microhardness is affected by filler content, diluent concentration and the diluent agent tested (decreasing order). In the main microhardness values of all resins increased with filler content. Concerning the influence of diluent concentration; an increase in microhardness was found, except for the samples containing TEGDMA. At low diluent concentration (85/15), resins containing TEGDMA as diluent exhibited higher hardness while for high diluent concentration (10/90 or 0/100) the best performance was found for CH₃ Bis-GMA resins (Table 2).

Similar microhardness values could be obtained for unfilled resins containing 40 wt% CH₃ Bis-GMA or TEGDMA and about 58% CF₃ Bis-GMA or TEGDMA; microhardness of resins with comonomer concentrations higher than those values was found to be better than for the Bis-GMA/TEGDMA resins with the same TEGDMA concentration (Table 2). For 35 wt% loaded resins, CH₃ Bis-GMA and CF₃ Bis-GMA systems become increasingly different, in this case similar microhardness values could be obtained for resins containing 35 wt% CH₃ Bis-GMA or TEGDMA and about 59% CF₃ Bis-GMA or TEGDMA (Table 2).

Discussion

Mechanical properties of composite resins are related to the polymer matrix, the filler, the coupling agent and the photoinitiator system. It was shown here, for the present materials, that the filler content, the composition and the dilution of the polymer matrix, influence flexural strength, modulus of elasticity and microhardness, and an extremely high reliability on the ANOVA results was obtained (Table 3).

Diluent concentration

According to the presented results, flexural strength and microhardness improve when the flexibility of the starting comonomer system increases, which may be produced by the dilution and/or by increasing the flexibility of the monomer being used as diluent. Present data may be related to the higher DC achieved for the polymer matrix; on methacrylate resins, the corresponding mechanical properties were found to depend on DC [17], which depends on the nature of the polymerizing monomers, in such a manner that more flexible monomer molecules give rise to increased DC [18-20]. The flexibility of the monomers may be probed by viscosity or Tₛ measurements and a good correlation was previously obtained between the concentration of Bis-GMA and Tₛ, and between Tₛ and DC in Bis-GMA/TEGDMA systems [4]. Even when increases in the concentration of the less viscous, more flexible comonomer, have raised the flexural strength of the resin, the Bis-GMA/TEGDMA matrix remains, in general, as the one with higher flexural strength for similar diluent concentrations. Table 2 shows higher results for flexural strength and microhardness in low-viscosity comonomer systems containing TEGDMA or CH₃ Bis-GMA, at 10/90 or 0/100 diluent concentrations, respectively. Concerning the trend for the properties of unfilled

<table>
<thead>
<tr>
<th>Dependent variables</th>
<th>Independent variables</th>
<th>F</th>
<th>Signification (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flexural strength, R=0.91</td>
<td>Main effect</td>
<td>65.5</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Diluent</td>
<td>98.0</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Diluent concentration</td>
<td>127.5</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Filler content</td>
<td>6.2</td>
<td>0.003</td>
</tr>
<tr>
<td>Young’s modulus, R=0.86</td>
<td>Main effect</td>
<td>72.0</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Diluent</td>
<td>64.1</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Diluent concentration</td>
<td>16.5</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Filler content</td>
<td>131.0</td>
<td>0.000</td>
</tr>
<tr>
<td>Microhardness VHN, R=0.76</td>
<td>Main effect</td>
<td>18.8</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Diluent</td>
<td>9.3</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Diluent concentration</td>
<td>14.8</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>Filler content</td>
<td>25.0</td>
<td>0.000</td>
</tr>
</tbody>
</table>

R, reliability of the test.
resins; an exception was found for TEGDMA at 10/90 diluent concentration, in specimens that contain the highest concentration of the more flexible monomer and, therefore, with the lowest viscosity (0.01 Pa s, Table 2), which is explained by the presence of a thick unpolymerized surface layer at the end of the irradiation period. It is also reasonable to expect a higher level of molecular oxygen in less viscous resins, which is known to strongly inhibit radical-induced polymerization because of its high reactivity toward radical species [20]. This inhibition effect is particularly pronounced when the monomer mixture is in contact with air, in which case the polymerization rate is reduced near the exposed surface, as expected [9]. DC also depends on the filler content, namely, because the inhibitor effect of oxygen decreases by raising the filler loading; therefore, an improvement in the mechanical properties is expected when increasing the filler percentage (Table 2).

DC and flexibility of comonomer starting systems is not necessarily positively correlated with mechanical properties [10]. In this study the modulus of elasticity of Bis-GMA/TEGDMA resins was found to be unaffected by the content of TEGDMA. Concerning resins containing Bis-GMA analogues, a decrease in modulus of elasticity is related to a decrease in Bis-GMA concentration. This result may be associated with the ability of Bis-GMA to form hydrogen bonds in the copolymer, which presumably is the outcome of restricted sliding of the polymer segments relative to each other, as previously stated for UDMA [10]. Also, this lack of correlation between DC and modulus of elasticity may be explained by the presence of much stiffer Bis-GMA in the polymer network [10]. In resins containing TEGDMA this effect is not so pronounced because DC increases with TEGDMA contents.

Filler

ANOVA data analysis shows that filler content had a significant effect on the mechanical properties evaluated. Information provided by past research suggests that the filler plays an important role in the properties of composite resins [21,22]. Overall, microhardness, flexural strength and modulus of elasticity increase for higher loaded resins (Table 2); however, a non-linear behavior was obtained for the filler effect on flexural strength of Bis-GMA/TEGDMA 10/90 resins that may be related to sedimentation of the filler particles, facilitated by the very low-viscosity of the resin matrices (Table 1). In general, the mechanical properties improve when the filler content is augmented. In the present study, the improvement of the mechanical properties is not so evident, because low filler contents were used intentionally (compared to 80-85% filler loading, generally found in commercially available resin composite) in order to facilitate the evaluation of the influence of the diluent on the mechanical properties, which otherwise would be difficult to ascertain.

Diluent

Microhardness and flexural strength are highly influenced by the DC of the polymer and a linear correlation was reported between these two properties and DC [17-19]. Tables 1 and 2 show that an increase in diluent concentration results in higher DC and, consequently, in the improvement of both properties. However, lower microhardness was obtained from resins with higher TEGDMA concentration, which may be due to the higher TEGDMA hydrophilicity, as compared with the Bis-GMA analogues (as microhardness is a surface property and specimens were stored in water for 1 week, water is expected to produce a higher reduction in mechanical properties of hydrophilic resins [23]). Therefore, higher microhardness was measured in resins containing higher Bis-GMA analogue concentration. Conversely, TEGDMA hydrophilicity seems not to affect flexural strength and modulus of elasticity, which are properties of the bulk and, consequently, less affected by interactions with water near the specimen surface.

Systems using TEGDMA as diluent have higher flexural strength, although systems with CH$_3$ Bis-GMA present clinically acceptable results. In all the tested specimens, the Young’s modulus was lower than the appropriate value, which should be comparable to that of mineralized dentin (14.7 GPa [24]); however, higher values are expected when using filler contents similar to that of commercially available resin composites. The null hypothesis should be rejected as differences in the mechanical properties of the different proposed resin matrices mixtures and filler contents do exist.

Within the limitations of an in vitro study (and taking into account that results were obtained in the presence of oxygen from the atmosphere), from flexural strength, modulus of elasticity, microhardness and from results about polymerization kinetics [11,13] and physico-chemical properties of these materials [12], it may be concluded that the analogue CH$_3$ Bis-GMA, which allows the
preparation of medium-viscosity resins, is a good candidate to replace TEGDMA in Bis-GMA mixtures. This conclusion is in agreement with recently reported results about mechanical properties of experimental hybrid resin composites based on TEGDMA:UDMA:Bis-GMA resins [25]. It was found that viscosity should be adjusted in order to achieve a balance between DC and mechanical properties and that (30:33:33 wt%) resins with medium-viscosity, provided optimum mechanical properties [25].

Further research is now in progress to evaluate physico-chemical properties of the systems containing Bis-GMA analogues after a higher filler loading, in order to obtain the resin composition with the best performance for its application as dental restorative materials.

Conclusions

In general, materials with CH$_3$ Bis-GMA diluent showed an enhanced microhardness, while overall, better flexural strength was obtained with TEGDMA based matrices, but few differences were obtained when compared to resin matrices using high CH$_3$ Bis-GMA concentration. Results are explained by an increase in the extent of polymerization due to the higher flexibility of the less viscous comonomer starting system and the hydrophobic character of the Bis-GMA analogues.

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References


