

Physical and Mechanical Properties of Resins Blends Containing a Monomethacrylate with Low-polymerization Shrinkage

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Abstract

Objectives The aim of this study was to evaluate the Knoop hardness (KH), cross-link density (CLD), water sorption (WS), water solubility (WSB), and volumetric shrinkage (VS) of experimental resins blends containing a monomethacrylate with low-polymerization shrinkage.

Materials and Methods A blend of bisphenol glycidyl methacrylate (BisGMA) as base monomer was formulated with (Bis-GMA)/triethyleneglycol dimethacrylate (TEGDMA), Bis-GMA/isobornyl methacrylate (IBOMA), or Bis-GMA/TEGDMA/IBOMA in different concentrations (40, 50, or 60 wt%). The camphorquinone (CQ)/2-(dimethylamino) ethyl methacrylate (DMAEMA) was used as the photoinitiator system. The KH and CLD were measured at the top surface using an indenter. For WS and WSB, the volume of the samples was calculated in mm³. The samples were transferred to desiccators until a constant mass was obtained (m1) and were subsequently immersed in distilled water until no alteration in mass was detected (m2). The samples were reconditioned to constant mass in desiccators (m3). WS and WSB were determined using the equations $m2 - m3/V$ and $m1 - m3/V$, respectively. VS results were calculated with the density parameters before and after curing.

Statistical Analysis Data were submitted to ANOVA and Tukey's test ($\alpha = 0.05$).

Results The resins containing IBOMA showed lower VS results. TEGDMA 40% and TEGDMA/IBOMA 20/20 wt% showed higher KH values. The IBOMA groups showed lower CLD, while TEGDMA groups had higher values of CLD. The BisGMA/TEGDMA resin presented the highest values of WS, and for WSB, all groups showed no significant differences among themselves.

Conclusion The monomethacrylate with low-polymerization shrinkage IBOMA used alone or in combination with TEGDMA may decrease VS, WS, and CLD values.

Keywords

- ▶ methacrylate monomers
- ▶ dental resin
- ▶ curing performance

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Introduction

Composite resins are highly successful restorative materials in dentistry.^{1,2} However, there are factors concerning the deleterious processes caused by the stress generated during the polymerization reaction.¹ Dental structures are routinely restored with dental restorative materials for aesthetic or functional problems caused by several factors such as tooth decay and traumas. The restorative materials represent one of the many successes of modern dental research in biomaterials.¹⁻³

Dental composites are derived from methacrylate networks, and the base monomer most currently used in these composites is bisphenol glycidyl methacrylate (Bis-GMA), known to be somewhat volatile, low diffusivity between tissues and low shrinkage.² The high viscosity of Bis-GMA monomers requires the addition of low-molecular weight monomer to obtain a suitable viscosity and improve mobility of the monomers during the polymerization reaction, increasing the degree of conversion^{4,5}, in addition to providing the incorporation of inorganic particle fillers.^{4,6}

Due to its low viscosity and ability to increase the degree of conversion, triethyleneglycol dimethacrylate (TEGDMA) is a diluent monomer widely added to the base monomer.^{4,7} However, TEGDMA has high volumetric shrinkage (VS).⁸ Still, the addition of diluent TEGDMA in greater proportion increases the polymerization shrinkage and water WS of the matrix,⁹ potentially leading to gap formation, marginal pigmentation, and secondary caries. Many alternative monomers with reactive diluents' intention of partial or total substitution of TEGDMA have often been exploited as a mean to reduce these problems.^{10,11}

Studies have been developed to evaluate physical and mechanical properties of resins blends.¹⁰⁻¹⁶ The isobornyl methacrylate (IBOMA) is a monomethacrylate that has low viscosity and polymerization shrinkage. Studies show that their use in synthesizing nanogels for matrix resins aiming to reduce shrinkage and polymerization stress^{15,16} is also used as comonomers thinners matrix composites because of their low viscosity, low polymerization shrinkage, and high hydrophobicity.¹⁷ Besides, this comonomer has low water WS, which can increase the durability of the polymer due to the resistance to degradation, particularly in the oral environment.^{4,7}

The phenomena of WS and WSB may be precursors to a variety of chemical and physical processes that promote biological concerns and have deleterious effects on the structure and function of resin matrixes.¹⁸ Polymer structure quality such as the degree of conversion and cross-link density (CLD) resulting from the photoactivation mode may lead to differences in WS and WSB.^{4,7,19}

Thus, it would be interesting to know the potential of experimental resin blends for dental resins. The aim of this study was to evaluate the physical and mechanical properties of experimental resin blends using Bis-GMA as monomer base, IBOMA as reactive diluent monomer alone or in combination with TEGDMA with different proportions. The hypothesis tested in this study is that the addition of alternative diluent monomer (IBOMA) may decrease the water WS and WSB and improve the KH and CLD of experimental resins.

Materials and Methods

Resin Preparation

Nine experimental resin formulations were tested in this study. The resin matrix consisted of bisphenol glycidyl methacrylate (BisGMA - Sigma-Aldrich Inc, St Louis, MO, USA) as base monomer and two diluent reactive co-monomers: triethyleneglycol dimethacrylate (TEGDMA - Sigma-Aldrich Inc, St Louis, MO, USA) and isobornyl methacrylate (IBOMA - Sigma-Aldrich Inc, St Louis, MO, USA). The structure of these molecules of monomers is showed in the ►Fig. 1. The diluent comonomers were mixed with the base monomers in nine different proportions, as described in ►Table 1. The photoinitiator system was composed of camphorquinone (CQ-0.5 wt%, Sigma-Aldrich Inc, St Louis, MO, USA and 2-(dimethylamino) ethyl methacrylate (DMAEMA-1 wt%; Sigma-Aldrich Inc, St Louis, MO, USA). Also, the inhibitor BHT (butylated hydroxytoluene; Sigma-Aldrich Inc, St Louis, MO, USA) was added to the organic matrix in a concentration of 0.1 wt% to avoid spontaneous polymerization of the monomers.¹¹

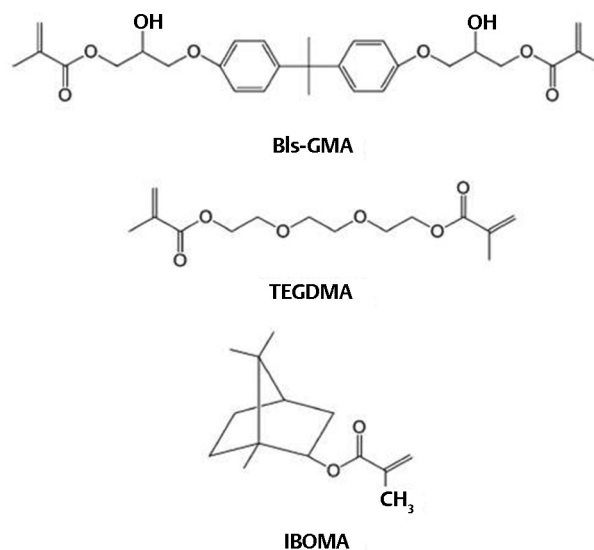


Fig. 1 Bisphenol glycidyl methacrylate (Bis-GMA), triethyleneglycol dimethacrylate (TEGDMA), and isobornyl methacrylate (IBOMA) molecule.

Table 1 Composition of the experimental resin blends

Resin	Bis-GMA%	TEGDMA%	IBOMA%
Bis50-TEG50	50	50	–
Bis60-TEG40	60	40	–
Bis40-TEG60	40	60	–
Bis50-IBO50	50	–	50
Bis60-IBO40	60	–	40
Bis40-IBO60	40	–	60
Bis50-TEG25-IBO25	50	25	25
Bis60-TEG20-IBO20	60	20	20
Bis40-TEG30-IBO30	40	30	30

Abbreviations: Bis-GMA, bisphenol glycidyl methacrylate; IBOMA, isobornyl methacrylate; TEGDMA, triethyleneglycol dimethacrylate.

Knoop Hardness (KH)

For the KH test, circular samples ($n = 10$) were prepared (2 mm thickness \times 5 mm diameter) and light cured by a LED curing unit (Bluephase G2, 1200 mW/cm²) over 60 s. The total energy dose was standardized at 72 J. After light-curing procedures, the specimens were dry stored at 37°C for 24 hours in light-proof containers. Thereafter, the top surface was wet-polished with 1,200-grit SiC paper to obtain a planar surface. KH measurements were taken using an indenter (HMV-2, Shimadzu, Tokyo, Japan), under a load of 490 N for 15 seconds. Five readings were performed for each specimen. The Knoop hardness number (KHN, in kilogram-force per square millimeter) was recorded as the average of the five indentations. Data were submitted to one-way ANOVA test followed by Tukey's test ($\alpha=0.05$).

Cross-link Density (CLD)

After completion of the KH test, samples of each resin ($n = 10$) were used to test CLD. These samples were immersed in 100% ethanol, for 24 hours, to indirectly evaluate the CLD and the elution of monomers by KH mean. The KH measurements were taken on top surface using an indenter (HMV-2, Shimadzu, Tokyo, Japan) under a load of 490 N (equivalent to 50 gf) for 15 seconds. Five readings were performed for each sample. The KHN was recorded as the average of the five indentations. Data were submitted to the one-way ANOVA test, followed by Tukey's test ($\alpha = 0.05$). Additionally, the percentage decrease values of KH obtained for each experimental resin was calculated.

Sorption and Solubility

This study was performed in compliance with ISO 4049:2000²⁰ standard specifications (except for the specimen dimensions and curing protocol) as follows: To test the WS and WSB, circular samples (2 mm thickness \times 5 mm diameter) were prepared ($n = 5$) and light cured by LED curing unit (Bluephase G2, 1200 mW/cm²) over 60 s. The total energy dose was standardized at 72 J. The disks were stored in desiccators containing silica gel at 37°C. The samples were weighted daily in an analytical balance (Tel Marke, Bel Quimis, São Paulo, SP, Brazil), accurate to 0.001 mg, constituting a weighing cycle every 24 hours. The complete cycle was repeated until a constant mass (m_1) was obtained (2 days of no weight change). Thickness (four measurements at four equidistant points on the circumference) and diameter (two measurements at the right angles) of each specimen were measured using a digital electronic caliper (Mitutoyo Corporation, Tokyo, Japan). The mean values were used to calculate the volume (V) of each specimen (in mm³). Thereafter, the samples were stored in plastic containers with distilled water at 37°C for 7 days. The volume of immersion water was 6 mL per specimen. Samples were again weighted daily after being carefully wiped with an absorbent paper. When constant weight was obtained (2 days of no weight change), this value was recorded as m_2 . After this weighing, the samples were returned to the first desiccator. The entire mass reconditioning cycle was repeated and the constant

mass (2 days of no weight change) was recorded as m_3 . The values for WS and WSB, in micrograms per cubic millimeters, were calculated using the following equations:

$$WS = (m_2 - m_3) / V$$

$$WSB = (m_1 - m_3) / V$$

Volumetric Shrinkage (VS)

The VS was determined by measuring the resin density before (ρ_u) and after (ρ_c) light curing ($n = 10$) with the help of Archimedes' principle. The mass (m) of the uncured sample was measured on a precision balance, the volume (v) was measured with a pipette, and the initial density (ρ_u) was calculated as follows:

$$\rho_u = m / v$$

After light curing was performed for 60 s (Bluephase G2, 1200 mW/cm²), the final mass of the sample was measured in air and water, and the final density (ρ_c) was calculated. The VS measurement was made after 24 hours of dry storage at 37°C. The VS (vol%) was calculated by the following equation:

$$VS = (\rho_c - \rho_u / \rho_c) \times 100$$

where ρ_c is the final density (cured) and ρ_u is the initial density (uncured).¹⁵

Statistical Analyses

The data were analyzed by one-way ANOVA and posthoc Tukey's tests. Statistical significance was established at $\alpha = 0.05$ for all tests.

Results

The KH and CLD values are shown in ►Table 2 and ►Fig. 2. The resin Bis-GMA/TEGDMA 60/40% by weight and Bis-GMA/TEGDMA/IBOMA 60/20/20% by weight showed the highest values of KH, and Bis-GMA/IBOMA 40/60 wt% showed the lowest values. The IBOMA groups had the lowest means for CLD, while the TEGDMA groups showed higher values of CLD. The groups of resins where the two reactive diluents monomers were present had intermediate values. The hardness decrease for TEGDMA groups ranged from 45.65 to 54.92%; for IBOMA groups, it ranged from 74.05 to 81.02%; for TEGDMA-IBOMA groups, it ranged from 63.66 to 69.39%.

The WS and WSB data are listed in ►Table 3. The resins that had TEGDMA as diluent monomer showed the highest values of WS, and for WSB, all groups showed no significant differences among themselves.

The VS data are listed in ►Table 4. The resins that had IBOMA as diluent monomer showed the lowest values of VS.

Discussion

The hypothesis was rejected, because IBOMA used as monomer diluent showed lower VS and WS values, but similar WBS values and lower KH and CLD values when compared with

Table 2 Means and standard deviation of the KHN, CLD (KHN), and hardness decrease (%) for the experimental resin blends

Resins	Hardness (KHN)	CLD (KHN)	%
Bis50-TEG50	31.1 (4.1) AB	16.9 (1.8) A	45.65
Bis60-TEG40	35.5 (4.8) A	16.0 (2.0) A	54.92
Bis40-TEG60	31.4 (5.7) AB	16.8 (2.0) A	46.49
Bis50-IBO50	26.7 (3.7) BC	6.6 (0.9) C	75.28
Bis60-IBO40	31.1 (3.8) AB	5.9 (0.6) C	81.02
Bis40-IBO60	23.9 (2.8) C	6.2 (0.6) C	74.05
Bis50-TEG25-IBO25	31.1 (3.3) AB	10.4 (0.9) B	66.55
Bis60-TEG20-IBO20	33.0 (2.2) A	10.1 (0.6) B	69.39
Bis40-TEG30-IBO30	32.2 (4.5) AB	11.7 (0.9) B	63.66

Abbreviations: cross-link density (CLD); KHN, Knoop hardness.

Distinct letters are statistically different for each column ($p < 0.05$).

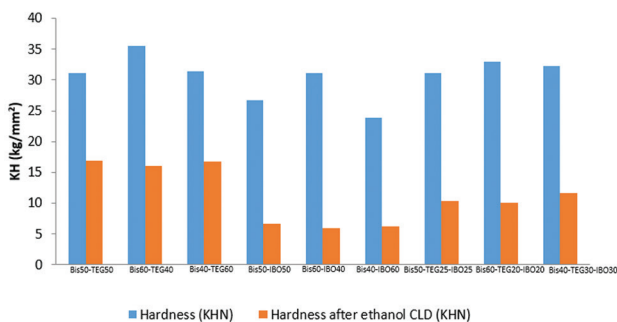


Fig. 2 Graphic presenting the cross-link density survey with the Knoop hardness before and after immersion in absolute ethanol. Knoop hardness reduction (%) presented above the columns.

Table 3 Means and standard deviation of the water sorption and solubility for the experimental resin blends

Resins	WS	WSB
Bis50-TEG50	41.4 (8.5) A	1.28 (2.86) A
Bis60-TEG40	35.5 (5.1) A	3.23 (6.76) A
Bis40-TEG60	48.4 (4.2) A	2.46 (6.88) A
Bis50-IBO50	15.3 (3.2) C	5.76 (8.35) A
Bis60-IBO40	22.9 (6.2) BC	3.52 (3.22) A
Bis40-IBO60	15.4 (4.7) C	10.17 (8.08) A
Bis50-TEG25-IBO25	29.2 (4.2) B	6.47 (8.85) A
Bis60-TEG20-IBO20	26.2 (5.3) BC	2.59 (7.13) A
Bis40-TEG30-IBO30	24.6 (4.8) BC	4.63 (5.37) A
		$\rho = 0.1559$

Abbreviations: WSB, water solubility; WS, water sorption.

Bis-GMA/TEGDMA resins. According to the results obtained, it can be verified that the IBOMA monomer decreased the VS values of the experimental dental resins. Overall, the resins with IBOMA (R5, R6, R7 and R9) showed lower VS values when compared with traditional BisGMA/TEGDMA dental resins, showing the potential for decreasing the polymerization shrinkage of IBOMA.

Table 4 Means and standard deviation for the VS% for the experimental resin blends

Resins	VS (%)
Bis50-TEG50	7.17 (0.36) BC
Bis60-TEG40	7.51 (0.23) AB
Bis40-TEG60	8.36 (0.27) A
Bis50-IBO50	6.36 (0.37) CD
Bis60-IBO40	4.03 (0.47) F
Bis40-IBO60	3.90 (0.97) F
Bis50-TEG25-IBO25	5.06 (0.26) E
Bis60-TEG20-IBO20	6.37 (0.57) CD
Bis40-TEG30-IBO30	5.72 (0.24) DE

Abbreviation: VS, volumetric shrinkage.

Distinct letters are statistically different ($p < 0.05$).

WSB in resin-based materials is a diffusion-controlled process and occurs mainly in the resin matrix.²¹ In this study, it was high values of WS were observed when the reactive diluent monomer TEGDMA was present in the resin matrix. Higher TEGDMA content in the matrix is responsible for increasing the WS of the composites.²² The WS of the copolymer is influenced by the hydrophilicity^{23,24} and CLD of the copolymer.²⁵

The influence of the composition on CLD of experimental composites containing different variations of TEGDMA/Bis-GMA, using hardness test before and after immersion in absolute ethanol, was examined. They observed that the variation in the composite composition influenced the CLD.²⁶ Also, a decrease in the hydrophilicity and an increase in the CLD of a copolymer could reduce the WS of the matrix.^{23,24} However, the CLDs of the Bis-GMA/IBOMA and Bis-GMA/IBOMA/TEGDMA were lower than that of the Bis-GMA/TEGDMA. The IBOMA is considered more hydrophobic than TEGDMA, which would lead to lower values of WS; however, on the other hand, it presents low ability to form crosslink among the polymer chains. The IBOMA is a monomethacrylate, presents low polymerization degree and, therefore, has fewer sites for crosslink in the polymer chain in formation.²⁷

In this study, the resins with IBOMA alone had lower KH when compared with the TEGDMA groups. This fact can be explained because monomethacrylates such as IBOMA tend to form linear polymers when polymerized alone or in resin blends, unlike what happens with the TEGDMA, which is known as conventional crosslinkers in polymers.⁹

Similar to the present study, Favarão et al said¹¹ the IBOMA associated with TEGDMA showed good or intermediate physical and mechanical properties. Also, it could be an alternative to improve the organic matrix of the composites, since it showed similar KH values when compared with TEGDMA groups. However, it was promising mainly because it can reduce the polymerization contraction. The results of the present study corroborate other studies that show that experimental resin blends can be promising for the development new dental composites.^{12-16,27} However, further investigations should be conducted to clarify not only the durability of this type of resin blend, analyzing marginal adaptation and bond strength, but also get an interesting formulation for the dental practice. Another important factor is the inclusion of inorganic filler particles for evaluating the performance of IBOMA as reactive diluent monomer in dental resins.

Conclusion

The monomethacrylate with low-polymerization shrinkage IBOMA used alone or in combination with TEGDMA may decrease VS, WS and CLD values. Thus, it can be used as a blend for dental resins.

Conflict of Interest

None declared.

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