Properties of 2,2-Bis[*p*-(2′-hydroxy-3′-methacryloxy propoxy)phenyl]propane/Isobornyl (Meth)acrylate Copolymers

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ABSTRACT: Isobornyl acrylate (IBOA) and isobornyl methacrylate (IBOMA) were used to replace triethylene glycol dimethacrylate (TEGDMA) as reactive diluents in dental restorative materials. Photopolymerization behaviors of mixtures of IBO(M)A and 2,2-bis[*p*-(2′-hydroxy-3′-methacryloxy propoxy)phenyl]propane (Bis-GMA) were investigated by Fourier transform infrared spectroscopy. The degree of conversion, volume shrinkage, contact angle, water sorption, water solubility, flexural strength, and modulus values of the Bis-GMA/IBO(M)A formulations were measured and compared with those of a Bis-GMA/TEGDMA formulation. The results illustrate that the degree of conversion, volume shrinkage, contact angle, water sorption, flexural strength, and modulus values of the Bis-GMA/IBO(M)A systems were all lower than those of the Bis-GMA/TEGDMA system; the water solubility values of the Bis-GMA/IBO(M)A systems were higher than that of the Bis-GMA/TEGDMA system. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: dental polymers; FT-IR; photopolymerization

INTRODUCTION

Dental restorative materials usually consist of a base resin, a reactive diluent, a photoinitiator system, and inorganic fillers. Most base resins and reactive diluents are dimethacrylate monomers.[1] 2,2-Bis[*p*-(2′-hydroxy-3′-methacryloxy propoxy)phenyl]propane (Bis-GMA; as shown in Fig. 1) is one of the most commonly used monomers in dental restorative materials.[2] Compared with monomers such as methyl methacrylate, Bis-GMA possesses advantages of a lower volatility and diffusivity into tissues and less volumetric shrinkage.[2] The disadvantage of Bis-GMA is its high viscosity and low vinyl conversion under ambient polymerization conditions.[3] To overcome these deficiencies, a low-viscosity reactive diluent, such as triethylene glycol dimethacrylate (TEGDMA; structure is shown in Fig. 1), is added. Recently, the Bis-GMA/TEGDMA system has been the most commonly used monomer mixture in dental restorative materials.[4,5] However, the addition of the smaller sized diluent TEGDMA increases polymerization shrinkage and water sorption of the materials.[6–8] To solve these problems, many diluents with lower polymerization shrinkage and water sorption values have been synthesized.[7,8] However, these diluents increase the viscosity of the dental resin system because of their higher molecular weights.

Isobornyl acrylate (IBOA) and isobornyl methacrylate (IBOMA; as shown in Fig. 1) are two traditional monomethacrylates with low viscosity and shrinkage values. Lots of articles have been published on the use of IBOA and IBOMA as reactive diluents in coatings.[9–12] With regard to dental resin systems, Elliott and Bowman[13] studied the polymerization kinetic behavior of Bis-GMA/IBOMA, and no further studies have been undertaken to investigate whether IBOA and IBOMA could be used as diluents in dental restorative materials.

In this research, we chose IBOA and IBOMA as diluents to replace TEGDMA in the Bis-GMA/TEGDMA system because of their low polymerization shrinkage and high hydrophobicity values with the aim of reducing the polymerization shrinkage and water sorption of the dental resin. The double-bond conversion (DC), water solubility, and mechanical properties were also investigated to evaluate the possibility of using IBOA and IBOMA as reactive diluents in dental restorative materials.

EXPERIMENTAL

Materials

Bis-GMA (92%) was purchased from Aldrich Chemical Co. (St. Louis, MO). TEGDMA (92%) was purchased
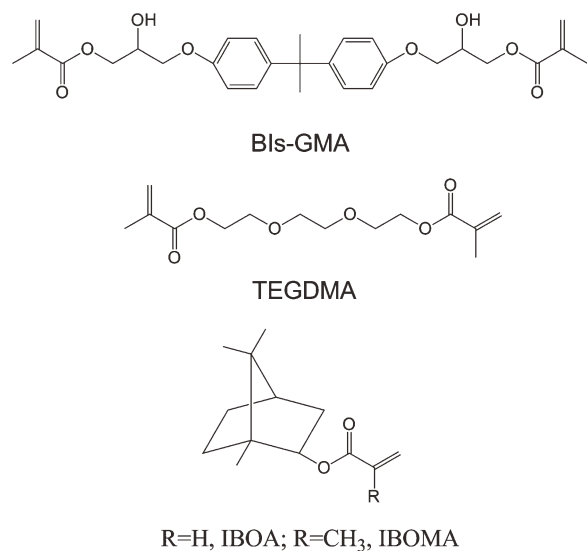
Figure 1 Structural formulas of Bis-GMA, TEGDMA, and IBO(M)A.

from Shuangjian Co. (Guangzhou, People's Republic of China). IBOA and IBOMA were purchased from Sartomer Co.(Guangzhou, People's Republic of China). Camphoroquinone (CQ; 99%) was purchased from Alfa Aesar Co. (Ward Hill, MA). 2-(*N*,*N*-Dimethylamino)ethyl methacrylate (DMAEMA; 99%) was purchased from Acros Organic Co. (Geel, Belgium).

Preparation of the resin formulations

The photocured resin formulations were mixtures of Bis-GMA, TEGDMA [or IBO(M)A], CQ, and DMAEMA. CQ and DMAEMA were used as a photoinitiator system. Their mass ratio of Bis-GMA/TEGDMA [or IBO(M)A]/CQ/DMAEMA was 49.3 : 49.3 : 0.7 : 0.7 w/w. All of the resin formulations were stored in the dark before use.

Measurement of the DC

The DC of every formulation was measured by a Vector33 Fourier transform infrared spectroscope (Bruker Co., Rheinstetten, Germany). Each sample was coated on a KBr plate, covered with a polyethylene film, and irradiated with visible light. The DCs were determined from the ratio of the calculated areas of two absorption bands (1635 cm^{-1} for C=C and 1608 cm^{-1} for aromatic rings as an internal standard) before and after exposure. DC was then calculated with the following equation:

$$C(t) = \frac{(A_{C=C}/A_{Ph})_0 - (A_{C=C}/A_{Ph})_t}{(A_{C=C}/A_{Ph})_0} \qquad (1)$$

where $A_{C=C}$ and A_{Ph} are the absorbance peak areas of methacrylate C=C at 1636 cm^{-1} and the phenyl

ring at 1608 cm^{-1}, respectively; $(A_{C=C}/A_{Ph})_0$ and $(A_{C=C}/A_{Ph})_t$ are the normalized absorbances of the functional groups at the radiation times 0 and t, respectively; and $C(t)$ is the conversion of methacrylate C=C as a function of the radiation time.

Measurement of the polymerization shrinkage

Polymerization shrinkage was determined by the differences in the density of the resin before and after curing. First, the density of the uncured resin was determined. A 10-mL density bottle was weighed, filled with uncured resin, and weighed again. The same bottle was then emptied, thoroughly washed and dried, filled with distilled water, and weighed again. This procedure was repeated five times. The density of the resin before curing (D_r) was then calculated as follows:

$$D_r = (M_r/M_w) \times D(T) \qquad (2)$$

where $D(T)$ is the density of water at the room temperature, M_r is the mass of the uncured resin, and M_w is the mass of water.

Second, the density of the cured resin was determined. Resins were poured into a Teflon mold with a size of $25 \times 2 \times 2$ mm^3 and then light-cured for 5 min with a dental light source at room temperature and with about a 5-mm distance between the light tip and the radiometer face. Five specimens for each resin were prepared. The cured resin specimen was removed and weighed to obtain the mass of the cured resin (M_s). A 10-mL density bottle was filled with distilled water and weighed to obtain the mass of water. The cured resin was put into the bottle, spilled water was gently wiped with a soft absorbent paper, and then, the bottle with water and cured resin was weighed to obtain M_{sw} (mass of bottle with water and cured resin). The density of the resin after curing (D_s) was calculated as follows:

$$D_s = \frac{M_s \times D(T)}{M_w + M_s - M_{sw}} \qquad (3)$$

Hence, the polymerization shrinkage (S) was calculated as follows:

$$S = \frac{D_s - D_r}{D_s} \times 100\% \qquad (4)$$

Measurement of the contact angle

The contact angle was measured on disc-shaped specimens (15 ± 0.1 mm $\times$ 1.0 ± 0.1 mm) of every resin formulation (number of specimens (n) = 5). The specimens were photopolymerized on each side for 300 s. Three 2-µL droplets of double-distilled water were placed on predetermined areas (polished with 1200-grit silica carbide paper) of every disc
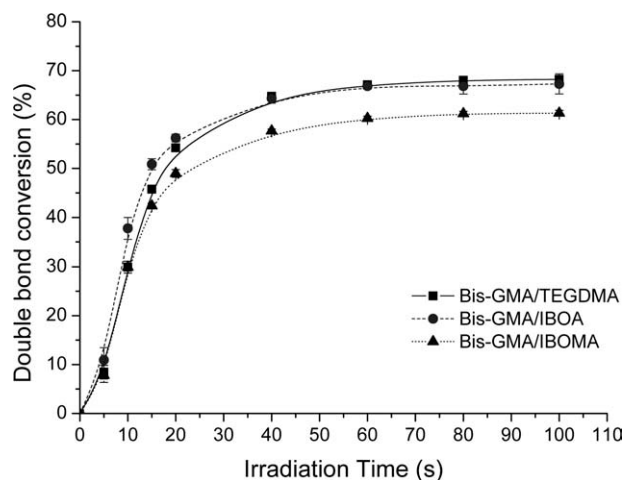
Figure 2 DCs of different systems.

specimen for a total of 15 readings per tested resin material. The contact angle was then measured 20 s after drop placement with a DSA100 optical contact angle measuring instrument (Kruss Co., Hamburg, Germany) at room temperature.

Measurement of the water sorption and solubility

Resins were added to a cylindrical Teflon mold with an internal diameter of 15 mm and a height of 1.0 mm and then light-cured for 5 min with a dental light source. Three specimens of each sample were prepared. The specimens were placed in a desiccator at room temperature under normal pressure and weighed every 24 h until a constant mass (M_1) was obtained (i.e., the variation was less than 0.001 g in any 24-h period). Then, the specimens were immersed in distilled water. At fixed time intervals, they were removed, blotted dry to remove excess water, weighed, and returned to the water. The equilibrium mass (M_2) was obtained when there was no significant change in the mass. The specimens were then dried at 40°C until their mass was constant, and the result was recorded as M_3. The water sorption (WS) and solubility (SL) were then calculated with the following formulas:

$$WS = \frac{M_2 - M_3}{V} \times 100\% \quad (5)$$

$$SL = \frac{M_1 - M_3}{V} \times 100\% \quad (6)$$

where V is the volume of the specimen.

Three-point bending test

We prepared the samples by injecting the resins into Teflon molds, covering the open sides with polyethylene films, and irradiating each side for 300 s. The

sample average dimensions were $20 \times 2 \times 2$ mm^3, and five specimens were prepared for each formulation. A three-point bending test was carried out to evaluate the flexural strength of the cured resin with a GT-TCS-2000 universal testing machine (Dongguan Gao Tie Co., Ltd., Dongguan, China) at a crosshead speed of 1.00 mm/min.

Statistical analysis

The results were analyzed and compared with a one-way analysis of variance and a Tukey test at a significance level of 0.05.

RESULTS AND DISCUSSION

Photopolymerization behavior

Figure 2 shows the curves of DC versus the irradiation time of the Bis-GMA/IBO(M)A formulations and Bis-GMA/TEGDMA formulation. As shown in Figure 2, DC increased significantly with increasing radiation time, and we obtained a maximum at 60 s of radiation time; then, DC did not increase obviously with prolonged radiation time. From Figure 2 and Table I, it could bee seen that Bis-GMA/IBOA and Bis-GMA/TEGDMA had comparable DCs ($p > 0.05$), and Bis-GMA/IBOMA had a relatively lower DC ($p < 0.05$).

Polymerization shrinkage

The volume shrinkage of polymerization originated from interactions between molecules before and after polymerization. The interactions between monomers were weak van der Waals interactions, but these were replaced by strong covalent bonds after polymerization. Thus, the intermolecular distance between molecules after polymerization became smaller than that between the monomers.[14–16] As usual, polymerization shrinkage was measured through the density change of the resin before and after curing. The variation of density and the final polymerization shrinkage of every resin formulation are shown in Table II. The shrinkages of Bis-GMA/IBOA (5.62%) and Bis-GMA/IBOMA (4.05%) were

TABLE I
DCs of Every Resin Formulation

Formulation	DC at 60 s of irradiation time (%)	DC at 100 s of irradiation time (%)
Bis-GMA/TEGDMA	67.1 ± 0.2[a]	68.2 ± 0.2[a]
Bis-GMA/IBOA	66.8 ± 0.4[a]	67.3 ± 2.1[a]
Bis-GMA/IBOMA	60.2 ± 0.5[b]	61.3 ± 0.6[b]

Superscripted lowercase letters indicate statistical differences within a column (Tukey's test, $p = 0.05$).

TABLE II
Polymerization Shrinkage Values of the Different Resin Systems

Formulation	Density before curing (g/cm^3)	Density after curing (g/cm^3)	Shrinkage (%)
Bis-GMA/TEGDMA	1.1184 ± 0.0008	1.2262 ± 0.0002	8.79 ± 0.76
Bis-GMA/IBOA	1.0720 ± 0.0047	1.1358 ± 0.0009	5.62 ± 0.42
Bis-GMA/IBOMA	1.0927 ± 0.0080	1.1389 ± 0.0011	4.05 ± 0.71

much lower than that of Bis-GMA/TEGDMA (8.79%). It has been reported that the polymerization shrinkage is directly influenced by the concentration and conversion of double bonds; a lower double-bond concentration and DC generate less polymerization shrinkage.[17–19] In this study, the double-bond concentrations of the diluents were 4.73×10^{-3} mol/mL (IBOA), 4.43×10^{-3} mol/mL (IBOMA), and 7.64×10^{-3} mol/mL (TEGDMA). Therefore, at the same DC, the shrinkage of Bis-GMA/IBOA was lower than that of Bis-GMA/TEGDMA because of its lower double-bond concentration. Moreover, the DC and double-bond concentration of Bis-GMA/IBOMA were both lower than those of the other two resin system, so it showed the lowest shrinkage.

Contact angle, water sorption, and solubility

The contact angle, water sorption, and water solubility are summarized in Table III. As shown in Table III, the contact angle of the copolymer increased when we replaced TEGDMA with IBOA or IBOMA as the reactive diluent in the Bis-GMA-based resin system ($p < 0.05$), and there was no significant difference in the contact angle between the Bis-GMA/IBOA copolymer and the Bis-GMA/IBOMA copolymer ($p > 0.05$). The water sorption of the Bis-GMA/TEGDMA copolymer was higher than those of the Bis-GMA/IBOA copolymer and Bis-GMA/IBOMA copolymer ($p < 0.05$), and the water sorption values of the Bis-GMA/IBOA copolymer and Bis-GMA/IBOMA copolymer were nearly the same ($p > 0.05$). The copolymers studied in this work had different water solubility values ($p < 0.05$); the sequence of these values was Bis-GMA/TEGDMA < Bis-GMA/IBOA < Bis-GMA/IBOMA.

It was reported that the water sorption of the copolymer is influenced by the hydrophilicity[20] and crosslinking density of the copolymer.[21] A decrease in the hydrophilicity and an increase in the crosslinking density of a copolymer could reduce the water sorption of the copolymer. In this work, the relative hydrophilicities of the copolymers were investigated by a comparison of the contact angles made when droplets of distilled water were placed on the polymerized resin surface.[22–24] From the results of the contact angle, we could see that the hydrophilicity values of the Bis-GMA/IBOA copolymer and Bis-GMA/IBOMA copolymer were much lower than that of the Bis-GMA/TEGDMA copolymer because there was one hydrophobic aliphatic cycle structure in both IBOA and IBOMA, and it could make the water sorption values of Bis-GMA/IBOA and Bis-GMA/IBOMA lower than that of the Bis-GMA/TEGDMA copolymer. However, the crosslinking densities of the Bis-GMA/IBOA copolymer and Bis-GMA/IBOMA copolymer were lower than that of the Bis-GMA/TEGDMA copolymer because there was only one double bond in the IBOA and IBOMA structures, and this induced higher water sorption. The final water sorption values of the Bis-GMA/IBOA copolymer and Bis-GMA/IBOMA copolymer were lower than that of Bis-GMA/TEGDMA; this was mainly attributed to the lower hydrophilicity values of the Bis-GMA/IBOA copolymer and Bis-GMA/IBOMA copolymer. Although hydrophilic properties are important to dental application because hydrophilic resins are able to achieve high immediate bonding strength to dentin, water sorption induced by hydrophilic resins weaken the strength over time.[25] In this work, hydrophobic IBO(M)A decreased the strength of the resin–dentin bond but might be more stable than hydrophilic resins. More work should be done to prove this further.

The water solubility of the copolymers was related to the amount of the unreacted monomers in the

TABLE III
Properties of the Cured Resins

Formulation	Contact angle (°)	Water sorption (%)	Water solubility (%)	Flexural strength (MPa)	Flexural modulus (MPa)
Bis-GMA/TEGDMA	82.1 ± 4.4^a	3.90 ± 0.01^a	0.07 ± 0.05^a	119.1 ± 2.9^a	2538.6 ± 399.2^a
Bis-GMA/IBOA	110.8 ± 10.6^b	1.26 ± 0.01^b	0.29 ± 0.02^b	71.1 ± 1.3^b	1514.9 ± 85.5^b
Bis-GMA/IBOMA	112.5 ± 5.5^b	1.31 ± 0.04^b	0.69 ± 0.11^c	63.6 ± 3.5^c	1257.7 ± 60.0^c

Superscripted lowercase letters indicate statistical differences within a column (Tukey's test, $p = 0.05$).

crosslinking network[26] and the characteristics of the network and monomer. Because it had the lowest DC, there were more unreacted monomers left in the Bis-GMA/IBOMA copolymer, and this induced its highest water solubility. A difunctional methacrylate molecule binds to the polymer network if at least one of the two methacrylate groups reacts. However, for a monofunctional methacrylate molecule to be combined, only one methacrylate group should react. That is, when DC is the same, the unbound monomer content of a dimethacrylate resin must be lower than that of the monomethacrylate resin. Therefore, there were more unreacted monomers left in the Bis-GMA/IBOA copolymer, even though it had a similar DC as the Bis-GMA/TEGDMA copolymer, and this made the water solubility of the former higher than that of the latter. The higher water solubility values of the Bis-GMA/IBOA copolymer and Bis-GMA/IBOMA copolymer might be a disadvantage compared to that of the Bis-GMA/TEGDMA copolymer because the release of unreacted monomers from the copolymer may stimulate the growth of bacteria[27] and promote allergic reactions.[28]

Flexural strength and modulus

The flexural strength and modulus values of the Bis-GMA/IBO(M)A copolymers and Bis-GMA/TEGDMA copolymer are shown in Table III. As shown in Table III, the sequence of the flexural strength and modulus values was Bis-GMA/TEGDMA > Bis-GMA/IBOA > Bis-GMA/IBOMA ($p < 0.05$). The flexural strength and modulus values were found to be dependent on the crosslinking density of the copolymer and the nature of the monomers.[29] In this work, the aliphatic cycle structure of IBOA and IBOMA reinforced the polymer chain, but the flexural strength and modulus of Bis-GMA/IBO(M)A was still lower than that of Bis-GMA/TEGDMA; this might have been mainly due to their lower crosslinking densities, which were induced by the monofunctional structure of IBOA and IBOMA.

CONCLUSIONS

Monomethacrylates IBOA and IBOMA were used to replace TEGDMA as reactive diluents in dental restorative materials. Compared with the Bis-GMA/TEGDMA system, the IBO(M)A/TEGDMA systems had some advantages, such as lower polymerization shrinkage and lower water sorption values. However, the drawbacks of the IBO(M)A/TEGDMA copolymers, including lower DCs, higher water solubilities, and lower mechanical properties, might limit their application in dental restorative materials.

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