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Characteristics of Novel Dental Composites Containing 2,2-Bis[4-(2-methoxy-3-methacryloyloxy propoxy) phenyl] propane as a Base Resin

J. W. Kim,† L. U. Kim,† C. K. Kim,*,† B. H. Cho,‡ and O. Y. Kim§

School of Chemical Engineering and Materials Science, Chung-Ang University, 221 Huksuk-dong, Dongjak-gu, Seoul, 156-756, Korea, Department of Conservative Dentistry and Dental Research Institute, College of Dentistry, Seoul National University. 28-2 Yongon-dong, Jongno-gu, Seoul, Korea, and Department of Polymer Science and Engineering, Dankook University, Korea

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Many dental restorative dental composites still utilize 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (Bis-GMA) as base resin. The high viscosity of Bis-GMA necessitates dilution with dimethacrylate ethers of low viscosity such as triethylene glycol dimethacrylate (TEGDMA). However, increased amounts of the TEGDMA have adverse effects on properties such as water uptake and curing shrinkage. The viscosity of the base resin should be as low as possible to enable the preparation of dental composites with a minimum content of diluent. To overcome the disadvantage of Bis-GMA, i.e., its high viscosity caused by hydrogen bonding between hydroxyl groups, 2,2-bis[4-(2-methoxy-3-methacryloyloxy propoxy) phenyl propane (Bis-M-GMA) was prepared by substituting methoxy groups for hydroxyl groups in Bis-GMA. The viscosity of Bis-GMA was dramatically decreased from 574 (Pa.s) to 3.7 (Pa.s) by substitution of methoxy group. Consequently, the amount of TEGDMA included in the resin matrix could be minimized. Dental composites were prepared from Bis-M-GMA (or Bis-GMA) mixtures with TEGDMA filled with 75 wt % filler. Comparing the curing shrinkage of dental composite containing Bis-M-GMA with that prepared from Bis-GMA, the reduction in curing shrinkage was about 47%. Dental composites prepared from new resin matrixes also exhibited low water uptake and better properties in mechanical strength.

Introduction

Resin composites are widely used in esthetic restorative treatments. Since their commercial introduction for restoring anterior teeth in the mid-1960s, their characteristics such as the physical properties, manipulative qualities, durability, and wear resistance have improved remarkably.[1−2] The scope of applications has expanded continuously from small anterior restorations to large posterior restorations and even fixed partial dentures.[3−4] Dental composites are composed of a soft organic matrix and hard inorganic fillers. Restorative dentistry is fraught with problems brought about by the inherent volumetric shrinkage that accompanies polymerization of composite resin matrices. These complications include post-operative sensitivity, marginal discoloration, secondary caries, and pulpal pathoses.[5−6]

The organic matrix generally contains 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (Bis-GMA), as a base resin, and triethylene glycol dimethacrylate (TEGDMA), as a diluent. 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA) is also often used as a base resin. A disadvantage of Bis-GMA is its high viscosity caused by hydrogen bonding between hydroxyl groups in the alkyl chain, necessitating a diluent monomer. A diluent monomer such as TEGDMA reduces the viscosity of the composite resin even though this inclusion increases the amount of water sorption.[7−11]

Another important issue of the monomer phase is that it undergoes polymerization shrinkage. The volumetric shrinkage of composite resins during polymerization arises from two different factors: the van der Waals distance between the monomer molecules is replaced by a covalent bond during polymerization, and the intermolecular distance between the polymer chains becomes smaller than that between the monomers.[12] The shrinkage stresses generated from polymerization of the composite resin are assumed to cause defects or debonding at the tooth−restorative interface.[13−18] Therefore, eliminating or reducing the amount of volumetric contraction during polymerization is one of the most important issues in the development of new monomers for dental composites. Polymerization shrinkage can be reduced by utilizing monomers of large molar volume such as Bis-GMA and by the inclusion of inorganic fillers. The diluent monomer will increase shrinkage because its molar volume is lower than that of Bis-GMA. Therefore the viscosity of the base resin should be as low as possible to fabricate composite resin with a minimum content of diluent and a maximum content of inorganic fillers.

Numerous studies aimed at developing resin composites with a low level of curing shrinkage have been performed.[9−11,19−31] Research has been directed toward producing low viscosity Bis-GMA alternatives requiring a lower concentration of diluent monomer.[9−11,19−22] These attempts have been somewhat successful in reducing the amount of curing shrinkage, but there are still problems with the mechanical properties and water uptake. Another approach toward minimizing the extent of polymerization shrinkage incorporates a free radical polymerizable spiro orthocarbonate monomer into the composite resin formulations with a conventional dimethacrylate monomer.[23−31] Composite polymers formed by the ring opening reaction of a

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* To whom correspondence should be addressed. E-mail: ckkim@cau.ac.kr.

† School of Chemical Engineering and Materials Science.

‡ Department of Conservative Dentistry and Dental Research Institute.

§ Department of Polymer Science and Engineering.

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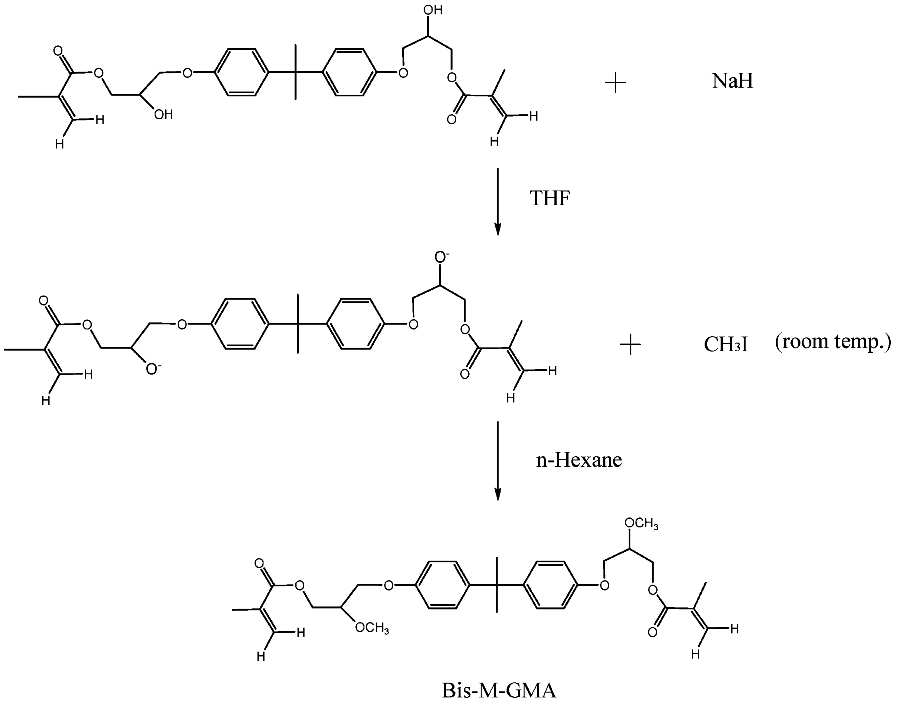
Scheme 1. Synthesis of Bis-M-GMA



spirocyclic monomer are considered to be most promising. However, their application in the composite resins was limited due to their poor mechanical properties and various side reactions of the spirocyclic monomers except for the ring opening reaction.[27−31]

In this study, 2,2-bis[4-(2-methoxy-3-methacryloyloxy propoxy) phenyl] propane (Bis-M-GMA) was prepared as a new base resin by substituting the methoxy groups for hydroxyl groups in the Bis-GMA. Since Bis-M-GMA possesses decreased viscosity and increased molar volume compared to Bis-GMA, a new dental composite with a low curing shrinkage and excellent mechanical properties in an aqueous environment may be expected with Bis-M-GMA. To confirm this hypothesis, viscosities and curing characteristics of resin matrices containing Bis-M-GMA were studied and then mechanical strength of dental composites was explored.

Materials and Procedures

Bis-GMA (99%, Polysciences Inc., USA) was used as a base resin, triethylene glycol dimethacrylate (TEGDMA, 3G grade, Aldrich Chemical Co., U.S.A.) as a diluent, camphorquinone (CQ, 99%, Aldrich Chemical Co., U.S.A.) as an initiator, and ethyl 4-dimethylaminobenzoate (EDMAB, 99+%, Aldrich Chemical Co., U.S.A.) as an accelerator. A mixture of radio-opaque barium silicate (H-MAF, Hansol Chemience, Korea, 1 μm primary particle size) and amorphous fumed silica (VC-20, Vericom Co., Korea, 0.05 μm primary particle size) were used as an inorganic filler for the composite resin. γ-Methacryloxypropyltrimethoxysilane (γ-MPS, 98%, Aldrich Chemical Co., USA) was used, without further purification, as the silane coupling agent for hydrophobic treatment of the filler.[32−33]

The new Bis-GMA derivative, i.e., Bis-M-GMA, was prepared in this laboratory by substituting methoxy group for hydroxyl group in Bis-GMA. Scheme 1 shows the preparation route for Bis-M-GMA. All reactions were carried out under an inert atmosphere of nitrogen. Methyl iodine (CH_3I, 3 mol) was added dropwise over 30 min to the solution of Bis-GMA (1 mol) and NaH (2.4 mol) in tetrahydrofuran (THF, 300 mL). After stirring for 5 h at 30 °C, the resulting mixture was mixed with dichloromethane (300 mL) and then transferred through a sintered glass funnel containing a small pad of silica gel. The resulting organic solution was washed with water (5 × 500 mL), dried over $MgSO_4$, and concentrated by vacuum filtration. The molecular structure of Bis-M-GMA was confirmed by FT-IR (Nicolet Magna 750, U.S.A.), ^{1}H NMR (Varian Gemini 2000, 300 MHz, U.S.A.), and GC/MS (Micromass Autospec, U.K.) analyses. Bis-M-GMA was placed in a KBr vessel for FT-IR analysis. ^{1}H NMR was registered with chloroform-*d* ($CDCl_3$, 100.0 atom % D, Aldrich Chemical Co., U.S.A.) as the solvent and tetramethylsilane (TMS, 99.9+%, NMR grade, Aldrich Chemical Co., U.S.A.) as the internal standard. Electron impact (EI, 70 eV) was used as the ionization method for mass spectrometry.

Monomer mixtures were prepared with Bis-GMA (or Bis-M-GMA) as the base resin, TEGDMA as the diluent, 0.75 wt % CQ as the initiator, and 1 wt % EDMAB as the accelerator. Note that, to examine the exact volumetric shrinkage caused by the polymerization of the monomers, the samples were prepared without the fillers normally included in composite resins. The monomer mixtures were placed in a DSC (differential scanning calorimeter, TA Instruments, TA-2100, U.S.A.) sample pan (6 mm diameter × 2 mm thickness) and polymerized by irradiating with visible light from a light source (λ_{max} 460 nm, intensity 600 mW/cm^2, VIP Junior Curing Light, BISCO Inc., U.S.A.) under a nitrogen-purged condition. The time required for the curing reaction was measured by DSC, with the time between onset and completion of the heat capacity changes defined as the curing time for the polymerization reaction.[22] The degree of conversion values were also studied with DSC adapted for photopolymerization measurements at a temperature of 36 °C under constant nitrogen flow as described elsewhere.[34] The densities of the monomer mixtures were measured with a liquid dilatometer [Anton Paar Co., DMA-500] and those of the resulting polymers with a solid dilatometer [Mettler Toledo Co., AX205]. The amount of curing shrinkage ($\Delta\upsilon_{sp}$) was calculated as follows:

$$\Delta\upsilon_{sp} = \frac{100(\upsilon_{sp,m} - \upsilon_{sp,p})}{\upsilon_{sp,m}} \qquad (1)$$

where $\upsilon_{sp,m}$ and $\upsilon_{sp,p}$ are the specific volumes of the monomer and polymer, respectively. Water uptake was determined according to the method described in ADA Specification No. 27 resin-based filling materials. Specimen disks 12 mm in diameter and 1 mm in thickness were fabricated in an aluminum mold between two glass plates by irradiating with visible light. Five specimen disks were prepared for each resin. The rheological measurements were carried out in a rheometer (model: Physica MCR 500, Anton Parr, Germany; geometry: 25 mm parallel plate). The measurements were made at 25 °C in the shear rate range of 0.1×10^2 to 4×10^3 s^{-1}. The data on shear stress (τ_w) and shear rates ($\dot{\gamma}$) were obtained. The viscosities of monomers and their mixtures (η) were evaluated from eq 2

$$\eta = \frac{\tau_w}{\dot{\gamma}} \tag{2}$$

The polymeric dental restorative composites were fabricated using surface-treated fillers and a resin matrix. The composites contained 75 wt % filler (70 wt % of barium silicate and 5 wt % of fumed silica) and were mixed vigorously in a kneader, followed by degassing at 30 °C for 1 day under a 1 mmHg vacuum. The diametral tensile strength (DTS) and flexural strength of the dental composites were then investigated. The DTS values were measured by compression with a universal testing machine (UTM, Instron Co., model 4469, load cell 1000 kg) with a crosshead speed of 1 mm/min, in accordance with ADA Specification No. 27. The cylinder-type specimens (8 mm diameter × 4 mm height), which had been cured with visible light in a Teflon mold, were broken by diametral tension. Reported DTS values are average one from the measurement of five replicated specimen calculated by using eq 3

$$\mathrm{DTS} = \frac{2P}{\pi DT} \tag{3}$$

where P, D, and T were load at fracture, diameter of specimen, and thickness of specimen, respectively.

The flexural strength (FS) was measured in accordance with International Standard Organization (ISO) Specification No. 4049, with testing being carried out by three-point loading. The maximum load was measured by pressing the center of the cured rectangular bar (25 mm length × 2 mm width × 2 mm height) while it was mounted between supports (20 mm length) of UTM. Each experiment was performed at least five times, and data are reported as the means of these values. The flexural strength of specimen is given by

$$\mathrm{FS} = \frac{3Fl}{(2bh^2)} \tag{4}$$

where F, l, b, and h are maximum load, distance between supports, specimen width, and specimen height, respectively. The data for the curing time, curing shrinkage, and degree of conversion of the monomer mixtures, and those for the DTS and the FS of experimental dental composites were analyzed by One-Way ANOVA and Two-Way ANOVA, respectively. Tukey's test was performed post hoc at a 5% level of significance. All statistical analyses were done using SigmaStat (version 2.03; Jandel Scientific Software, Chicago, IL).

Result and Discussion

Characterization of Bis-M-GMA. The molecular structure of Bis-M-GMA was confirmed by FT-IR, GC-mass, and ^{1}H NMR. Figure 1 exhibits FT-IR spectra of Bis-GMA and Bis-M-GMA. At 3458 cm^{-1}, the broad adsorption band corresponds to $-OH$ of the Bis-GMA. Disappearance of this signal in Bis-M-GMA indicates the completion of the methoxylation with replacement of the $-H$ in the $-OH$ group by $-CH_3$. Spectral analysis also reveals the presence of carbonyl and vinyl groups, as shown by adsorption bands at stretching frequencies of 1750 and 1640 cm^{-1}, respectively. Figure 2 shows the ^{1}H NMR spectrum of the Bis-M-GMA prepared by reacting Bis-GMA with methyl iodine. The spectrum of the Bis-M-GMA is exactly the same with that of Bis-GMA[22] except the peak at 3.40 ppm representing the protons from the methoxy groups. The peak corresponding to the proton in the hydroxyl groups (2.0 ppm) in Bis-GMA is not observed in the Bis-M-GMA spectrum. However, it may not be clear evidence that hydroxyl groups in Bis-GMA are replaced with methoxy groups because the peak corresponding to the hydroxyl groups is very small and overlapped with the peak representing the protons from the methyl group from methacrylate. Figure 3 exhibits the GS/MS chart of the Bis-M-GMA. The molecular weight of Bis-M-GMA (=540 g/mol) was confirmed using the GC-mass chart. The level of impurities in the final products examined using HPLC were negligible.

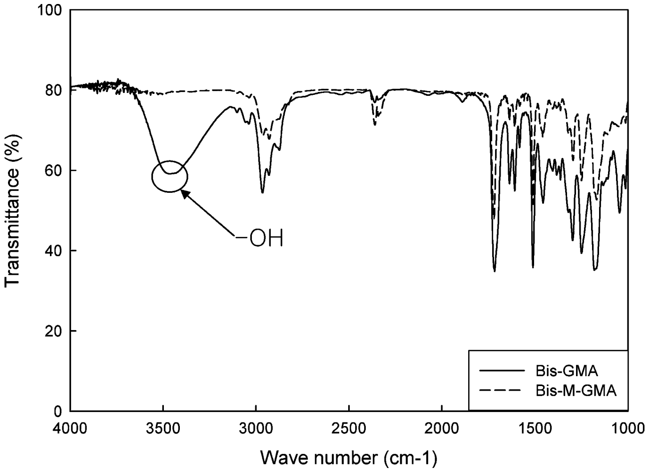


Figure 1. FT-IR spectra of Bis-GMA and Bis-M-GMA.

Viscosities of Bis-GMA, Bis-M-GMA, TEGDMA, and their Mixtures. Many dental restorative composites still utilize Bis-GMA as the main component of the polymerizable monomer. The high viscosity of Bis-GMA necessitates dilution with dimethacrylate ethers of low viscosity such as TEGDMA to achieve high filler loading for a successful composite. However, increased amounts of the TEGDMA have adverse effects on properties such as water uptake and curing shrinkage.[7−11,35−36] Figure 4 exhibits the measured viscosities of Bis-GMA, TEGDMA, and their mixtures as a function of shear rate. Viscosity of Bis-GMA (=574 Pa s) is about 60 000 times higher than that of TEGDMA (=0.0086 Pa s), even though molecular weight of the former (=512 g/mol) is only about 1.8 times higher than that of the latter (=286 g/mol). It means that Bis-GMA behaves as a supramolecule because of intermolecular association that stems from hydrogen bonding between Bis-GMA molecules. A typical feature of many associating systems is the strong shear rate dependence of the viscosity.[37] In many cases, Newtonian behavior is observed at low shear rates, whereas at higher shear rates, a progressive shear thinning occurs. Shear thinning begins at the shear rates at which shear forces disrupt the hydrogen-bonded network by reducing the number of interchain bonds, lowering the resistance to the flow as well as the viscosity. The intermolecular junctions are disrupted at a rate faster than their rate of reformation, resulting in a decrease in the junction density and hence a drop of viscosity. Bis-GMA exhibits a typical feature of an associating system as shown in Figure 4. Newtonian behavior is observed at low shear rates, whereas at higher shear rates, a progressive shear thinning occurs. The Bis-GMA mixture containing 5 wt % TEGDMA also exhibits the same behavior. In TEGDMA and Bis-GMA mixtures containing more than or equal to 10 wt % TEGDMA, on the other hand, a typical Newtonian behavior, i.e, constant viscosity regardless of shear rate, is observed.

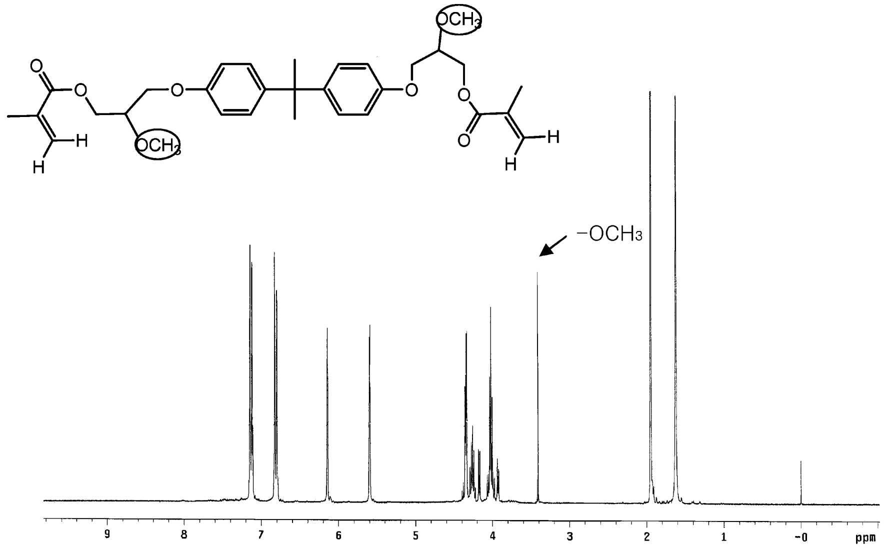


Figure 2. ^{1}H NMR spectrum of the Bis-M-GMA.

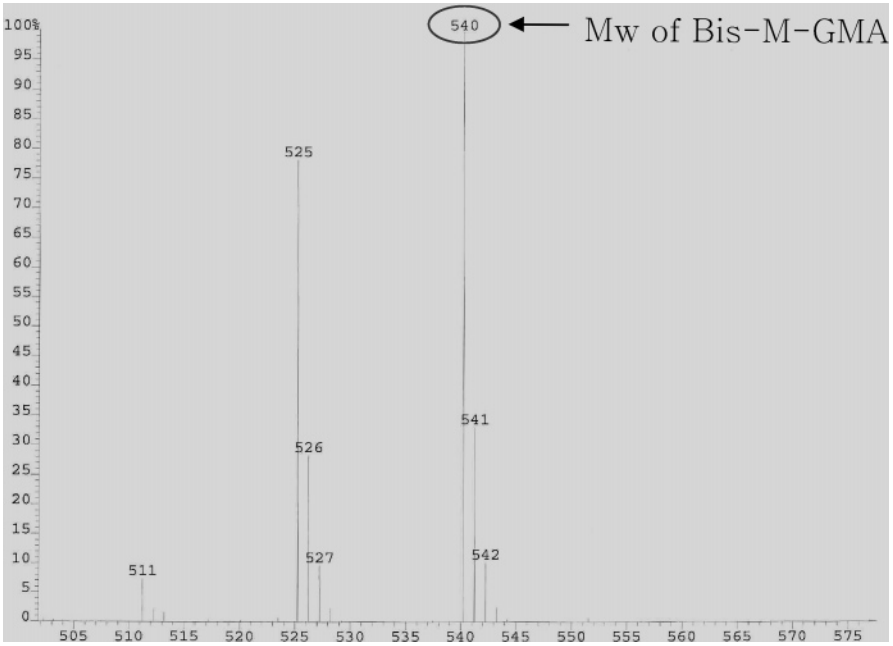


Figure 3. GC/MS chart of the Bis-M-GMA.

The relative degree of shear thinning for the Bis-GMA and its mixture may be characterized with a simple power law, which is given by

$$\eta = \dot{\gamma}^{n-1} \tag{5}$$

where n is the power law index. The values of n, determined from the shear thinning parts of the curves, for the Bis-GMA and Bis-GMA/TEGDMA = 95/5 were −0.56 and −0.27, respectively. The abnormal values of the n obtained here indicate the decrease of shear stress with increasing shear rate. Note that the n value is generally ranging from 0 to 1. Figure 5 exhibits shear stresses as a function of shear rates for Bis-GMA and its mixtures with TEGDMA. Bis-GMA/TEGDMA = 90/10 and Bis-GMA/TEGDMA = 80/20 mixtures exhibit a continuous increase of shear stress with increasing shear rates, whereas Bis-GMA and the Bis-GMA/TEGDMA = 95/5 mixture exhibit the decrease of shear stress with increasing shear rates where shear thinning occurs. The continuous decline in the shear stress at higher shear rate may stem from continuous disruption of intermolecular association. The power law indices obtained here indicate that increasing diluent concentration demotes the shear thinning effect of the mixture systems.

The hydrogen bonding between Bis-GMA may be interfered by increasing TEGDMA content of the mixtures. Because of this, the shear thinning effect is not observed when mixtures contain more than 10 wt % of TEGDMA (see Figure 4). Figure 6 shows changes in viscosity with mixture composition. Note that the plateau values, i.e, viscosities at the Newtonian region, were used in this plot. The rapid decline in the viscosities of Bis-GMA mixtures, i.e., huge negative deviation from the additive rule, is observed by adding TEGDMA. TEGDMA having very low viscosity also can act as lubricant in the mixture.[38] Not only disruption of intermolecular association but also lubrication caused by the presence of TEGDMA results in a sharp decline in the mixture viscosity.

The viscosity of Bis-M-GMA obtained by substituting methoxy groups for hydroxyl groups in Bis-GMA is explored. Figure 7 shows the measured viscosities of Bis-M-GMA and its mixtures with TEGDMA as a function of shear rate. The

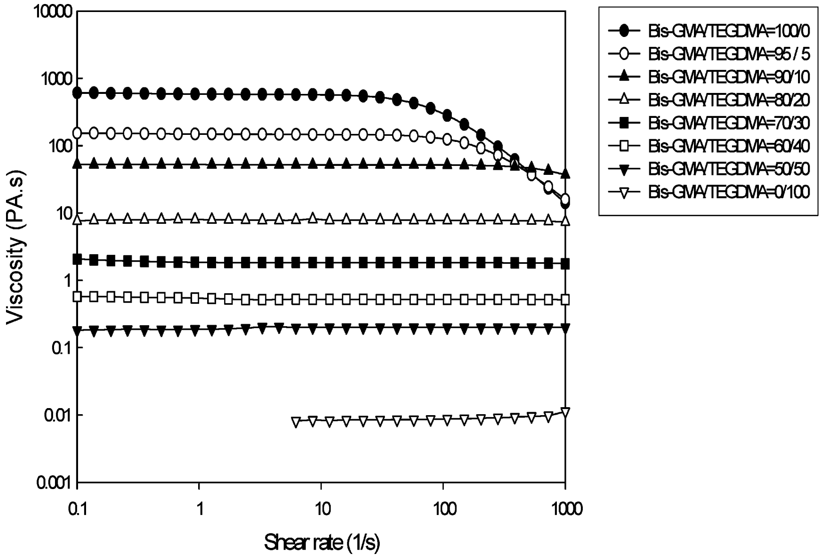


Figure 4. Measured viscosities of Bis-GMA, TEGDMA, and their mixtures as a function of shear rate.

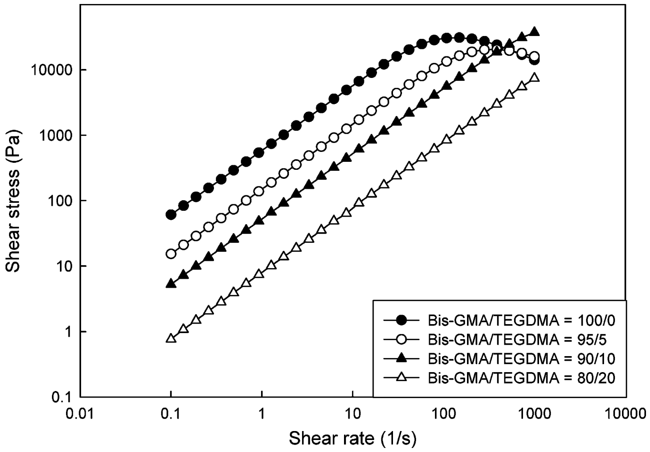


Figure 5. Shear stresses of for Bis-GMA and its mixtures with TEGDMA as a function of shear rates.

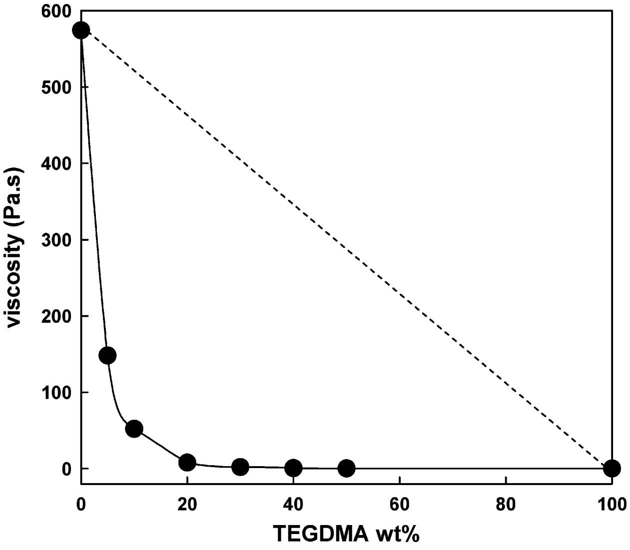


Figure 6. Changes in viscosity of the Bis-GMA/TEGDMA mixtures as a fuction of TEGDMA content.

high viscosity of Bis-GMA is abruptly decreased from 574 to 3.7 (Pa s) by substituting methoxy groups for hydroxyl groups in Bis-GMA. Furthermore, Bis-M-GMA exhibits Newtonian behavior regardless of the shear rates. These results can be attributed to the disappearance of network junctions, i.e, hydrogen bondings between molecules, caused by methoxy substitution. The amounts of diluent, which should be added to the base resin to reduce viscosity of the resin matrix, can be minimized by using Bis-M-GMA instead of Bis-GMA. Viscosities of Bis-M-GMA mixtures with TEGDMA are compared with that of the Bis-GMA/TEGDMA = 70/30 mixture. Note that the content of the Bis-GMA was kept to 70 wt % because commercial products of the resin composites are approximately composed of Bis-GMA/TEGDMA = 70/30 mixture. As shown in Figure 7, viscosities of Bis-M-GMA mixture containing 5 wt % of TEGDMA are nearly the same with those of Bis-GMA/TEGDMA = 70/30 mixture. It means that adverse effects caused by TEGDMA on the properties of dental composite such as water uptake and curing shrinkage can be minimized by substituting Bis-M-GMA for Bis-GMA. Properties of the dental composites prepared from Bis-M-GMA mixtures with TEGDMA will be discussed in the next section.

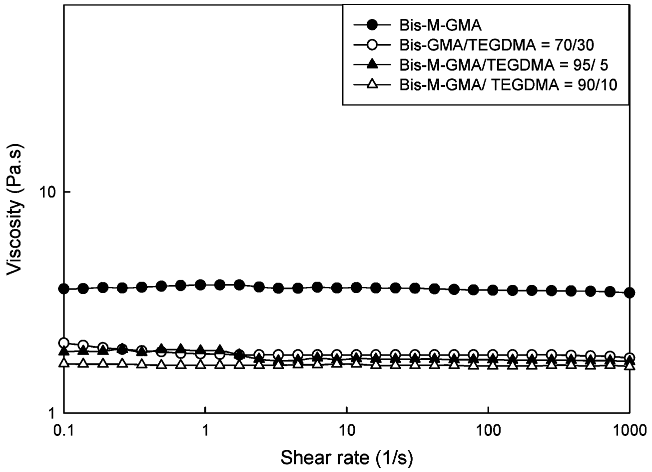


Figure 7. Measured viscosities of Bis-M-GMA, its mixtures with TEGDMA, and the Bis-GMA/TEGDMA = 70/30 mixture as a function of shear rate.

Curing Characteristics of Monomer Mixtures. The curing characteristics of the monomers and their mixtures are listed in Table 1. The curing time of the Bis-M-GMA required for polymerization was significantly shorter than that of the Bis-GMA ($p < 0.05$). This might stem from the reduction in the viscosity of the Bis-M-GMA. The amount of curing shrinkage

Table 1. Curing Characteristics, Viscosity, and Water Uptake of Various Resins and Their Mixtures^{a}

monomer	density (g/cm^3) monomer	density (g/cm^3) polymer	curing time (s, $n = 5$)^{b}	curing shrinkage (%, $n = 5$)^{b}	degree of conversion (%, $n = 5$)^{b}	viscosity (Pa s)	equilibrium water uptake (wt %, $n = 5$)^{b}
Bis-GMA	1.1563	1.2190	46.00 ± 0.75^{a}	5.16 ± 0.31^{c}	65.5 ± 0.8^{e}	574	3.11 ± 0.12^{c}
Bis-M-GMA	1.1185	1.1727	36.23 ± 0.96^{b}	4.58 ± 0.18^{d}	70.3 ± 0.7^{d}	3.65	0.87 ± 0.08^{e}
TEGDMA	1.0739	1.2239	56.50 ± 0.79^{b}	12.32 ± 1.31^{a}	82.3 ± 0.4^{a}	0.0086	6.02 ± 0.20^{a}
Bis-GMA/TEGDMA= 70/30	1.1474	1.2270	31.13 ± 1.13^{d}	7.04 ± 0.80^{b}	74.1 ± 0.5^{c}	1.86	4.1 ± 0.15^{b}
Bis-M-GMA/TEGDMA= 95/5	1.0739	1.2239	33.32 ± 1.46^{c}	4.26 ± 0.11^{d}	75.5 ± 0.3^{b}	1.79	1.1 ± 0.12^{d}

[a] The same superscripts mean that there was no significant difference between the experimental groups (Tukey test; $p < 0.05$). [b] The data are presented as mean ± standard deviation, and n is the number of specimens.

Table 2. Properties of the Dental Composites^{a}

monomer mixture	time of measurements^{b}	equilibrium water uptake (%)	curing shrinkage (%)	DTS^{c} (MPa)	FS^{c} (MPa)
Bis-GMA/TEGDMA = 70/30	before		1.94 ± 0.23	45.2 ± 1.4	149.8 ± 3.5
	after	1.2		32.1 ± 1.4	110.4 ± 3.3
Bis-M-GMA/TEGDMA = 95/5	before		1.01 ± 0.17	49.2 ± 1.1	161.0 ± 4.1
	after	0.32		42.9 ± 1.7	147.8 ± 3.6

[a] Five specimens were tested for each property. [b] Mechanical properties were examined before and after water uptake. [c] The results of Two-Way ANOVA suggested that the interaction effect of "monomer mixture × water uptake" is expected in both the measurements of DTS and FS ($p < 0.001$).

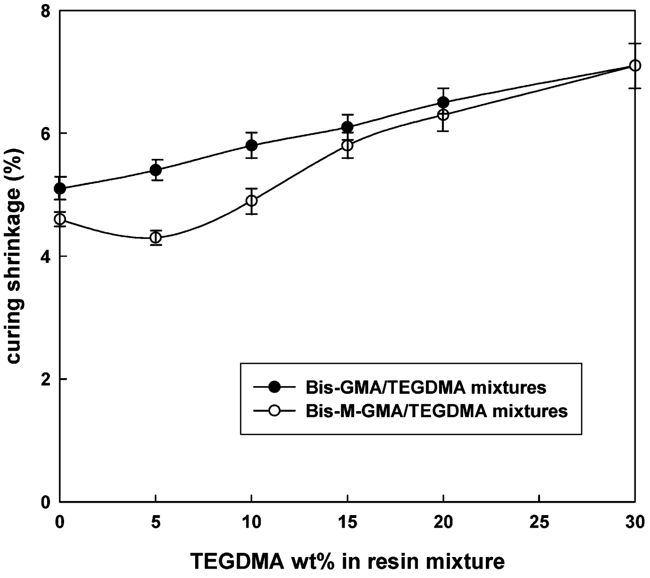


Figure 8. Curing shrinkage of Bis-GMA mixtures (or Bis-M-GMA mixtures) with TEGDMA.

was decreased as a result of substituting methoxy groups for hydroxyl groups of the Bis-GMA ($p < 0.05$). Close molecular packing caused by the strong specific interactions that originate from polar groups such as hydroxyl groups and carbonyl groups increases the density of molecule. Because of this, the density of Bis-M-GMA is lower than that of Bis-GMA as listed in Table 1. The differences in the molecular packing may affect the amount of volumetric shrinkage caused by polymerization. Loose chain packing of Bis-M-GMA is favorable to decrease the amount of curing shrinkage. The equilibrium water sorption of the resulting polymers is also listed in Table 1. As expected, the absence of the hydroxyl groups in the Bis-M-GMA results in significantly lower water uptake ($p < 0.05$).

To examine the properties of monomer mixtures containing TEGDMA as diluent, in this study, a monomer mixture of TEGDMA (30 wt %) and Bis-GMA (70 wt %) was used as the control of the base resin. The curing time of the mixtures required for polymerization is significantly shorter than that of the Bis-GMA or that of TEGDMA ($p < 0.05$, Table 1). Figure 8 exhibits curing shrinkage of Bis-GMA mixtures (or Bis-M-GMA mixtures) containing up to 30 wt % of TEGDMA. The curing shrinkage of the Bis-M-GMA mixture is smaller than that of the Bis-GMA mixture when mixtures contains less than 10 wt % of TEGDMA, whereas both mixtures containing more than 10 wt % of TEGDMA exhibit similar curing shrinkage. Since the viscosity of Bis-M-GMA/TEGDMA = 95/5 mixture is nearly the same with that of the base resin used as the control (Bis-GMA/TEGDMA = 70/30 mixture), the curing shrinkages of both mixtures are compared here. The curing shrinkage of the former is 4.3%, whereas that of the latter is 7.0%; that is, the reduction in curing shrinkage is 40%. Note that although the difference was not significant ($p > 0.05$), the curing shrinkage of the Bis-M-GMA/TEGDMA = 95/5 mixture is slightly smaller than that of Bis-M-GMA. Addition of a small amount of TEGDMA, which has a different molecular structure than Bis-M-GMA, may hinder close chain packing of formed polymer. Because of this, the adverse effect of TEGDMA on curing shrinkage could be minimized by adding a minimum amount of TEGDMA into the monomer mixture containing Bis-M-GMA as a base resin. The equilibrium water uptake of the polymers containing Bis-M-GMA is also significantly lower than that of the polymers containing Bis-GMA ($p < 0.05$) because of the expected hydrophobic effects due to the presence of methoxy groups in Bis-M-GMA. It means that polymerization with the mixtures containing Bis-M-GMA and TEGDMA can be a promising strategy for obtaining a dental composite resin with a low amount of curing shrinkage and water uptake as described next section.

Characteristics of Composite Resins. The curing characteristics and mechanical properties of the resin composite containing 75 wt % filler (70 wt % of barium silicate and 5 wt % of fumed silica) are examined, and the results are listed in Table 2. As expected, the amount of curing shrinkage of the resin composite prepared from the Bis-M-GMA/TEGDMA = 95/5 mixture is significantly lower than that prepared from the Bis-GMA/TEGDMA = 70/30 mixture ($p < 0.05$). The reduction in the amount of volumetric shrinkage is about 47% (from 1.9% to 1.0%). The diametral tensile strength and flexural strength of the resin composite prepared from the Bis-M-GMA/TEGDMA = 95/5 mixture are significantly higher than those of the resin composite prepared from the Bis-GMA/TEGDMA = 70/30 mixture ($p < 0.05$). Furthermore, comparing the mechanical strength in an aqueous condition of dental composite containing Bis-M-GMA with that prepared from Bis-GMA, the decline of mechanical strength of the former is significantly smaller than that of the latter ($p < 0.001$, Two-Way ANOVA, Table 2). The results explored here indicate that a dental composite resin with a low amount of volumetric shrinkage as well as excellent mechanical properties in an aqueous environment can be obtained by using the mixture of Bis-M-GMA and TEGDMA as a base resin.

Summary

New resin matrices were examined to develop dental composites having low volumetric shrinkage and excellent mechanical properties in an aqueous environment. To minimize diluent (TEGDMA) content in the resin matrix by reducing the viscosity of the base resin, Bis-M-GMA synthesized by substituting methoxy groups for hydroxyl groups in Bis-GMA was explored as a base resin. The molecular structure of the Bis-M-GMA prepared here was confirmed with FT-IR, ^{1}H NMR, and GC-mass. The viscosity of Bis-GMA was dramatically decreased from 574 to 3.7 (Pa s) by substituting methoxy groups for hydroxyl groups. Consequently, content of TEGDMA in the resin matrix (Bis-GMA/TEGDMA = 70/30) can be reduced from 30 wt % to 5 wt % by replacing base resin from Bis-GMA to Bis-M-GMA. Properties of the dental composites prepared from Bis-M-GMA/TEGDMA mixtures filled with 75 wt % filler were examined. Comparing the curing shrinkage of dental composite containing Bis-M-GMA with that prepared from Bis-GMA, the reduction in volumetric shrinkage was about 47%. Furthermore, the former exhibited better mechanical strength and lower water uptake than the latter.

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