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Dental Restorative Composites Fabricated from a Novel Organic Matrix without an Additional Diluent

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Commercial organic matrixes of dental composites generally include diluents such as triethylene glycol dimethacrylate (TEGDMA) to reduce viscosity. However, the diluent exhibits adverse effects such as curing shrinkage and diminished mechanical properties of the dental composites. To overcome these adverse effects, organic monomers that can be used as an organic matrix may be developed. In this study, various novel organic monomers were developed by substituting alkoxy for hydroxyl groups in 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy)phenyl]propane (bis-GMA). Viscosities of the alkoxy-substituted monomers were decreased by increasing substituent size. The viscosity of 2,2-bis[4-(2-ethoxy-3-methacryloyloxy propoxy)phenyl]propane (bis-E-GMA) was higher than the control organic matrix (70 wt % bis-GMA and 30 wt % TEGDMA). However, those of 2,2-bis[4-(2-propoxy-3-methacryloyloxy propoxy)phenyl]propane (bis-Pr-GMA), 2,2-bis[4-(2-butoxy-3-methacryloyloxy propoxy)phenyl]propane (bis-B-GMA), and 2,2-bis[4-(2-pentoxy-3-methacryloyloxy propoxy)phenyl]propane (bis-P-GMA) were lower than the control organic matrix. To this end, these monomers could be used as organic matrixes of dental composites without an additional diluent. Among these monomers, bis-B-GMA exhibited the lowest curing shrinkage. In comparison to the control organic matrix, the curing shrinkage of the bis-B-GMA dental composite was approximately 40%. Additionally, dental composites prepared from bis-B-GMA exhibited excellent mechanical properties.

Introduction

Polymeric dental composites are widely used in esthetic restorative treatments. The scope of applications has continuously expanded from small anterior restorations to large posterior restorations, including fixed partial dentures.[1−6] Dental composites are composed of soft, organic matrix and hard, inorganic fillers. Restorative dentistry is fraught with problems from curing shrinkage that accompanies polymerization of composites. Commercial organic matrixes generally contain 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. A disadvantage of bis-GMA is a high viscosity caused by hydrogen bonding between hydroxyl groups in the alkyl chain, necessitating a diluent monomer. The shrinkage stress generated from polymerization of the composite matrix is assumed to cause defects or debonding at the tooth−restorative interface.[7−12] Therefore, eliminating or reducing the curing contraction is one of the most important issues in the development of new monomers for dental composites. Although the inclusion of TEGDMA reduces the viscosity of the composite resin, the diluent increases curing shrinkage and water sorption.[13−15]

To overcome adverse diluent effects on the properties of the resin composites, an organic monomer that can be used as an organic matrix may be developed. To date, no such organic materials have been developed. Numerous studies aimed at developing bis-GMA alternatives with lower viscosities have been performed.[16−26] Bis-GMA alternatives, such as dimethacrylate monomers of propoxylated-diphenol, silylated bis-GMA derivatives, and ethoxy and methyl siloxy analogues of bis-GMA, have been examined. These attempts have been partially successful in reducing viscosity; however, a low concentration of diluent monomer is still required.

Several key strategies can be employed to develop a novel organic monomer for use an organic matrix. To fabricate a composite with a maximal content of inorganic fillers, the viscosity of an organic monomer should be reduced to produce resin matrix without an additional diluent. Removal of the hydroxyl groups in bis-GMA (removal of hydrogen bonding between molecules) may be an effective strategy for viscosity reduction.[20,27] Steric hindrance from chain packing of the polymer during the curing reaction should be increased. For example, a bulky group substitution for hydrogen on the phenyl ring in the bis-GMA would increase steric hindrance.[28] Additionally, the molar volume of the organic monomer should be as high as possible.

Among these issues, reduction in the viscosity of the organic monomer may be the most important. Since the high viscosity of bis-GMA stems from hydrogen bonding between hydroxyl groups in the alkyl chain, hydroxyl groups should be replaced with proper organic groups. In previous research,[20] 2,2-bis[4-(2-methoxy-3-methacryloyloxy propoxy)phenyl]propane (bis-M-GMA) was synthesized by substituting methoxy for hydroxyl groups. The viscosity of bis-GMA decreased from 574 (Pa s) to 3.7 (Pa s). However, the bis-M-GMA still required approximately 5 wt % TEGDMA since the viscosity was higher than commercially available organic matrix composed of 70 wt

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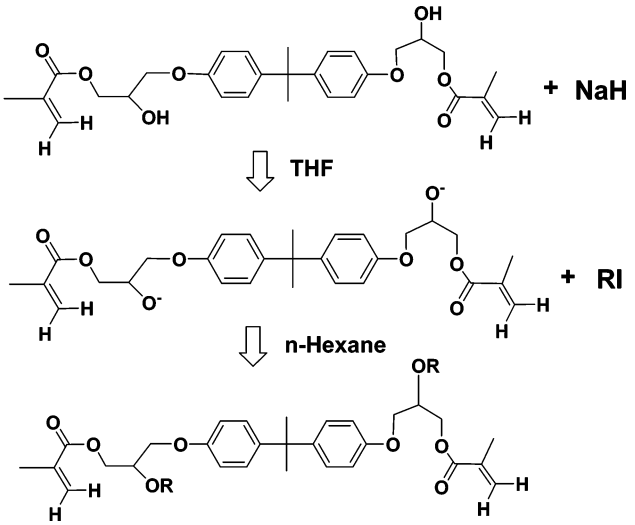
Scheme 1. Synthetic Route of the Alkoxy-Substituted Organic Monomer[a]



[a] Note that RI stands for alkyl iodine.

% bis-GMA and 30 wt % TEGMDA. Other organic monomers with viscosities lower than bis-M-GMA should be developed for use as organic matrixes. The viscosity of the organic monomer depends on the molar volume, specific interactions between organic monomers, and intermolecular distance (free volume). The viscosity of the organic monomer is increased through increasing the molar volume and specific interactions, but it is decreased by increasing the free volume.

In this study, novel organic monomers, i.e., 2,2-bis[4-(2-ethoxy-3-methacryloyloxy propoxy)phenyl]propane (bis-E-GMA), 2,2-bis[4-(2-propoxy-3-methacryloyloxy propoxy)-phenyl]propane (bis-Pr-GMA), 2,2-bis[4-(2-butoxy-3-methacryloyloxy propoxy)phenyl]propane (bis-B-GMA), and 2,2-bis[4-(2-pentoxy-3-methacryloyloxy propoxy)phenyl]propane (bis-P-GMA) were prepared by substituting alkoxy for hydroxyl groups in bis-GMA. The viscosity and curing characteristics, such as curing shrinkage, required curing time, and degree of polymerization, were investigated. Mechanical properties and curing characteristics of dental composites fabricated from the monomers were also investigated.

Materials and Procedures

Bis-GMA (99%, Polysciences Inc., U.S.A.) was used as a base resin, 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-40, Vericom Co., Korea, 0.04 μm primary particle size) was used as inorganic fillers for the composite resin. γ-Methacryloxypropyltrimethoxysilane (γ-MPS, Aldrich Chemical Co., U.S.A.) was used as a silane coupling agent for the hydrophobic treatment of the filler.[21]

The new organic monomers, bis-E-GMA, bis-Pr-GMA, bis-B-GMA, and bis-P-GMA were prepared by substituting alkoxy for hydroxyl groups in bis-GMA. The reaction procedure for synthesis of the organic monomers is shown in Scheme 1. All reactions were performed under an inert nitrogen atmosphere. Over 30 min, alkyl iodine (3 mol) was added dropwise to a 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 combined with dichloromethane (300 mL) and 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 the organic monomer was confirmed by ^1H NMR (Varian Gemini 2000, 300 MHz, U.S.A.) and GC/MS (model HP-6890, Hewlett-Packard, U.S.A.) analysis. ^1H 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. Main fragmentation peaks were reported with their relative intensity. Analytical HPLC was performed with an instrument equipped with a UV detector set at 254 nm (model LC-2500, Futecs, Korea). Octadecylsilane-coated columns (4.6 mm × 250 mm) with 5 μm particle size were used.

An organic matrix containing 0.75 wt % CQ and 1 wt % EDMAB was placed in a differential scanning calorimeter (DSC, 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 curing time was measured with the DSC since the time between onset and completion of the heat capacity changes during polymerization.[20,28] The degree of conversion was studied with the DSC adapted for photopolymerization measurements. Experiments were performed at 36 °C under constant nitrogen flow, as described elsewhere.[29] The densities of the organic matrixes were measured with a liquid dilatometer [Anton Paar Co., DMA-500]. The density of the cured polymers were measured with a solid dilatometer [Mettler Toledo Co., AX205]. The volumetric shrinkage ($\Delta\upsilon_{sp}$) was calculated as follows:

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

where $\upsilon_{sp,m}$ and $\upsilon_{sp,p}$ are the specific volumes of the organic matrix and resulting polymer, respectively. Water uptake was determined according to the ADA Specification No. 27 method describing organic matrix-based filling materials. The viscosities of the organic matrixes and composites were measured with a rheometer (model Physica MCR 500, Anton Parr, Germany; geometry: 25 mm parallel plate). The measurements were performed at 25 °C over the shear rate range of 0.1×10^2 to 4×10^3 s^{-1}.

The dental composites were fabricated using surface-treated fillers and a resin matrix. The composites contained 75 wt % filler (65 wt % barium silicate and 10 wt % fumed silica) and were mixed in a twin extruder (Bau Tech, model BA-11, *L*/*D* ratio = 40), followed by degassing at 30 °C for 1 day under a 1 mm of Hg vacuum. The diametral tensile strength (DTS) and flexural strength (FS) 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) using a crosshead speed of 1 mm/min, in accordance with ADA Specification No. 27. The FS was measured in accordance with International Standard Organization (ISO) Specification No. 4049, using a three-point loading test. The maximum load was measured by pressing the center of the cured rectangular bar (25 mm length × 2 mm width × 2 mm height) when mounted between UTM supports (20 mm length).

The data for the curing time, curing shrinkage, and water uptake of monomers and experimental dental composites 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).

Results and Discussion

Characterization of New Organic Monomers. The molecular structure of synthesized organic monomers was confirmed

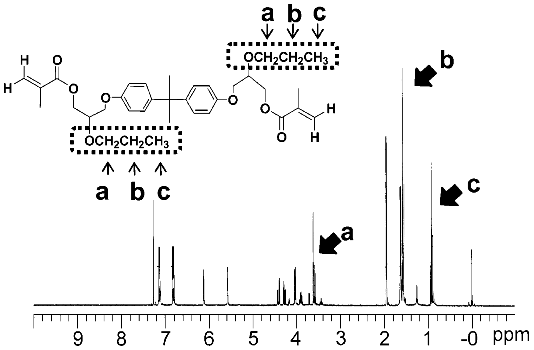


Figure 1. ^{1}H NMR spectrum of the bis-Pr-GMA.

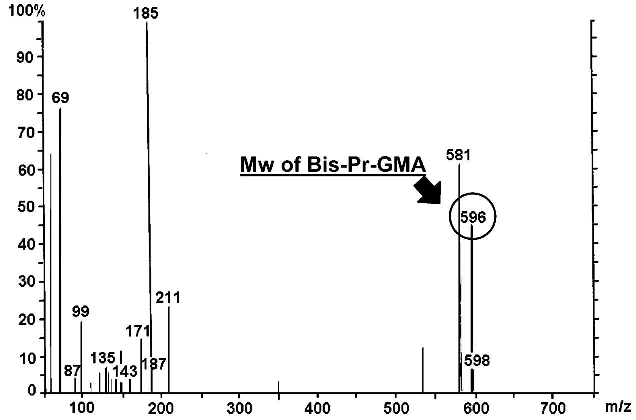


Figure 2. GC/MS chart of the bis-Pr-GMA.

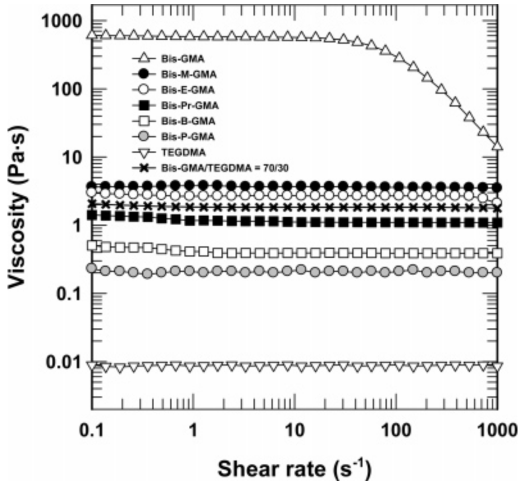


Figure 3. Measured viscosities of bis-GMA, TEGDMA, and alkoxy-substituted organic monomers as a function of shear rate.

by ^{1}H NMR and GC/MS analysis. The ^{1}H NMR spectrum of Figure 1 indicates that bis-Pr-GMA is similar to bis-GMA, except for the peaks at 0.96, 1.52, and 3.48 ppm, representing the protons from propoxy groups.[28] Figure 2 shows the GC/MS chart of bis-Pr-GMA. The molecular weight of bis-Pr-GMA (596 g/mol) was confirmed using the GC/mass chart. HPLC indicated that the impurities in the final products were negligible.

Characteristics of the Organic Monomers. Figure 3 depicts the viscosities of bis-GMA, TEGDMA, control organic matrix, and alkoxy-substituted bis-GMA monomers as a function of shear rate. A monomer mixture of TEGDMA (30 wt %) and bis-GMA (70 wt %) was used as a control organic matrix because commercial products were approximately similar in composition. The viscosity of bis-GMA (574 Pa s) was approximately 60 000 times higher than that of TEGDMA (0.0086 Pa s). Bis-GMA behaved like a supramolecule due to the intermolecular association caused by hydrogen bonding between the bis-GMA molecules.[20,27] The addition of TEGDMA to bis-GMA resulted in a sharp decline in viscosity due to the disruption of intermolecular association between bis-GMA molecules. For example, the viscosity of the control organic matrix (70 wt % bis-GMA and 30 wt % TEGDMA) used was 1.86 Pa s.[20] The high-viscosity bis-GMA was abruptly decreased from 574 to 3.71 Pa s through substitution of methoxy groups for hydroxyl groups in bis-GMA. The amount of diluent, which would be added to reduce the viscosity of the resin matrix, can be reduced by using bis-M-GMA (the organic monomer obtained through substitution of methoxy groups for hydroxyl groups in bis-GMA) instead of bis-GMA. The viscosity of the bis-M-GMA mixture containing 5 wt % TEGDMA was nearly the same as that of the control organic matrix.[20] However, the adverse effects of TEGDMA on the dental composite properties cannot be entirely removed since bis-M-GMA still requires TEGDMA for organic matrix development.

To produce organic monomers with a viscosity lower than bis-M-GMA, hydroxyl groups were replaced by bulkier alkoxy groups. As shown in Figure 3, the viscosity of the organic monomers gradually decreased with increasing substituent size. The viscosity of the bis-E-GMA (2.68 Pa s) remained higher than that of the control organic matrix. Bis-E-GMA required 2 wt % TEGDMA to produce the organic matrix. The viscosity of the organic monomers with subtituents bulkier than ethoxy groups (bis-Pr-GMA, bis-B-GMA, and bis-P-GMA) was lower than that of the control organic matrix. To elucidate the reduction of viscosity with increasing substituent size, the fractional free volume of the organic monomers was calculated, as listed in Table 1.[30] The fractional free volume increased with increasing substituent size, suggesting that loose molecular packing results in viscosity reduction of the organic monomer, even though the molar volume of the organic monomer increases. These organic monomers may be used as an organic matrix without an additional diluent if the curing characteristics and properties satisfy requirements as dental composites.

Curing characteristics of the organic monomers are listed in Table 1. Curing shrinkage of the alkoxy-substituted monomers was lower than that of bis-GMA (or TEGDMA). Upon polymerization, the curing shrinkage of the alkoxy-substituted monomers first decreased with substituent size, followed by a minimum from a butoxy substituent, and then increased. Curing time increased with increasing substituent size, and the effects of substituent size on the degree of polymerization were negligible. Although bis-P-GMA had the lowest viscosity among the organic monomers, it required the longest curing time (124 s). As listed in Table 1, the equilibrium water uptake of the alkoxy-substituted polymers was significantly lower than that of the polymers produced from the control organic matrix (4.1 wt %).[20] The lower equilibrium water uptake may be expected due to the hydrophobic effects of the alkoxy groups in the new organic monomers.

Characteristics of Composite Resins. After preparing dental composites containing 25 wt % organic matrix and 75 wt % inorganic fillers [65 wt % radio-opaque barium silicate (1 μm primary particle size) and 10 wt % of silica nanoparticles (40 nm)], their properties were investigated. As listed in Table 2, the curing shrinkage and curing time exhibited trends similar to those of the organic matrixes. The curing shrinkage of the alkoxy-substituted organic matrixes was significantly lower than that of the control organic mixture. The reduction of volumetric shrinkage was approximately 50% (from 1.9% to 0.97%) when bis-B-GMA was used as the organic matrix.

Table 1. Curing Characteristics, Viscosity, and Water Uptake of Various Organic Monomers[a]

monomer	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]	fractional free volume
bis-GMA	46 ± 0.8[e]	5.2 ± 0.2[d]	64.5 ± 0.8[e]	574	3.11 ± 0.12	0.1481
TEGDMA	57 ± 0.8[d]	12.3 ± 1.3[c]	82.3 ± 0.4[c]	0.0086	6.02 ± 0.20	
bis-M-GMA	36 ± 1.0[f]	4.6 ± 0.2[e]	70.3 ± 0.7[d]	3.65	0.87 ± 0.07	0.1611
bis-E-GMA	33 ± 1.1[g]	4.6 ± 0.2[e]	71.2 ± 0.6[d]	2.685	0.82 ± 0.06	0.1655
bis-Pr-GMA	36 ± 1.4[f]	4.3 ± 0.1[f]	70.6 ± 0.7[d]	1.188	0.78 ± 0.06	0.1808
bis-B-GMA	56 ± 2.1[d]	3.9 ± 0.1[g]	71.5 ± 0.7[d]	0.402	0.75 ± 0.07	0.1870
bis-P-GMA	124 ± 4.5[c]	4.2 ± 0.1[f]	70.8 ± 0.6[d]	0.211	0.72 ± 0.05	0.1964
bis-GMA/TEGDMA = 70/30	31 ± 1.1	7.0 ± 0.8	74.1 ± 0.5	1.86	4.1 ± 0.15	
bis-M-GMA/TEGDMA = 95/5	33 ± 1.2	4.3 ± 0.1	75.5 ± 0.3	1.79	1.1 ± 0.12	
bis-E-GMA/TEGDMA = 98/2	31 ± 0.9	4.5 ± 0.1	75.2 ± 0.4	1.82	0.88 ± 0.10	

[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 the mean ± standard deviation, and n is the number of specimens.

Table 2. Properties of the Dental Composites

monomer mixture	time of measurement[a]	equilibrium water uptake	curing shrinkage (%, $n = 5$)	DTS (MPa, $n = 5$)[b]	FS (MPa, $n = 5$)[b]
bis-GMA/TEGDMA = 70/30	before		1.94 ± 0.14	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		1.05 ± 0.08	49.2 ± 1.1	161.0 ± 4.1
	after	0.32		42.9 ± 1.7	147.8 ± 3.6
bis-E-GMA/TEGDMA = 98/2	before		1.10 ± 0.08	51.5 ± 1.2	160.5 ± 4.0
	after	0.23		46.7 ± 1.5	154.5 ± 3.7
bis-Pr-GMA	before		1.09 ± 0.05	54.6 ± 1.6	164.6 ± 3.7
	after	0.20		51.5 ± 1.3	158.7 ± 4.0
bis-B-GMA	before		0.97 ± 0.06	53.4 ± 1.8	161.5 ± 3.6
	after	0.20		51.0 ± 1.6	156.4 ± 4.0
bis-B-GMA[c]	before		0.80 ± 0.05	59.7 ± 1.6	167.2 ± 3.4
	after	0.18		57.8 ± 1.8	163.4 ± 3.7
bis-P-GMA	before		1.05 ± 0.07	50.0 ± 1.4	157.2 ± 4.0
	after	0.18		47.2 ± 1.5	152.8 ± 3.5

[a] Mechanical properties were examined before and after water uptake. [b] The results of two-way ANOVA suggested that the interaction effect of “monomer mixture x water uptake” is expected in both the measurements of DTS and FS ($p < 0.001$). [c] Dental composite contains 80 wt % inorganic fillers. Note that other dental composites prepared contained 75 wt % inorganic fillers.

Commercially available dental composites generally contain less than 75 wt % inorganic fillers.[31−33] The high viscosity of the organic matrix limited the increase of the filler content in the dental composite, even though the decrease of the curing shrinkage can be expected by increasing the content of the filler. Dental composites containing 80 wt % inorganic fillers [70 wt % radio-opaque barium silicate (1 μm primary particle size) and 10 wt % silica nanoparticles (40 nm)] were produced when bis-B-GMA was used as an organic matrix. As shown in Figure 4, the viscosity of this dental composite was similar to that of the control dental composites (75 wt % inorganic fillers and 25 wt % bis-GMA/TEGDMA = 70/30 mixture). In this case, the curing shrinkage of the dental composite was reduced by approximately 60%. The DTS and FS of the composite prepared from alkoxy-substituted organic matrix were significantly higher than that of the resin composite prepared from the control mixture. The decrease in mechanical strength under aqueous conditions was significantly smaller for dental composites containing the alkoxy-substituted organic matrix than bis-GMA mixture.

Summary

To overcome the adverse effects when a diluent is included in an organic matrix of a dental composite, organic monomers that can function as an organic matrix were developed. To use an organic monomer as a resin matrix, the viscosity should be lower than that of the control resin matrix (70 wt % bis-GMA and 30 wt % TEGDMA). Various organic monomers were synthesized by substituting alkoxy groups for hydroxyl groups in bis-GMA. The viscosities of the monomers decreased with increasing substituent size. Among these organic monomers, the viscosities of bis-Pr-GMA, bis-B-GMA, and bis-P-GMA were lower than that of the control resin matrix. Among these monomers, bis-B-GMA exhibited the lowest curing shrinkage.

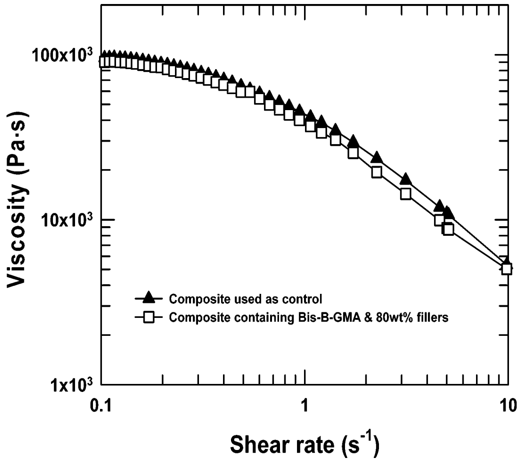


Figure 4. Measured viscosities of the dental composite used as control and those of the dental composite composed of 20 wt % bis-B-GMA and 80 wt % fillers.

The curing shrinkage of the bis-B-GMA matrix was 3.9%, whereas that of the control organic matrix was 7.0%. Additionally, dental composites prepared from bis-B-GMA exhibited the lowest curing shrinkage as well as excellent mechanical properties. In comparison to the curing shrinkage of the dental composite prepared from the control organic matrix, bis-B-GMA reduction was approximately 60%.

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References and Notes

(1) Bowen, R. L. U.S. Patent 3,066,112, 1962.
(2) Bowen, R. L. U.S. Patents 3,194,783 and 3,194,784, 1965.
(3) Leinfelder, K. F. *J. Am. Dent. Assoc.* **1991**, *122*, 65−70.
(4) Moszner, N.; Salz, U. *Prog. Polym. Sci.* **2001**, *26*, 535−542.
(5) Sanda, F.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 323−332.
(6) Schulz, H.; Madler, L.; Pratsinis, S. E.; Burtscher, P.; Moszner, N. *Adv. Funct. Mater.* **2005**, *15*, 830−838.
(7) Full, C. A.; Hollander, W. R. *J. Dent. Child.* **1993**, *60*, 57−60.
(8) Ferracane, J. L. *J. Am. Dent. Assoc.* **1992**, *123*, 53−58.
(9) Hansel, C.; Leyhausen, G.; Mai, U. E. H.; Geurtsen, W. *Dent. Mater.* **1998**, *77*, 60−67.
(10) Oysaed, H.; Ruyter, I. *J. Biomed. Mater. Res.* **1986**, *20*, 261−272.
(11) Dickens, S. H.; Cho, B. H. *Dent. Mater.* **2005**, *21*, 354−364.
(12) Santos, C.; Clarke, R. L.; Braden, M.; Guitian, F.; Davy, K. W. M. *Biomaterials* **2002**, *23*, 1897−1904.
(13) Bailey, W. J.; Sun, R. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1972**, *13*, 281−282.
(14) Endo, T.; Bailey, W. J. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 25−28.
(15) Davy, K. W. M.; Braden, M. *Biomaterials* **1991**, *12*, 406−418.
(16) Sandner, B.; Baudach, S.; Davy, K. W. M.; Braden, M.; Clarke, R. L. *J. Mater. Sci. Mater. Med.* **1997**, *8*, 39−44.
(17) Kalachandra, S.; Sankarapandian, M.; Shobha, H. K.; Tayor, D. F.; Mcgrath, J. E. *J. Mater. Sci. Mater. Med.* **1997**, *8*, 283−286.
(18) Sankarapandian, M.; Shobha, H. K.; Kalachandra, S.; Mcgrath, J. E. *J. Mater. Sci. Mater. Med.* **1997**, *8*, 465−468.
(19) Davy, K. W. M.; Kalachandra, S.; Pandain, M. S.; Braden, M. *Biomaterials* **1998**, *19*, 2002−2014.
(20) Kim, J. W.; Kim, L. U.; Kim, C. K.; Cho, B. H.; Kim, O. Y. *Biomacromolecules* **2006**, *7*, 154−160.
(21) Kim, L. U.; Kim, J. W.; Kim, C. K. *Biomacromolecules* **2006**, *7*, 2680−2687.
(22) Davy, K. W. M.; Anseau, M. R.; Odlyha, M.; Foster, G. M. *Polym. Int.* **1997**, *43*, 143−154.
(23) Shobha, H. K.; Sankarapandian, M.; Kalachandra, S.; Taylor, T. F. *J. Mater. Sci. Mater. Med.* **1997**, *8*, 385−389.
(24) Pereira, S. G.; Nunes, T. G.; Kalachandra, S. *Biomaterials* **2002**, *23*, 3799−3806.
(25) Stansbury, J. W.; Antonucci, J. M. *Dent. Mater.* **1999**, *15*, 166−173.
(26) Pereira, S. G.; Osorio, R.; Toledano, M.; Nunes, T. G. *Dent. Mater.* **2005**, *21*, 823−830.
(27) Nystrom, B.; Kjoniksen, A.; Iversen, C. *Adv. Colloid Interface Sci.* **1999**, *79*, 81−103.
(28) Kim, Y.; Kim, C. K.; Cho, B. H.; Um, J. M.; Son, H.; Kim, O. Y. *J. Biomed. Mater. Res., Part B* **2004**, *70B* (1), 82−90.
(29) Emami, N.; Soderholm, K.-J. M. *J. Mater. Sci. Mater. Med.* **2005**, *16*, 47−52.
(30) Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: 1990; Chapter 18.
(31) Ferracane, J. L. *Crit. Rev. Oral Biol. Med.* **1995**, *6*, 302−318.
(32) Lohbauer, U.; Frankenberger, R.; Kramer, N.; Petschelt, A. *J. Biomed. Mater. Res., Part B* **2005**, *71B*, 114−120.
(33) Lee, Y. K.; Lim, B. S.; Rhee, S. H.; Yang, H. C.; Power, J. M. *J. Biomed. Mater. Res., Part B* **2004**, *70B*, 16−21.

BM070345A