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Effects of Molecular Structure of the Resins on the Volumetric Shrinkage and the Mechanical Strength of Dental Restorative Composites

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To prepare a dental composite that has a low amount of curing shrinkage and excellent mechanical strength, various 2,2-bis[4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (Bis-GMA) derivatives were synthesized via molecular structure design, and afterward, properties of their mixtures were explored. Bis-GMA derivatives, which were obtained by substituting methyl groups for hydrogen on the phenyl ring in the Bis-GMA, exhibited lower curing shrinkage than Bis-GMA, whereas their viscosities were higher than that of Bis-GMA. Other Bis-GMA derivatives, which contained a glycidyl methacrylate as a molecular end group exhibited reduced curing shrinkage and viscosity. Methoxy substitution for hydroxyl groups on the Bis-GMA derivatives was performed for the further reduction of the viscosity and curing shrinkage. Various resin mixtures, which had the same viscosity as the commercial one, were prepared, and their curing shrinkage was examined. A resin mixture containing 2,2-bis[3,5-dimethyl, 4-(2-methoxy-3-methacryloyloxy propoxy) phenyl] propane] (TMBis-M-GMA) as a base resin and 4-*tert*-butylphenoxy-2-methyoxypropyl methacrylate (t-BP-M-GMA) as a diluent exhibited the lowest curing shrinkage among them. The composite prepared from this resin mixture also exhibited the lowest curing shrinkage along with enhanced mechanical properties.

Introduction

Resins that exhibit a low amount of shrinkage or no shrinkage in volume upon polymerization are highly desirable in the application of various fields such as restorative dentistry, precision castings, and adhesives.[1−5] Especially, the development of new resins eliminating volume change during polymerization is essential in restorative dentistry. Various problems such as postoperative sensitivity, marginal discoloration, secondary caries, and pulpal pathoses still occur as a result of the inherent volumetric shrinkage resulting from the polymerization of the composite resin matrix.[5−7] The shrinkage stresses generated from the polymerization of the composite resin may be sufficiently concentrated to cause defects or debonding at the tooth−restorative interface.[8−14]

Volume shrinkage during polymerization results from the conversion of van der Waals distances between monomers to covalent bond lengths.[15] The van der Waals distance separates monomer molecules approximately three times greater than a covalent bond does. The organic matrix containing the classical monomers, i.e., 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, has been used in the past. 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 resin mixture even though this inclusion increases the amount of water sorption and curing shrinkage.[16−20] Today's dental composites are moving away from Bis-GMA and TEGDMA, replacing them at least in part with monomers such as ethoxylated bisphenol A dimethacrylate (Bis-EMA) and urethane dimethacrylate (UDMA), to reduce shrinkage and water sensitivity.

In the previous research,[21] we had explored various base resins to develop dental restorative composites having low curing shrinkage and excellent mechanical properties. Bis-GMA derivatives prepared by substituting the methyl groups for some or all of the four available positions onto the phenyl rings, i.e., 2,2-bis[3-methyl, 4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (DMBis-GMA) and 2,2-bis[3,5-dimethyl, 4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (TMBis-GMA), exhibited lower curing shrinkage than Bis-GMA. These results indicated that the incline of steric hindrance in the chain packing of formed polymer can be a promising strategy in reducing curing shrinkage. In this research, however, we did not consider the increase of viscosity caused by molecular weight change. Since viscosity increases with molecular weight, DM-Bis-GMA or TM-Bis-GMA may have higher viscosity than Bis-GMA. It means that these derivatives require a great amount of diluent that gives adverse effects on the curing shrinkage and mechanical properties. 2,2-Bis [4-(2-methoxy-3-methacryloyloxy propoxy) phenyl] propane] (Bis-M-GMA), which was prepared by substituting the methoxy groups for hydroxyl groups in Bis-GMA, has been also examined as a base resin.[22] Since Bis-M-GMA possesses abruptly decreased viscosity compared to Bis-GMA, a resin matrix containing only 5 wt % of TEGDMA as a diluent could be developed by using Bis-M-GMA as a base resin.

Several key strategies can be employed to develop dental restorative composites having reduced shrinkage. The viscosity of the base resin should be lowered to minimize the addition of diluent or to produce a resin matrix without diluent. Removal of hydroxyl groups in Bis-GMA, i.e., removal of hydrogen bonding between molecules, as well as reduction of molecular weight might be effective strategies for this purpose. Steric hindrance in the chain packing of the polymer formed by the curing reaction should be increased.[5] Bulky group substitution

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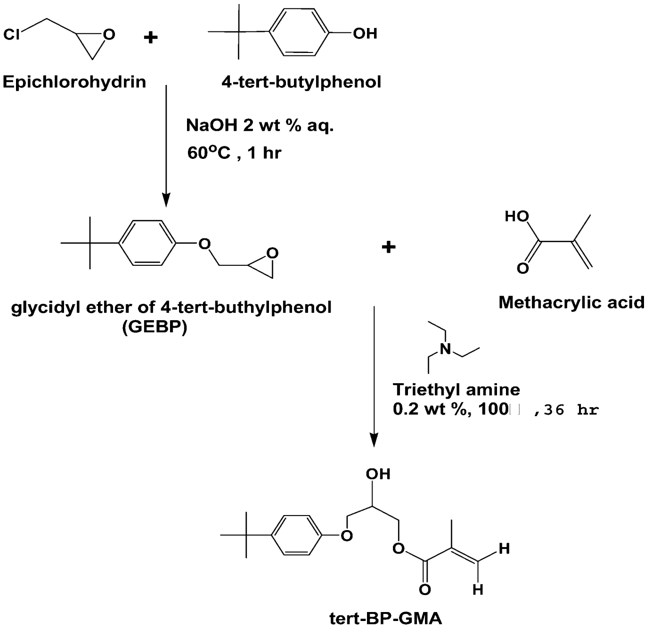
Scheme 1. Synthetic Procedure of t-BP-GMA



for hydrogen on the phenyl ring in the Bis-GMA could be an example. Reduction of the cross-linking density of the cured resin matrix also could be an effective strategy. Since most of the Bis-GMA derivatives developed previously contained glycidyl methacrylate at both ends of the molecule, the polymerization and cross-linking reaction that occurred during the curing process gave adverse effects in reducing volumetric shrinkage.[18−25] The use of a monomer with only one polymerizable group might be an effective way to reduce curing shrinkage. In this study, various Bis-GMA derivatives that consider the issues mentioned above were synthesized, and their mixtures were explored to develop resin matrixes having reduced curing shrinkage. Mechanical properties and curing characteristics of dental restorative composites prepared from them were also examined.

Materials and Procedures

Materials. Bis-GMA (99%, Polysciences Inc., USA) as a base resin, TEGDMA (3G grade, Aldrich Chemical Co., USA) as a diluent, camphorquinone (CQ, 99%, Aldrich Chemical Co.) as an initiator, and ethyl 4-dimethylaminobenzoate (EDMAB, 99+%, Aldrich Chemical Co.) as an accelerator were used. 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 preparation of the dental composites.

Synthesis of the Base Resins. Base resins prepared by substituting the methyl groups for some or all of the four available positions onto the phenyl rings, i.e., 2,2-bis[3-methyl, 4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (DMBis-GMA) and 2,2-bis[3,5-dimethyl, 4-(2-hydroxy-3-methacryloyloxy propoxy) phenyl] propane (TMBis-GMA), were synthesized at our laboratory as reported previously.[21] New base resins, i.e., 4-cumylphenoxy glycidyl methacrylate (CP-GMA) and 4-*tert*-butylphenoxy glycidyl methacrylate (t-BP-GMA), were also synthesized in the laboratory by changing bisphenol A used for the synthesis of Bis-GMA to 4-cumylphenol (or 4-*tert*-butylphenol). CP-GMA and t-BP-GMA were synthesized by a two-step reaction. Scheme 1 shows the preparation route for t-BP-GMA. 4-*tert*-Butylphenol (0.3 mol) was dissolved in aqueous solution containing 10 wt % NaOH and was reacted with epichlorohydrin (0.75 mol) at 60 °C for 2 h. The resulting glycidyl ether of the 4-*tert*-butylphenol (GEBP) was reacted at 60 °C for 1 day by adding an excess amount of methacrylic acid (0.75 mol) and triethylamine (0.2 wt % of methacrylic acid) as a catalyst. The resulting product was dissolved in dichloromethane (1 mol), was reacted with a 1 N NaOH aqueous solution (3 × 100 mL) to remove the unreacted methacrylic acid, and was reacted with 1 N HCl aqueous solution (3 × 100 mL) to remove triethylamine. The resulting organic solution was washed with water (5 × 500 mL), dried with $MgSO_4$, and was concentrated by vacuum filtration. CP-GMA was synthesized using the same procedure with t-BP-GMA.

Procedures for the Methoxy Substitution. Methoxy substitution for hydroxyl groups in various base resins was also performed. Details of the reaction procedures for methoxy substitution were described previously.[22] For the preparation of 4-*tert*-butylphenoxy-2-methyoxypropyl methacrylate (t-BP-M-GMA), methyl iodine (CH_3I, 3 mol) was added dropwise over 30 min to the solution of t-BP-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 was transferred through a sintered glass funnel containing a small pad of silica gel. Note that reactions were carried out under an inert atmosphere of nitrogen. The resulting organic solution was washed with water (5 × 500 mL), dried with $MgSO_4$, and concentrated by vacuum filtration.

Characterization of the Molecular Structure. The molecular structure of base resins synthesized here was confirmed by FT-IR (Nicolet Magna 750, USA), ^1H NMR (Varian Gemini 2000, 300 MHz, USA), and GC/MS (Micromass Autospec, U.K.) analyses. Base resins were placed in a KBr vessel for FT-IR 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.

Characterization of Resin Mixtures. Resin mixtures containing base resin, diluent, initiator (0.75 wt % CQ), and accelerator (1 wt % EDMAB) were prepared. Note that in order to examine the exact volumetric shrinkage caused by the polymerization the samples were prepared without fillers that are normally included in the composite resin. The resin mixtures were placed in a DSC sample pan (diameter x thickness = 6 mm × 2 mm) and polymerized by irradiating with visible light from a light source ($\lambda_{max} = 460$ nm, intensity: 600 mW/cm^2, VIP Junior Curing Light, BISCO Inc., U.S.A.). The time required for the curing reaction was measured using DSC (DSC-2010, TA Instrument, U.S.A.). The times when the onset and completion of the heat capacity changes occurred were defined as the curing time required for the polymerization reaction.[21−22] 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.[26] To calculate curing shrinkage, the densities of the monomer mixtures and those of the resulting polymers were measured using a liquid dilatometer [Anton Paar Co., DMA-500] and a solid dilatometer [Mettler Toledo Co., AX205], respectively. The curing shrinkage (Δv_{sp}) is given by

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

where $v_{sp,m}$ and $v_{sp,p}$ are the specific volume 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 I mm 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

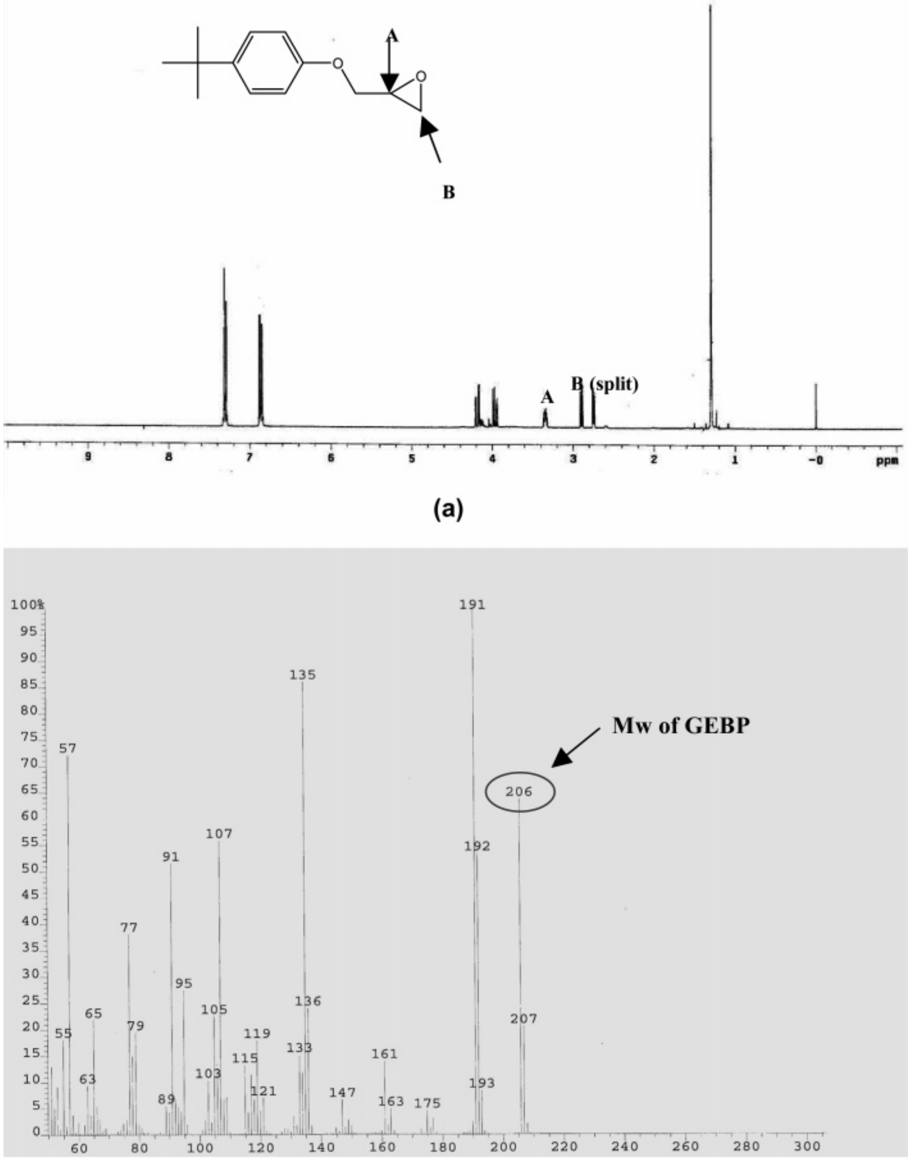
$$\eta = \frac{\tau_w}{\dot{\gamma}} \tag{2}$$

Preparation of the Dental Composites. The hydrophilic surface of the filler caused by hydroxyl end groups was treated with γ-MPS to improve interfacial adhesion between the resin matrix and filler.[27–28] γ-MPS (1 mol) was prehydrolyzed by reacting with a spreading solvent (100 mL) composed of deionized distilled water (70 wt %) and acetic acid (30 wt %) at 25 °C for 2 h. Filler (100 g) was continuously added to the γ-MPS solution and was stirred at 1000 rpm for 2 h. After removing unreacted γ-MPS by using an ultracentrifuge, the resulting product was further purified by freeze-drying at −50 °C for 2 days. The surface-treated filler was finally cured at 120 °C for 2 h to accomplish condensation reaction. For the fabrication of the polymeric dental restorative composites, 75 wt % of surface-treated fillers (70 wt % of barium silicate and 5 wt % of fumed silica) and 25 wt % of a resin matrix were mixed vigorously in a kneader, followed by degassing at 30 °C for 1 day under a 1 mmHg vacuum.

Mechanical Strength of the Dental Composites. 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 x 4 mm height), which had been cured with visible light in a Teflon mold, were broken by diametral tension. Reported DTS values are average numerical values from the measurement of five replicated specimen. The flexural strength (FS) was measured in accordance with International Standard Organization (ISO) Specification No. 4049, with the testing being carried out by three-point loading. The maximum load was measured by pressing the center of a cured rectangular bar (25 mm length x 2 mm width x 2 mm height) while it was mounted between supports (20 mm length) of UTM. Each experiment was performed at least five times, and data reported were the means of these values.

Results and Discussion

Characterization of Various Resins. The molecular structures of CP-GMA and t-BP-GMA were confirmed by GC-mass and ^{1}H NMR. Figure 1 shows the GS-mass chart and ^{1}H NMR spectrum of the GEBP, i.e., the intermediate prepared by reacting 4-*tert*-butylphenol with epichlorohydrin. The molecular weight of GEBP (=206 g/mol) was confirmed using the GC-mass chart.



(a)

(b)

Figure 1. ^{1}H NMR spectrum (a) and GC/MS chart (b) of glycidyl ether of the 4-*tert*-butylphenol (GEBP).

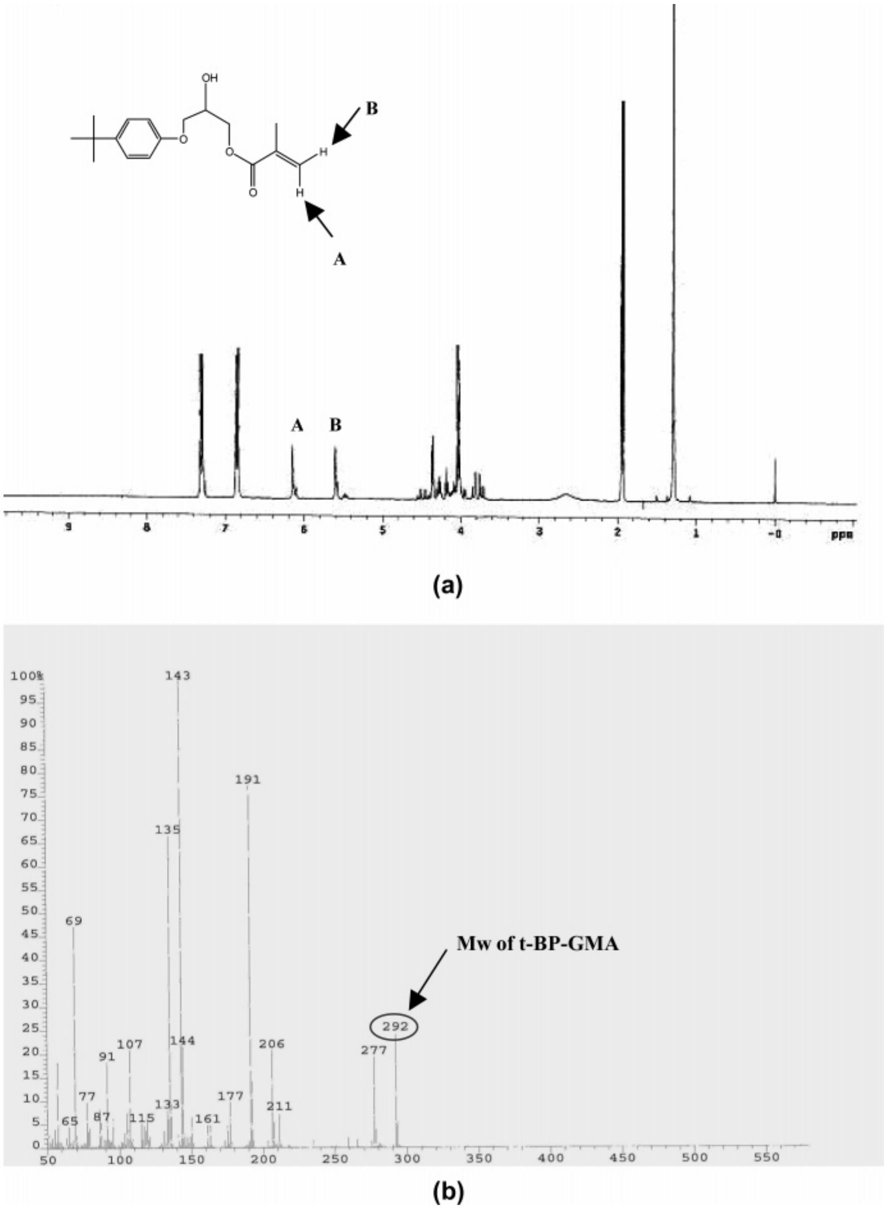


Figure 2. ^{1}H NMR spectrum (a) and GC/MS chart (b) of t-BP-GMA.

In the ^{1}H NMR spectrum, the peaks between 6.9 and 7.3 ppm are due to the aromatic protons. The peaks 2.73, 2.87, and 3.33 ppm represent the protons arising from the attached epoxy groups. The molecular structure of the final product, i.e., t-BP-GMA and its molecular weight (292 g/mol) were also confirmed using ^{1}H NMR and GC-mass (Figure 2). The peak at 1.95 ppm represents the protons from the methyl group in the methacrylate. The peaks at 5.61 and 6.15 ppm represent the proton in $=CH_2$. The molecular structure of CP-GMA was also confirmed in a similar manner.

Base resins substituting methoxy groups for hydroxyl groups such as 2,2-bis[3-methyl,4-(2-methoxy-3-methacryloyloxy propoxy) phenyl] propane] (DMBis-M-GMA), 2,2-bis[3,5-dimethyl, 4-(2-methoxy-3-methacryloyloxy propoxy) phenyl] propane] (TMBis-M-GMA), 4-cumylphenoxy-2-methyoxypropyl methacrylate (CP-M-GMA), and 4-*tert*-butylphenoxy-2-methyoxypropyl methacrylate (t-BP-M-GMA) were also prepared. The molecular structures of base resins containing methoxy groups were also confirmed by FT-IR, GC-mass, and ^{1}H NMR. For example, Figure 3 exhibits FT-IR spectra of t-BP-GMA and t-BP-M-GMA. At 3458 cm^{-1}, the broad adsorption band corresponds to $-$OH of the t-BP-GMA. Disappearance of this signal in t-BP-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 4a shows the ^{1}H NMR spectrum of the t-BP-M-GMA prepared by reacting t-BP-GMA with methyl iodide. The spectrum of the t-BP-M-GMA is exactly the same as that of t-BP-GMA, except for the peak at 3.53 ppm that represents the protons from the methoxy groups. The molecular weight of t-BP-M-GMA (306 g/mole, Figure 4b) was confirmed using the GC-mass chart. The levels of impurities in the final products examined using HPLC were negligible.

Viscosities of Base Resins. Some of the dental restorative composites still utilize Bis-GMA as the main component (or base resin) 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.[16−20] The viscosity of the base resin mainly depends on the molecular weight and

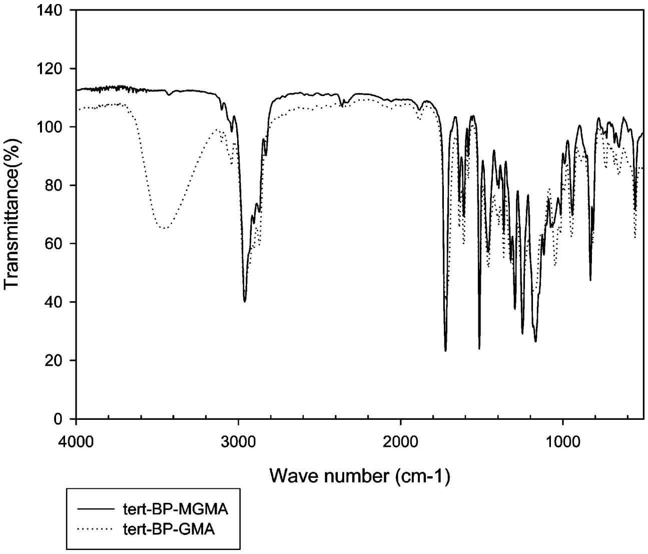


Figure 3. FT-IR spectra of t-BP-GMA and t-BP-M-GMA.

intermolecular interactions such as hydrogen bonding. Figure 5 exhibits changes in the viscosities with shear rate for the selected base resins. The viscosity of the base resin was increased with the molecular weight of the base resin. Among these resins, TMBis-GMA, DMBis-GMA, and Bis-GMA exhibited a non-Newtonian flow behavior at a high shear rate, which is observed when polymeric materials have a high molecular weight. It means that these resins behave like macromolecules, because of the intermolecular association stemming from the hydrogen bonding between the molecules.[22,29] 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.[29] The shear rate where shear thinning began was decreased by increasing the molecular weight. However, the value of shear stress at which shear thinning began was nearly the same (20 000 Pa) regardless of the kinds of base resins that were used. Note that shear stress was calculated from eq 2. It means that the strength of hydrogen bonding existing in base resins is nearly the same regardless of the molecular structure of the base resins. CP-GMA and t-BP-GMA did not exhibit shear thinning behavior, and their viscosities were significantly lower than Bis-GMA. It means that these resins do not behave like macromolecules, even though they contain a hydroxyl group. Since each molecule contains a hydroxyl group, behavior like macromolecules caused by hydrogen bonding might not be expected. Note that each molecule should have at least two hydroxyl groups such as Bis-GMA to form macromolecules caused by hydrogen bonding.

Viscosities of resins obtained by substituting methoxy groups for hydroxyl groups are listed in Table 1. Note that these resins did not exhibit shear thinning behavior. Comparing the viscosity of the methoxy substituted resin with that of the corresponding base resin, abrupt reduction in the viscosity was observed. For example, the viscosity of TMBis-GMA (= 1145 Pa•s) is about 130 times higher than that of TMBis-M-GMA (= 8.85 Pa•s). These results can be attributed to the disappearance of hydrogen bonding between molecules caused by methoxy substitution. A diluent such as TEGDMA should be added to the resin to reduce the viscosity of the resin matrix. 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. Since the viscosity of t-BP-M-GMA (0.023 Pa•s) is much lower than those of other resins developed here, it might be used as a diluent. Note that the viscosity of TEGDMA was 0.0086 Pa•s. Details related to the viscosities of mixtures, their curing characteristics, and mechanical properties of composites prepared from the mixtures containing resin developed here were described in the following sections.

Curing Characteristics of Base Resins. The curing characteristics of the resins developed here are listed in Table 1. The increase of the curing time with resin viscosity was observed when base resins contain hydroxyl groups. The curing shrinkages of the DMBis-GMA and TMBis-GMA that were obtained by phenyl ring substitution with methyl groups were reduced by increasing the number of methyl groups on the phenyl rings. It has stemmed from steric hindrance of chain packing as described previously.[21] The required curing time for the polymerization of the methoxy substituted base resin was shorter than that of the corresponding base resin. This might have stemmed from the reduction in the viscosity of the methoxy-substituted resins. The amount of curing shrinkage was also decreased as a result of methoxy substitution. Close molecular packing caused by the strong specific interactions that originate from the polar groups, such as hydroxyl groups and carbonyl groups, increases the density of the molecule. Because of this, the density of the methoxy-substituted base resin is lower than that of the corresponding base resin. Loose chain packing of methoxy-substituted resins is favorable to decreasing the curing shrinkage.

Curing Characteristics and Viscosity of Resin Mixtures. The resin mixture used as the control in this study consists of a monomer mixture of Bis-GMA (70 wt %) and TEGDMA (30 wt %). The curing characteristics of the resin mixtures and their viscosities were listed in Table 2.

To adjust the viscosity of the resin mixture, each base resin was mixed with various amounts of TEGDMA. For example, viscosities of TMBis-GMA mixtures containing various amounts of TEGDMA were examined as shown in Figure 6. The rapid decrease in the viscosities of TMBis-GMA mixtures is observed by adding TEGDMA. The TMBis-GMA/TEGDMA = 50/50 mixture exhibited nearly the same viscosity as the Bis-GMA/TEGDMA = 70/30 mixture. Since TMBis-GMA and DMBis-GMA required a greater amount of diluent than Bis-GMA, they were not effective in reducing the curing shrinkage of resin matrixes, even though they have a lower curing shrinkage than Bis-GMA. However, CP-GMA required only about 5 wt % TEGDMA. Since viscosity of the t-BP-GMA was slightly lower than that of the resin mixture used as the control, its mixture was not examined. As listed in Table 2, the curing shrinkage could be reduced effectively by using CP-GMA. However, resin mixture containing CP-GMA may not be used as a resin matrix, because the cross-linking density of the resulting polymer is too low to apply for a dental composite. Note that CP-GMA and t-BP-GMA contain only one reactive group at the end of a molecule.

The curing characteristics and viscosities of resin mixtures containing methoxy-substituted resins were also listed in Table 2. Since methoxy-substituted resin has a significantly lower viscosity than the corresponding base resin, the former required a small amount of diluent (TEGDMA) in preparing the resin mixture, which has the same viscosity with the resin mixture used as the control. Comparing the curing shrinkage of the resin mixture containing methoxy substituted resin with that of the

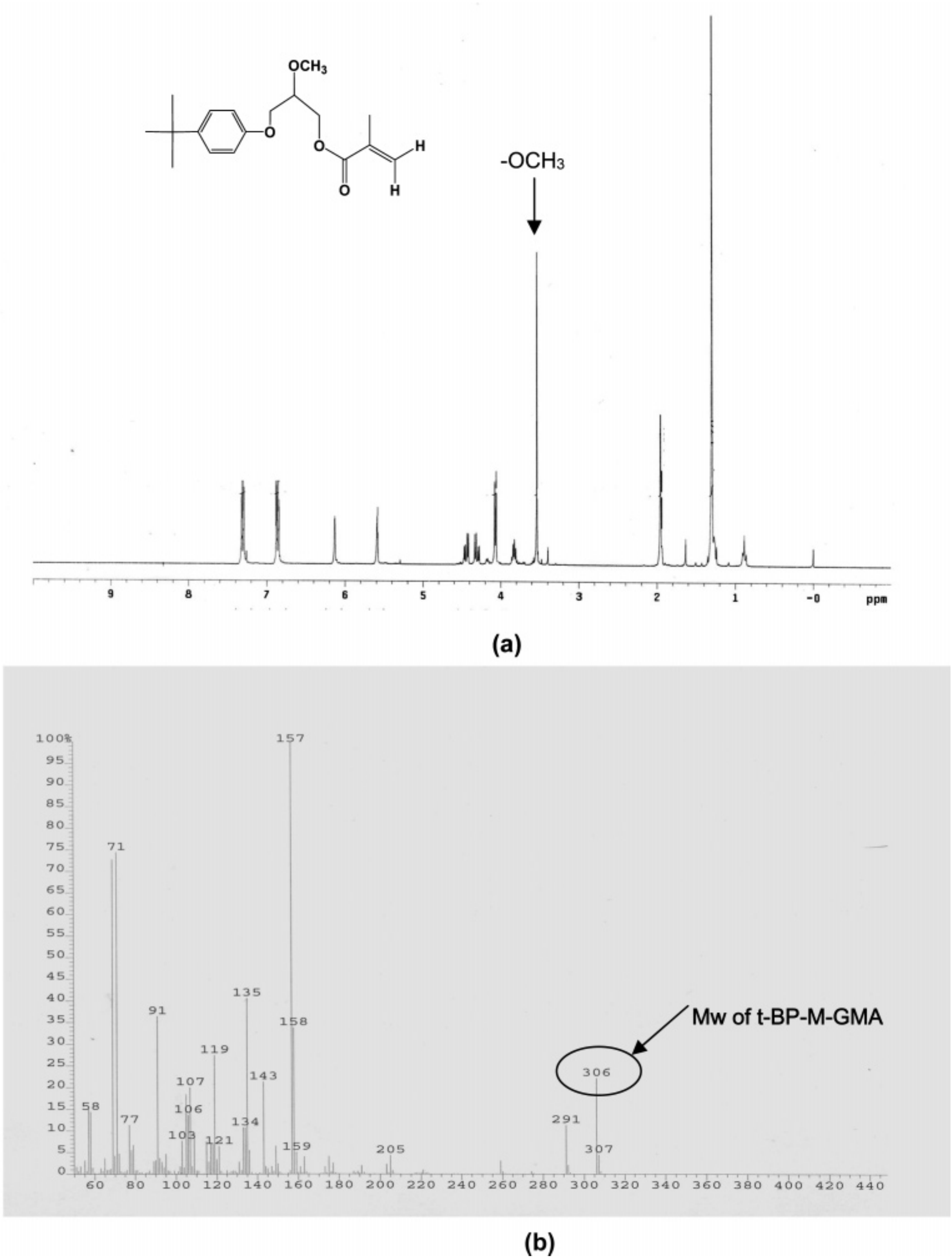


Figure 4. ^{1}H NMR spectrum (a) and GC/MS chart (b) of t-BP-M-GMA.

corresponding base resin mixture, significant reduction in the curing shrinkage was observed. Note that the t-BP-M-GMA (or CP-M-GMA) mixture with TEGDMA was not examined because the viscosity of t-BP-M-GMA (or that of CP-M-GMA) is lower than that of the resin mixture used as the control.

Since t-BP-M-GMA has the lowest viscosity among the resins prepared here, it was used as a diluent in the substitution of TEGDMA. Figure 7 exhibits the changes in viscosity of the TMBis-M-GMA/t-BP-M-GMA mixture as a function of t-BP-M-GMA content. When TM-Bis-GMA, which exhibits macromolecular flow behavior caused by hydrogen bonding, was mixed with TEGDMA, the rapid decline in the viscosities of mixtures, i.e., nearly exponential decay, was observed by adding TEGDMA (See Figure 6). Bis-GMA also exhibited a similar behavior with TM-Bis-GMA.[22] Disruption of intermolecular association among the TMBis-GMA (or Bis-GMA) molecules caused by the presence of TEGDMA resulted in a sharp decline in the mixture viscosity. However, in the viscosities of TMBis-M-GMA/t-BP-M-GMA mixtures, a parabolic decline was observed by increasing t-BP-M-GMA content. The absence of hydrogen bonding caused by methoxy substitution might be the reason for the observed viscosity behavior. A mixture of Bis-M-GMA (or DMBis-M-GMA) with t-BP-M-GMA also exhibited a similar behavior as the TMBis-M-GMA/t-BP-M-GMA mixture. The TMBis-M-GMA/t-BP-M-GMA mixture containing about 45 wt % of t-BP-M-GMA had nearly the same viscosity as the resin mixture used as the control. As listed in Table 2, the resin mixture composed of TMBis-M-GMA and t-BP-M-GMA has the smallest curing shrinkage among the resin mixtures prepared here. Dental monomers are usually difunctional to tie them into the polymer network, even if their conversion is not complete. A residual monomer that is not attached to the polymer matrix by either of its double bonds is subjected to extraction in vivo and presents a toxicity hazard. The amount of extractable difunctional monomer might be less than that of an extractable monofunctional monomer. Because of this shortcoming, an extraction study with the resin mixture composed of TMBis-M-GMA and t-BP-M-GMA is necessary for the practical application.

Table 1. Curing Characteristics, Viscosities, and Water Uptake of Various Base Resins[a]

monomer	curing time (s, *n* = 5)	curing shrinkage (%, *n* = 5)	degree of conversion (%, *n* = 5)	viscosity (Pa.s)	equilibrium water uptake (wt %, *n* = 5)
Bis-GMA	46.0 ± 0.8	5.1 ± 0.31	65.5 ± 0.8	574	3.11 ± 0.12
DMBis-GMA	49.1 ± 0.7	4.5 ± 0.20	63.7 ± 0.7	856	2.83 ± 0.15
TMBis-GMA	51.2 ± 0.8	3.8 ± 0.27	63.3 ± 0.8	1145	2.66 ± 0.17
CP-GMA	39.5 ± 0.5	3.5 ± 0.37	68.6 ± 0.9	4.84	1.72 ± 0.16
t-BP-GMA	36.5 ± 0.7	4.6 ± 0.29	71.8 ± 0.8	1.60	1.83 ± 0.12
Bis-M-GMA	36.2 ± 0.9	4.6 ± 0.18	70.3 ± 0.7	3.65	0.87 ± 0.08
DMBis-M-GMA	38.9 ± 0.9	4.0 ± 0.26	68.4 ± 0.9	5.78	0.76 ± 0.06
TMBis-M-GMA	40.3 ± 0.8	3.2 ± 0.34	67.1 ± 0.7	8.84	0.67 ± 0.05
CP-M-GMA	35.1 ± 0.8	3.1 ± 0.31	76.5 ± 0.9	0.082	0.81 ± 0.06
t-BP-M-GMA	34.8 ± 0.9	4.1 ± 0.35	78.1 ± 0.6	0.023	0.76 ± 0.04
TEGDMA	56.5 ± 0.8	12.3 ± 1.31	82.3 ± 0.4	0.0086	6.02 ± 0.20

[a] The data are presented as mean ± standard deviation, and *n* is the number of specimens.

Table 2. Curing Characteristics and Viscosities of Various Resin Mixtures[a]

monomer	curing time (s, *n* = 5)	curing shrinkage (%, *n* = 5)	degree of conversion (%, *n* = 5)	viscosity (Pa·s)
Bis-GMA/TEGDMA = 70/30	31.0 ± 0.8	7.0 ± 0.70	74.1 ± 0.5	1.86
DMBis-GMA/TEGDMA = 60/40	32.0 ± 0.7	7.4 ± 0.60	73.7 ± 0.6	1.87
TMBis-GMA/TEGDMA = 50/50	34.2 ± 0.8	7.8 ± 0.52	71.8 ± 0.8	1.79
CP-GMA/TEGDMA = 95/5	32.4 ± 0.8	3.8 ± 0.22	75.6 ± 0.9	1.90
Bis-M-GMA/TEGDMA = 95/5	33.3 ± 1.5	4.3 ± 0.17	75.5 ± 0.7	1.79
DMBis-M-GMA/TEGDMA = 92/8	34.1 ± 1.2	4.5 ± 0.20	72.4 ± 0.9	1.73
TMBis-M-GMA/TEGDMA = 88/12	35.6 ± 1.0	4.1 ± 0.16	74.1 ± 0.8	1.81
Bis-M-GMA/t-BP-M-GMA = 75/25	33.0 ± 0.9	4.4 ± 0.21	72.5 ± 0.8	1.89
DMBis-M-GMA/t-BP-M-GMA = 65/35	32.3 ± 1.1	4.3 ± 0.25	73.1 ± 0.6	1.80
TMBis-M-GMA/t-BP-M-GMA = 55/45	34.0 ± 1.2	3.7 ± 0.16	71.7 ± 0.7	1.88

[a] The data are presented as mean ± standard deviation, and *n* is the number of specimens.

Table 3. Properties of the Dental Composites[a]

monomer mixture	time of measurements	equilibrium water uptake[b] (%)	curing shrinkage (%)	DTS (MPa)	FS (MPa)
Bis-GMA/TEGDMA = 70/30	before		1.94 ± 0.23	45.2 ± 1.4	149.8 ± 5.5
	after	1.2		32.1 ± 2.5	110.4 ± 4.3
Bis-M-GMA/t-BP-M-GMA = 75/25	before		1.12 ± 0.23	51.5 ± 1.7	181.0 ± 5.1
	after	0.22		44.5 ± 2.8	161.0 ± 4.7
DMBis-M-GMA/t-BP-M-GMA = 65/35	before		1.15 ± 0.23	49.5 ± 1.5	174.0 ± 4.8
	after	0.20		43.7 ± 2.7	155.0 ± 6.1
TMBis-M-GMA/t-BP-M-GMA = 55/45	before		0.92 ± 0.17	53.2 ± 2.1	186.0 ± 5.4
	after	0.19		46.9 ± 2.4	173.8 ± 6.6

[a] Specimens examined here contain 75 wt % inorganic fillers, and five specimens were tested for each property. [b] Standard deviation was negligible.

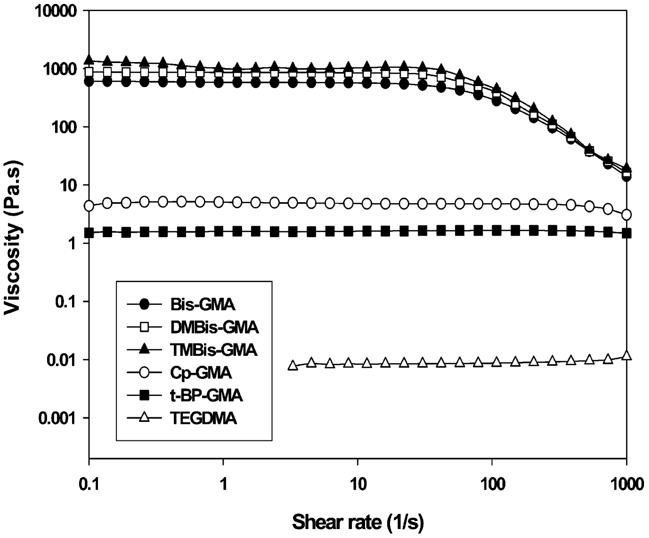


Figure 5. Measured viscosities of various base resins as a function of shear rate.

Characteristics of Resin Composites. The curing characteristics and mechanical properties of the resin composite containing 75 wt % filler were examined, and the results are listed in Table 3. Note that resin mixtures used for the preparation of the composites had nearly the same viscosity. As expected, the curing shrinkage and the curing time of the resin composites exhibited a similar trend with those of the resin mixtures. The curing shrinkage of the resin composite prepared from the resin matrix containing methoxy substituted resin was significantly lower than that prepared from the Bis-GMA/TEGDMA = 70/30 mixture. The decrease in the curing shrinkage of the composite prepared from the resin mixtures containing t-BP-M-GMA as diluent was remarkable. Especially, the composite prepared from the TMBis-M-GMA/t-BP-M-GMA = 55/45 resin mixture exhibited about 0.9% curing shrinkage, whereas that prepared from the Bis-GMA/TEGDMA = 70/30 mixture exhibited 1.9% curing shrinkage. The diametral tensile strength and the flexural strength of the former were higher than those of the latter, as it is listed in Table 3. Furthermore, when

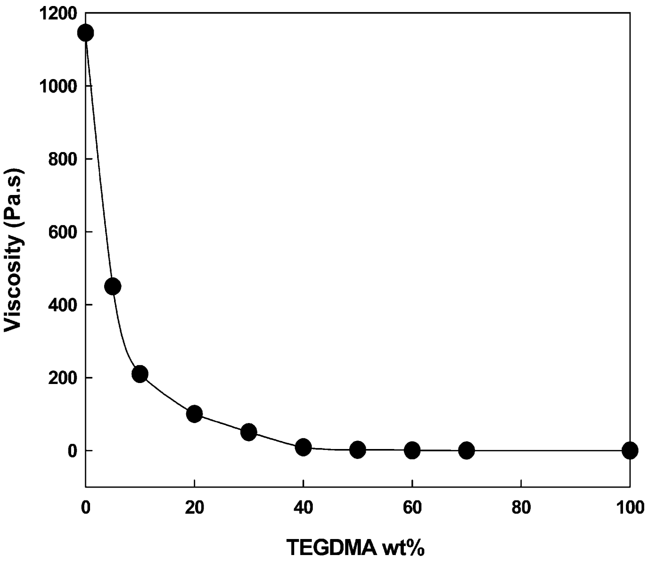


Figure 6. Changes in viscosity of the TMBis-GMA/TEGDMA mixtures as a function of TEGDMA content.

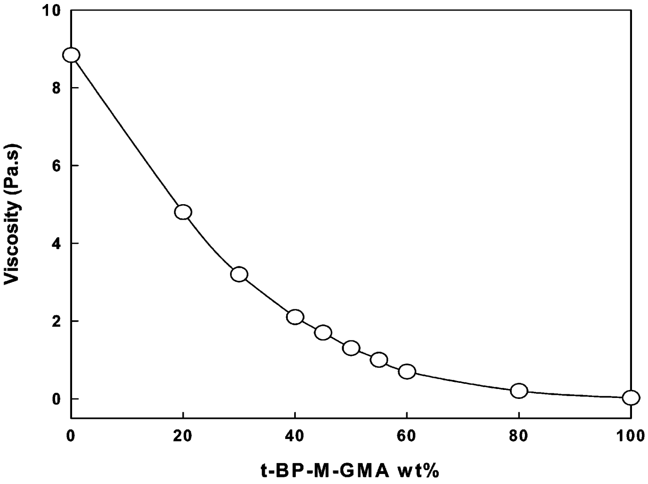


Figure 7. Changes in viscosity of the TMBis-M-GMA/t-BP-M-GMA mixtures as a function of t-BP-M-GMA content.

the mechanical strength of the former is compared with the latter after water absorption, the decrease of mechanical strength of the former is significantly smaller than that of the latter. In summary, methoxy substitution for hydroxyl groups in the base resin as well as addition of Bis-GMA derivative such as t-BP-M-GMA as a diluent could be a promising strategy for obtaining a dental composite that has reduced curing shrinkage along with excellent mechanical properties.

Summary

Various Bis-GMA derivatives were prepared to develop novel dental composites that have a low amount of curing shrinkage and excellent mechanical strength. Bis-GMA derivatives such as DMBis-GMA and TMBis-GMA was obtained by substituting the methyl groups for some or all of the four available positions onto the phenyl rings in bisphenol A, whereas other derivatives such as CP-GMA and t-BP-GMA were prepared by changing bisphenol A to 4-cumylphenol (or 4-*tert*-butylphenol). Methoxy substitution for hydroxyl groups in these Bis-GMA derivatives was also performed to reduce the viscosity. Various resin mixtures were examined to develop dental composite having a low amount of curing shrinkage. Among the resin mixtures that have nearly the same viscosity with the resin mixture that was used as a control, the TMBis-M-GMA/t-BP-M-GMA = 55/45 mixture exhibited the lowest curing shrinkage. When the curing shrinkage of a dental composite prepared from the TMBis-M-GMA/t-BP-M-GMA = 45/55 mixture is compared with that prepared from the resin mixture used as the control, reduction in the curing shrinkage was approximately 53%. Furthermore, the former exhibited a better mechanical strength than the latter. After water uptake, the latter exhibited a huge decrease in the mechanical strength, whereas the decrease in the mechanical strength of the former was negligible.

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