

Effects of Water Contents and Postcuring Conditions on Bis-GMA/TEGDMA Dental Restorative Composite Resins

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ABSTRACT: Dental restorative composite resins of the monomer bisphenol A glycerolate dimethacrylate (Bis-GMA/TEGDMA; 50/50, mass ratio), with different initial water contents in monomer mixtures and subject to various postcuring conditions, were prepared. The effects of water contents and postcuring conditions on photopolymerization rate, degree of methacrylate double bond conversion, and mechanical properties (flexural strength and elastic modulus) were systematically investigated. Within the scope of this investigation, the initial water content was not found to significantly affect the mechanical properties of the photocured composite resins. Nevertheless, the addition of distilled water into the monomer mixture slightly increased the degree of methacrylate double bond conversion, and slightly

slowed down the photocuring process, especially when the amount of water was oversaturated. Postcuring conditions of 37°C vapor or water aging increased the degree of methacrylate double bond conversion, but made the mechanical properties of the composite resins less desirable, especially under water-aging conditions. Postcuring treatment of the composite resins in a 100°C vacuum (~27.9 KPa) oven for 1 day improved both the flexural strength and the elastic modulus by at least 30%, but the improvements quickly diminished upon subsequent 37°C water aging. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 492–502, 2004

Key words: dental polymers; photopolymerization; aging; FTIR; kinetics

INTRODUCTION

Dental composites have been available for over four decades.^{1–4} Compared to dental amalgams, the composite resins have better esthetic properties and less safety concerns. Based upon a number of laboratory studies, the mechanical properties of the dental composites are not substantially different from those of dental amalgams.⁵ Therefore, composites have been widely accepted by the dental profession as a restorative material.

Dental restorative composites are composed of resin matrix and glass (or ceramic) fillers. The resin matrix is usually cured (hardened) by photoinitiated free-radical polymerization. The monomer bisphenol A glycerolate dimethacrylate (Bis-GMA), first introduced by Bowen,^{1–4} has been widely used as a base monomer. Bis-GMA is a very viscous, honeylike liquid. To improve its handling qualities, a low viscous

monomer, such as tri(ethylene glycol) dimethacrylate (TEGDMA), is added to Bis-GMA to decrease the viscosity.⁶ Reed and coworkers⁷ studied the photopolymerization kinetics, methacrylate double bond conversion, and photopolymerization-induced volumetric shrinkage of the visible light activated Bis-GMA/TEGDMA systems and demonstrated that Bis-GMA functioned to limit the shrinkage and enhance resin reactivity, whereas TEGDMA provided means to increase the methacrylate double bond conversion.

In each Bis-GMA molecule, as shown in Figure 1, there are two hydroxy groups, which make Bis-GMA quite hydrophilic and therefore able to promote water absorption. The absorbed water and its effects on the mechanical properties of the cured composites, as well as the rate of photopolymerization, especially after the composites are stored in a humid environment for a period of time (e.g., a few years of service), are a continuous concern. Earlier studies revealed that the dental composites made with Bis-GMA/TEGDMA resin filled with glass-modifying elements (e.g., quartz particles), experienced a severe reduction of mechanical properties during water aging. This reduction of mechanical properties was related to the leaching of filler components.^{8,9} The mechanism behind the leaching process during water aging was explained by a self-catalytic reaction.^{10,11} According to the theory proposed by Charles,¹² the leaking of sodium from the

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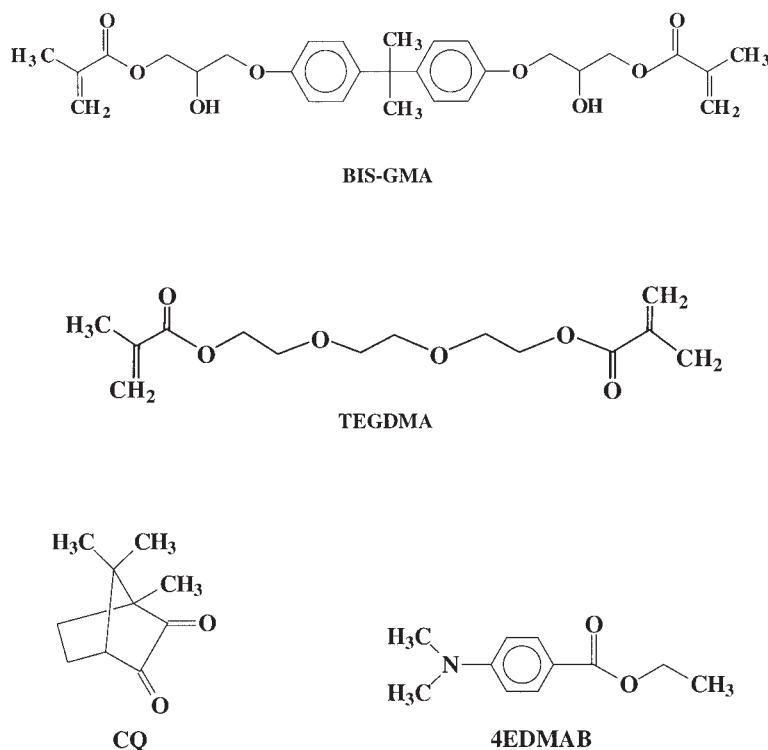


Figure 1 Molecular structures of monomers and photoinitiation system used in the work

glass filler caused an increase in hydroxy ion concentration at the glass/resin interface, and after reaching a critical pH value, these hydroxyl ions started to attack the silica network of the glass filler and caused significant decrease in mechanical properties, such as strength, fracture toughness, and wear properties.

However, very little research has been conducted to investigate the effects of initial water contents in monomers on the photopolymerization rate, the degree of methacrylate double bond conversion, and the mechanical properties of the neat composite resins (i.e., without filler) with various postcuring conditions. In this study, the above questions were systematically investigated by using 50/50 (mass/mass) mixtures of Bis-GMA/TEGDMA with different initial water contents and subjected to various postcuring conditions. Near-infrared spectroscopy (NIR) was employed to study the photopolymerization rate and the degrees of methacrylate double bond conversions; a universal mechanical testing machine (Instron) was used to characterize the mechanical properties of the cured composite resins and scanning electron microscopy (SEM) was used to observe the fracture surfaces.

EXPERIMENTAL

Materials

Bis-GMA and TEGDMA monomers (Fig. 1) were supplied by Esstech (Essington, PA). The commonly used photoinitiator camphorquinone (CQ) and coinitiator eth-

yl-4-(*N,N'*-dimethylamino) benzoate (4EDMAB), as shown in Figure 1, were selected as the visible light initiation system. CQ and 4EDMAB were purchased from Aldrich Chemical Company, Inc. (Milwaukee, WI). All materials were used as received without further purification.

Desiccation and formulation of monomer mixture systems

Except for the as-received condition, the monomer mixtures of Bis-GMA/TEGDMA (50/50, mass ratio) were dried by using the benzene azeotropic distillation method. Benzene, after being received from Aldrich Chemical Co., was desiccated by using a molecular sieve 4A (also received from Aldrich) for a week. Molecular sieve 4A was predesiccated in a 100°C vacuum oven (~ 27.9 KPa) for 5 days. The desiccated benzene was then mixed with Bis-GMA/TEGDMA mixture, and the solution was distilled at 50°C under a vacuum of about 1 Torr (133 Pa). The dried Bis-GMA/TEGDMA mixture was examined by NMR, and no water or benzene residue was identified. The dried Bis-GMA/TEGDMA mixture was subsequently added with different amounts of distilled water, using the formulations as described in Table I. Of the seven monomer mixture systems, Water 0, 1, 2, 3, 4, and 5 were clear mixtures, whereas Water 6 was a milky mixture, indicating the water was oversaturated. The initiator CQ (mass fraction of 0.2%) and the accelerator

TABLE I
Codes and Descriptions of the Monomer Mixture Systems Formulated in the Study

Code	Description
Water 0	As-received Bis-GMA/TEGDMA (50/50, mass/mass), no additional water added.
Water 1	Azeotropic dried Bis-GMA/TEGDMA (50/50, mass/mass), no additional water added.
Water 2	Azeotropic dried Bis-GMA/TEGDMA (50/50, mass/mass), 0.1% (mass fraction) additional water added.
Water 3	Azeotropic dried Bis-GMA/TEGDMA (50/50, mass/mass), 0.5% (mass fraction) additional water added.
Water 4	Azeotropic dried Bis-GMA/TEGDMA (50/50, mass/mass), 1.0% (mass fraction) additional water added.
Water 5	Azeotropic dried Bis-GMA/TEGDMA (50/50, mass/mass), 2.0% (mass fraction) additional water added.
Water 6	Azeotropic dried Bis-GMA/TEGDMA (50/50, mass/mass), 4.0% (mass fraction) additional water added.

4EDMAB (mass fraction of 0.8%) were added to each mixture system to allow for visible light curing.

Sample preparation and evaluation

Photopolymerization rate

The photopolymerization rate was studied based on the data acquired by the real-time near-infrared series runs (RT-NIR). RT-NIR refers to a technique collecting infrared spectra periodically (the time interval was 0.93 s in this study) *in situ* during a continuous reaction. By following the overtone of the vinyl band at $\sim 6167 \text{ cm}^{-1}$, the RT-NIR data provide valuable insight into photopolymerization rate and degree of methacrylate double bond conversion. The feasibility of this spectroscopic technique to monitor the curing behavior of dental methacrylate monomers was discussed in detail by Stansbury and Dickens.¹³

In this study, RT-NIR was conducted at ambient condition for 5 min, with four scans per spectrum at 8-wavenumber resolution. The curing light (MAX100, L. D. Caulk Co., Milford, DE) was manually turned on at 0.5 min and turned off at 1.5 min (i.e., the total photocuring time was 1.0 min). A Nicolet Magna-IRTM 550 FTIR (Nicolet Inc., Madison, WI) spectrometer continuously purged with dry air was employed to carry out the work. During the RT-NIR experiment, uncured neat resin was placed in a U-shaped Teflon® sample holder, with both sides covered by glass slides

(glass is transparent in the NIR region between 4000 and 6500 cm^{-1}). The glass slides were tightly attached to the sample holder by using small clamps. The dental curing light was placed directly above the sample holder. The relative uncertainty of the NIR intensity measurements was approximately $\pm 0.5\%$,¹⁴ based on the measurements of three independent runs for each monomer mixture system.

Flexural strength and elastic modulus

Flexural strength (FS) and elastic modulus (E_Y) of the photocured composite resins with various resin formulations (Table I), and subject to different postcuring conditions (Table II), were tested by using a standard three-point bending test method (ASTM F417-78, 1984). The bar-shaped specimens of the three-point bending test were prepared by using a homemade Teflon® mode, which had 12 bar-shaped pockets. Each pocket had a length of $\sim 25 \text{ mm}$, and a width and depth of $\sim 2.0 \text{ mm}$. The specimens were photocured for 2 min by using a TRIAD 2000 curing chamber, supplied by Dentsply International, Inc. (York, PA). After the photocuring, the specimens were taken out of the mode and carefully polished on all four sides with 2400-grit silicon carbide paper. The final dimensions of the specimens were then measured and recorded. The specimens were fractured in a three-point bending jig with a 20-mm span on a computer-

TABLE II
Codes and Descriptions of Various Postcuring Conditions

Code	Description
A	Ambient condition for 1 day.
B	Ambient condition for 1 day, then 37°C vapor chamber for 1 day.
C	Ambient condition for 1 day, then 37°C vapor chamber for 7 days.
D	Ambient condition for 1 day, then 37°C vapor chamber for 28 days.
E	Ambient condition for 1 day, then 37°C water for 1 day.
F	Ambient condition for 1 day, then 37°C water for 7 days.
G	Ambient condition for 1 day, then 37°C water for 28 days.
H	100°C, house vacuum ($\approx 27.9 \text{ KPa}$) for 1 day.
I	100°C, house vacuum ($\approx 27.9 \text{ KPa}$) for 1 day, then, 37°C water for 1 day.
J	100°C, house vacuum ($\approx 27.9 \text{ KPa}$) for 1 day, then, 37°C water for 7 days.
K	100°C, house vacuum ($\approx 27.9 \text{ KPa}$) for 1 day, then, 37°C water for 28 days.

controlled universal testing machine (model 5500R, Instron Corp., Canton, MA) at a crosshead speed of 0.5 mm per minute to record stress-strain curves. Six specimens, ~ 25 mm in length, 2 mm in width and thickness, were prepared and tested, for each resin formulation (Table I) under each postcuring condition (Table II). Calculations were made by using the formulas

$$FS = \frac{3PL}{2WT^2}$$

$$E_y = (P/d)(L^3/4WT^3)$$

where P is the load at fracture, L is the distance between two supports (which was set to be 20 mm), W is the width of the specimen, T is the thickness of the specimen, and d is the deflection, in millimeters, at load P .

Degree of methacrylate double bond conversion

For measuring the degrees of methacrylate double bonds conversions, three disc-shaped specimens of each resin formulation (Table I) under each postcuring condition (Table II) were prepared. The specimens were photocured by using the same procedure as described in the section above. Unlike the mode for making the three-point bending specimens, the home-made Teflon® mode for making the disc-shaped specimens had eight disk-shaped pockets. Each pocket had the diameter of ~ 6.3 mm and the depth of ~ 3.1 mm. Similar to the study of photopolymerization rate, NIR was used to measure the absorbance of methacrylate double bond. Prior to NIR measurement, the diameter and thickness of each specimen were carefully measured and recorded. The degree of double bond conversion was calculated by using the following equation. For each condition, three independent measurements were conducted

Degree of double bond conversion =

$$\left[1 - \frac{(\text{Absorbance of double bond after curing/Thickness})}{(\text{Absorbance of double bond before curing/Thickness})} \right] \times 100\%$$

It needs to be addressed that the use of the above equation to calculate the methacrylate double bond conversion does not take into account the photopolymerization-induced volumetric shrinkage, which would introduce a systematic error of ~ 3%. However, because the volumetric shrinkages of all the samples were similar, such a systematic error will not significantly affect the trends of the results.

Fracture surfaces

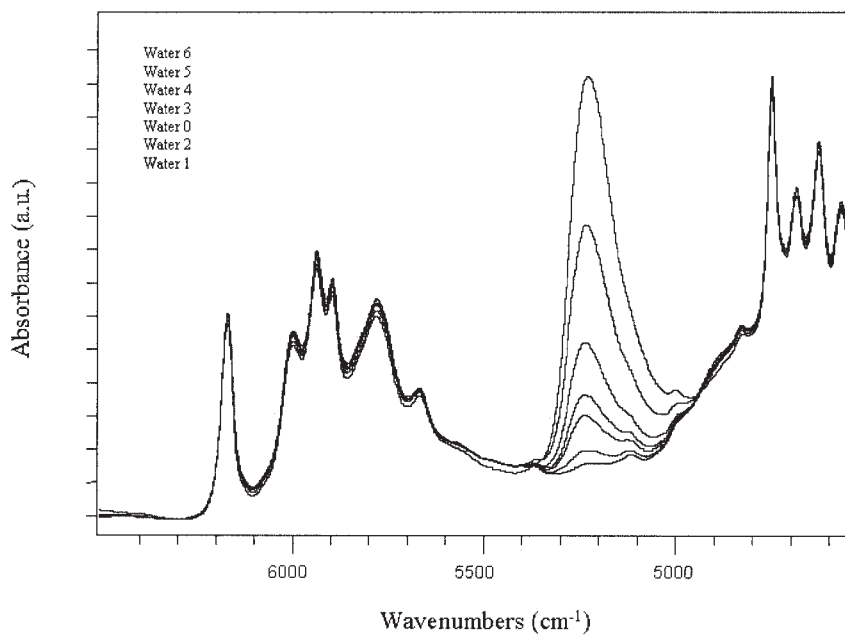
Fracture surfaces of the representative three-point bending specimens, with various resin formulations (Table I) and under different postcuring conditions (Table II), were examined by a SEM (model JSM-5300, JEOL, Peabody, MA). Prior to SEM observations, the samples were sputter coated with a thin layer (~ 5 nm) of gold to allow for better electrical conduction.

RESULTS AND DISCUSSION

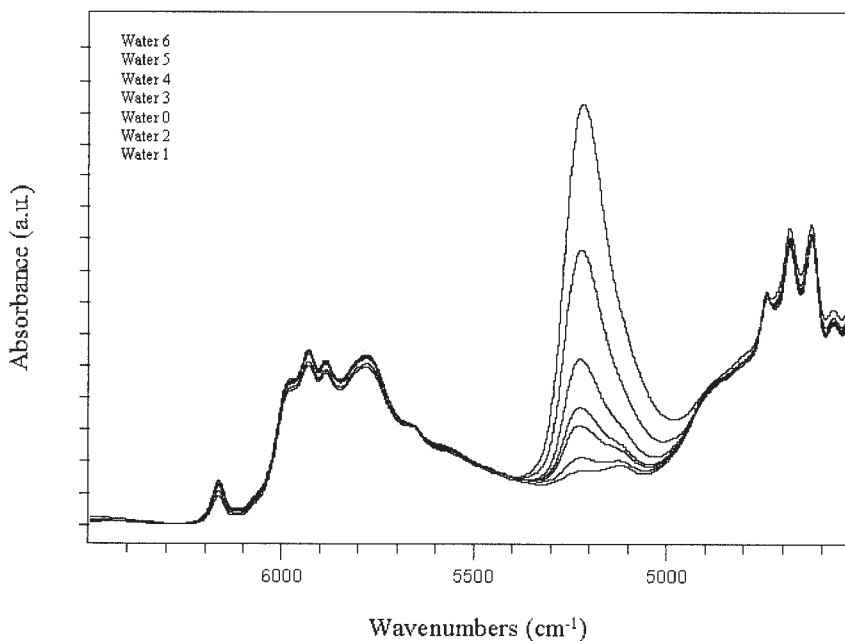
NIR and photopolymerization rate

NIR spectrum was composed of combination and overtone bands of fundamental bands that absorb in the mid-IR spectrum. Unlike mid-IR, most bands other than those from C—H, O—H, and N—H were too weak to register in the NIR region. The absorption of =C—H is located at about 4743 cm^{-1} , and the first overtone was located at about 6167 cm^{-1} . Because 4743 cm^{-1} was in the combination region, the baseline dropped sharply in the vicinity, and reliable peak area measurements were difficult. The overtone band at 6167 cm^{-1} was therefore selected for measuring the degree of methacrylate double bond conversion, even though it had lower absorptivity than the 4743 cm^{-1} combination band. The absorption of the phenyl structure in Bis-GMA was located at about 4623 cm^{-1} . This peak should remain the same before and after the photopolymerization and was suggested as an internal standard for the Bis-GMA/TEGDMA system.¹³ However, this peak along with its baseline could be significantly affected by the neighboring peaks and other conditions; to use it as the internal standard required careful calibration. In this study, instead of using the phenyl peak as the internal standard, the absorbance of the methacrylate double bond was normalized to the thickness of the specimen, based on the Beer-Lambert Law.

The NIR spectra of the samples (Table I) before and after the photopolymerization were shown in Figure 2(a and b), respectively. The spectra were in the order of Water 6, 5, 4, 3, 0, 2, and 1, from top to bottom in each plot. Such a sequence also represented the reduction of water content from high to low. As shown in Figure 2, for all samples, the intensity of absorption around 4743 and 6167 cm^{-1} , which were associated with the methacrylate double bonds, decreased significantly after photocuring, indicating that a majority of the methacrylate double bond had been polymerized. In addition, the intensity of absorption in the region from 5000 to 5300 cm^{-1} was severely affected by the water content. The higher the water content, the greater the intensity of the absorption. For the sample of Water 0, which referred to the Bis-GMA without azeotropic distillation, the water content was slightly less than that of the sample of Water 3. This indicated



(a)

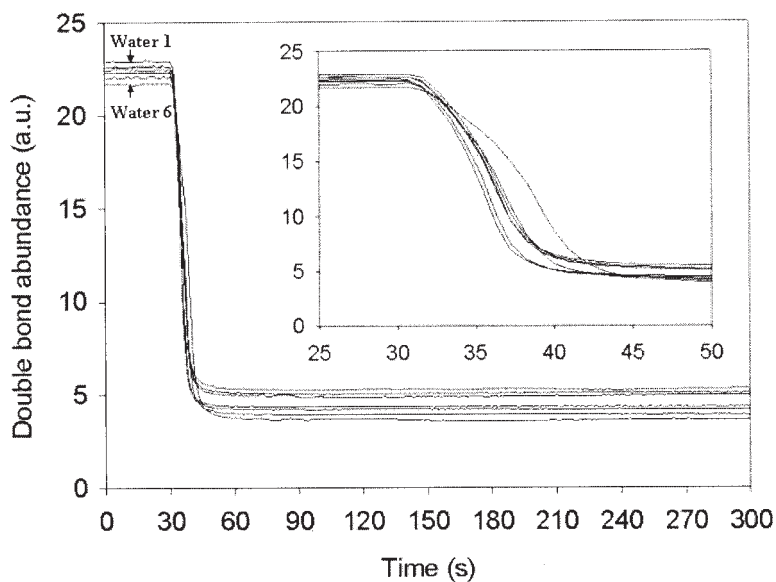


(b)

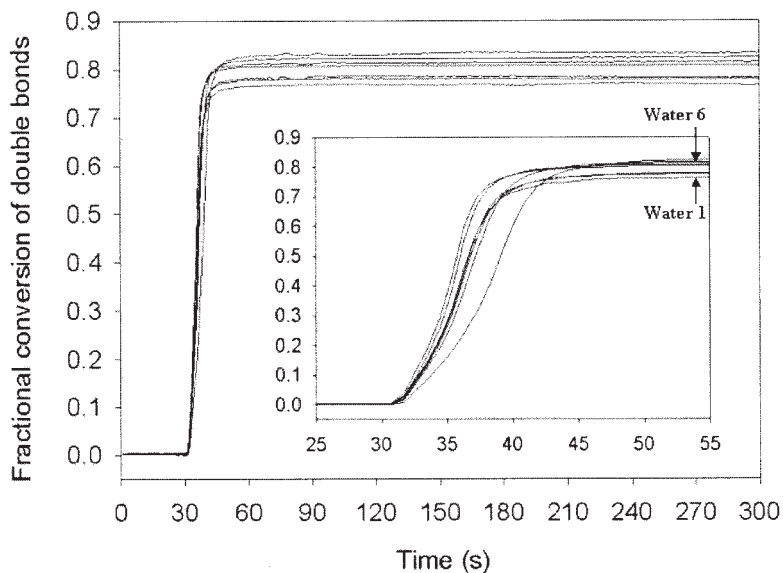
Figure 2 NIR spectra of the samples of Water 6, 5, 4, 3, 0, 2, and 1 (from top to bottom), (a) before and (b) after the photocuring.

that the monomer mixture made from as-received Bis-GMA/TEGDMA (50/50 mass ratio) had slightly $<0.5\%$ (mass fraction) water content. In addition, for the sample of Water 1, although the majority of water

was removed by azeotropic distillation, there was still a trace amount of water left. According to the previous research,^{14,15} the absorption of free water occurred at a higher wavenumber ($\sim 5250 \text{ cm}^{-1}$); while the absorp-



(a)



(b)

Figure 3 NIR photocuring profiles showing (a) double bond abundance, (b) fraction of double bond conversion, versus time. (The curves, from top to bottom in each plot, represented the samples of Water 1, 2, 0, 3, 4, 5, and 6, respectively.)

tion of hydrogen-bonded water occurred at a lower wavenumber ($\sim 5120 \text{ cm}^{-1}$). Thus, the majority of the residual water in Water 1 existed as the hydrogen-bonded water ($\sim 5120 \text{ cm}^{-1}$), whereas in the other samples, more water existed as the free water ($\sim 5250 \text{ cm}^{-1}$). This result also revealed that the azeotropic distillation could not completely remove the hydrogen-bonded water in the Bis-GMA/TEGDMA system. Meanwhile, it was also noticed that during photopolymerization the water peaks shifted $\sim 20 \text{ cm}^{-1}$ to the

higher wavenumbers and returned back after curing. The reason was that the polymerization reaction generated heat and caused the temperature to rise. The higher temperature weakened hydrogen bonds and caused more water to exist as free water (5250 cm^{-1}) instead of the hydrogen-bonded water (5120 cm^{-1}).

By following the intensity of the absorption of the methacrylate double bond (6100 to 6227 cm^{-1}), RT-NIR could provide information about the double bond abundance *in situ* with the reaction time. In Figure

3(a), the curves represented samples of Water 1, 2, 0, 3, 4, 5, 6, respectively, from top to bottom. As explained earlier, during the RT-NIR measurements, the curing light was manually turned on at about 0.5 min (30 s) and turned off at about 1.5 min (90 s). To better observe the variation of methacrylate double bond right after the light was turned on, the inset plot in Figure 3, which was the magnified region between the time periods from 25 to 50 s, was made. By using the double bond abundance before photocuring as reference, the fractional conversion of double bond versus the reaction time could be calculated, as shown in Figure 3(b). Figure 3(a, b) showed that the addition of distilled water to the Bis-GMA/TEGDMA (50/50, mass fraction) monomer mixture systems did not result in major changes during the photocuring process, either to the photopolymerization rate or to the methacrylate double bond conversion. Nevertheless, the addition of water caused some minor differences.¹ The initial uncured methacrylate double bond abundance decreased with water content. This was simply because the addition of water diluted the methacrylate double bonds.² The addition of water slightly increased the double bond conversion. This might be due to the addition of water slightly increasing the mobility of the methacrylate monomers.³ The addition of water slightly slowed down the curing process, especially when water was oversaturated (Water 6). Because slope of the curves at each point in the inset of Figure 3(b) was the polymerization rate at that specific time, the polymerization rate of Water 6 sample was slower than those of the others. This was because oversaturated water acted like a plasticizer and might hinder the chain propagation during the photopolymerization.

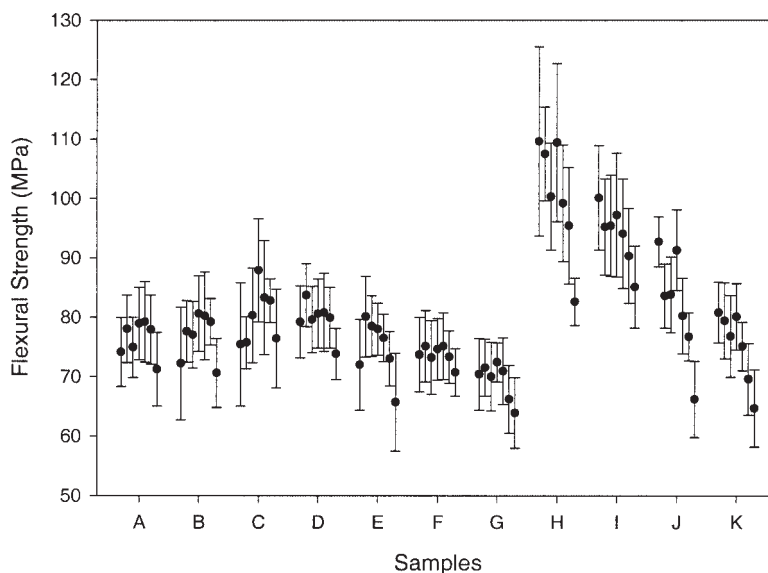
Mechanical properties

The mechanical properties of the cured resins with different initial water contents (Table I), and subjected to different postcuring conditions (Table II), were the focus of this study. As shown in Figure 4(a, b), the effects of water contents on both flexural strength and elastic modulus were complicated. In general, the samples without postcuring heating (A to G) had less distinguishable variations of mechanical properties, regardless of whether aging in vapor or water at 37°C for various periods of time. To the samples subjected to postcuring 100°C vacuum heating (H to K), although both flexural strength and elastic modulus were improved by at least 30%, the improvement quickly diminished upon the subsequent 37°C water aging.

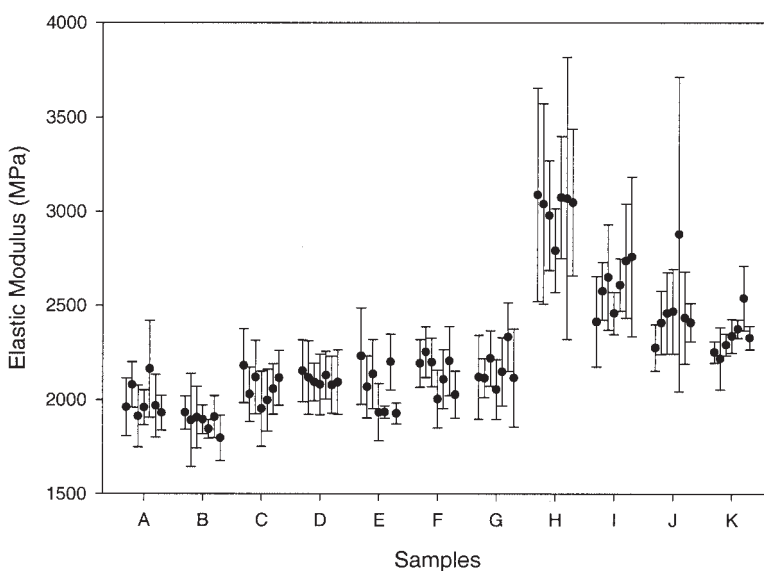
Previous work^{16,17} suggested that the water uptake of the cured resin at a given temperature consisted of two processes. First, the matrix took up moisture, and water entered the specimens from the surface. Then,

water molecules diffused into the composites through microflaws such as pores and cracks. As the water absorption process continued, soluble components and/or unreacted low-molecular-weight matters leached out, resulting in the formation of microvoids within the composites. In addition, the absorbed water was believed to be able to create new cracks due to large microstresses as a result of moisture absorption.^{16,17} In this study, the samples subjected to postcuring 100°C vacuum heating were found to have higher flexural strength and elastic modulus. This was because the high temperature resulted in further curing of the specimen. However, the further curing, which happened in a relatively short time period during the postcuring vacuum heating, might also result in the internal stress to develop locally, and generated voids and microflaws. After immersing these samples in water, the diffusion and penetration of water molecules into the composite resins were much easier and quicker. This was the reason the samples after postcuring vacuum heating suffered a faster reduction of mechanical properties upon subsequent water aging. In addition, the postcuring vacuum-heated samples also presented relatively larger standard deviations for both strength and modulus, indicating the voids and microflaws were formed randomly in the composite resins.

For the samples without postcuring vacuum heating, the moduli [A to G in Fig. 4(b)] were not found to have apparent differences upon vapor or water aging [one-way analysis of variance (ANOVA), $P > 0.05$]. This result suggested that the cured composite resins, regardless the initial water contents, were unlikely to uptake much water to get swollen and soft. Regarding the strength [A to G in Fig. 4(a)], the situations were a little more complicated. There was also no appreciable variation in the samples upon vapor aging, but for the samples upon water aging, the strength seemed to gradually decrease, but such reduction happened at a much slower rate than those of the vacuum-heated samples. This result suggested that vapor was less likely to make the soluble components and/or unreacted low-molecular-weight matters in the cured composite resins to leach out, but water could. Unlike the samples subjected to postcuring vacuum heating, the samples without postcuring vacuum heating had less voids and microflaws in the composite resins; therefore, the water uptake and component leaching out happened at a much slower rate. In addition, the postcuring vacuum heating removed absorbed and even hydrogen-bonded water, while the samples without postcured heating had the water left. The initial water in the composite resins might hinder the diffusion and penetration of the external water and prevent the fast decrease of the mechanical properties of the cured resins.



(a)



(b)

Figure 4 (a) Flexural strength and (b) elastic modulus, of the composite resins with different initial water contents, and subject to various postcuring conditions. (The seven data, from left to right in each postcuring condition, represented the samples of Water 0, 1, 2, 3, 4, 5, and 6, respectively.)

Figure 4(a) also showed that the water-oversaturated sample of Water 6, under all kinds of postcuring conditions, had lower flexural strength than the other water-undersaturated samples (paired different test, Water 1 to Water 6, $P < 0.05$). This result suggested that when the water content in the monomer system was oversaturated (Water 6), the water was likely to form clusters that functioned like microvoids, which resulted in lower strength. However, when the content of water was undersaturated (Water 0 to Water 5), it seemed there was no apparent dependence of flex-

ural strength on water content. This result implied that, when the resin was under saturation, the water molecules could tightly associate with the monomers and would not significantly affect the flexural strength of the cured composite resin.

Methacrylate double bond conversion

The degrees of the methacrylate double bond conversions with different initial water contents in the monomer systems (Table I), and with different postcuring

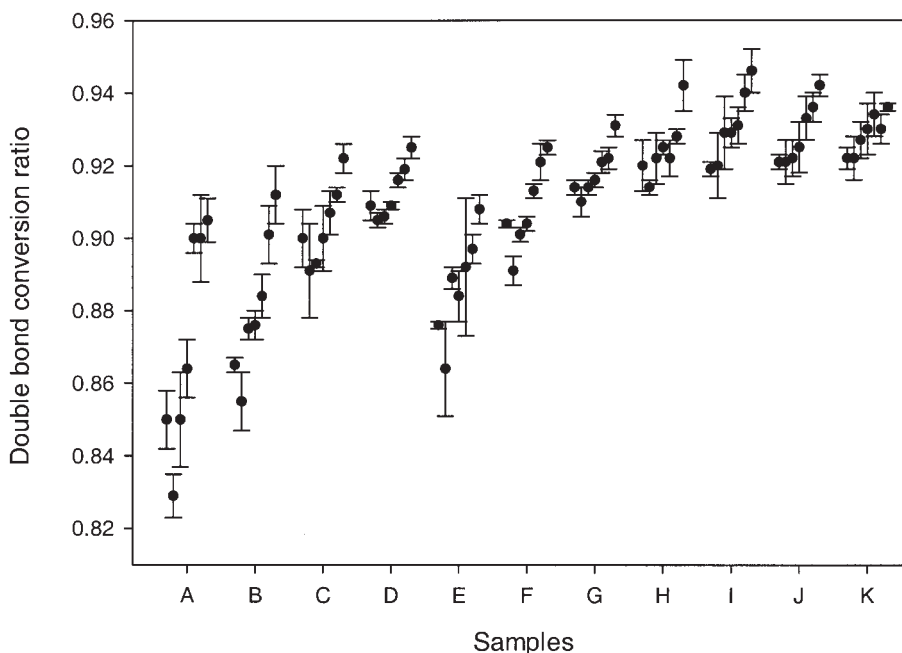


Figure 5 Methacrylate double bond conversions of the composite resins with different initial water contents and subject to various postcuring conditions. (The seven data, from left to right in each postcuring condition, represented the samples of Water 0, 1, 2, 3, 4, 5, and 6, respectively.)

conditions (Table II), were calculated by using the equation in Experimental and were shown in Figure 5. Figure 5 indicated the following: (1) under all kinds of postcuring conditions, the higher the initial water content, the higher the degree of double bond conversion; and (2) Water 6 system had the highest conversion among all systems ($P < 0.05$, ANOVA). This further confirmed the previous result (see above) that the addition of water into the monomer mixture improved the degree of methacrylate double bond conversion. Besides, for the samples without postcuring vacuum heating (A to G in Fig. 5), the longer the postcuring time, the higher the degree of double bond conversion. This revealed that the polymerization had continued after the photocuring for quite a long time, at least a month. Nevertheless, if the samples received postcuring 100°C vacuum heating (H to K in Fig. 5), the continuous polymerization did not happen. This was because during 100°C vacuum heating, most of the postcurable methacrylate double bonds reacted, and the composite resin could not be further cured. An interesting fact was, for conditions of D, G, H, I, J, and K in Figure 5, the degrees of methacrylate double bond conversions were about the same, but the mechanical properties were quite different (Fig. 4). The observation implied that (1) after the photopolymerization, the leftover amount of postcurable methacrylate double bonds could be further cured either by heating or by long-time aging, (2) the degree of methacrylate double conversion was not the only factor that determined the strength and modulus of the

cured resin. The relationship between the double bond conversion and the mechanical properties further depended on postcuring conditions.

Fracture surface

After three-point bending test, the specimens were collected for examination of the fracture surfaces by using a scanning electron microscope. Within the scope of this SEM observation, it seemed that different postcuring conditions had little SEM observable effect on the fracture surfaces. SEM images of the fracture surfaces from the samples of Water 0, 1, 2, 3, 4 and 5 were essentially indistinguishable. However, in the Water 6 samples, numerous water voids could be identified at the fracture surfaces (Fig. 6). These observations further indicated that in undersaturated systems (i.e., in Water 0, 1, 2, 3, 4, and 5), water molecules could mix homogeneously with Bis-GMA/TEGDMA [Fig. 6(a)]. Nevertheless, if the water was oversaturated (i.e., in Water 6), it was more likely to form sphere-shaped droplets with the average diameter of $\sim 10\text{--}50\ \mu\text{m}$ [Fig. 6(b)]. These water droplets might be the places where stress was accumulated during the flexural strength testing and perhaps was the reason the flexural strength of samples from the Water 6 system was lower than the other resin systems [as shown in Fig. 4(a)]. It also needed to address that the micropores and microcracks that had been postulated as the cause for loss of strength in postcuring vacuum-heated samples were not clearly observed within this

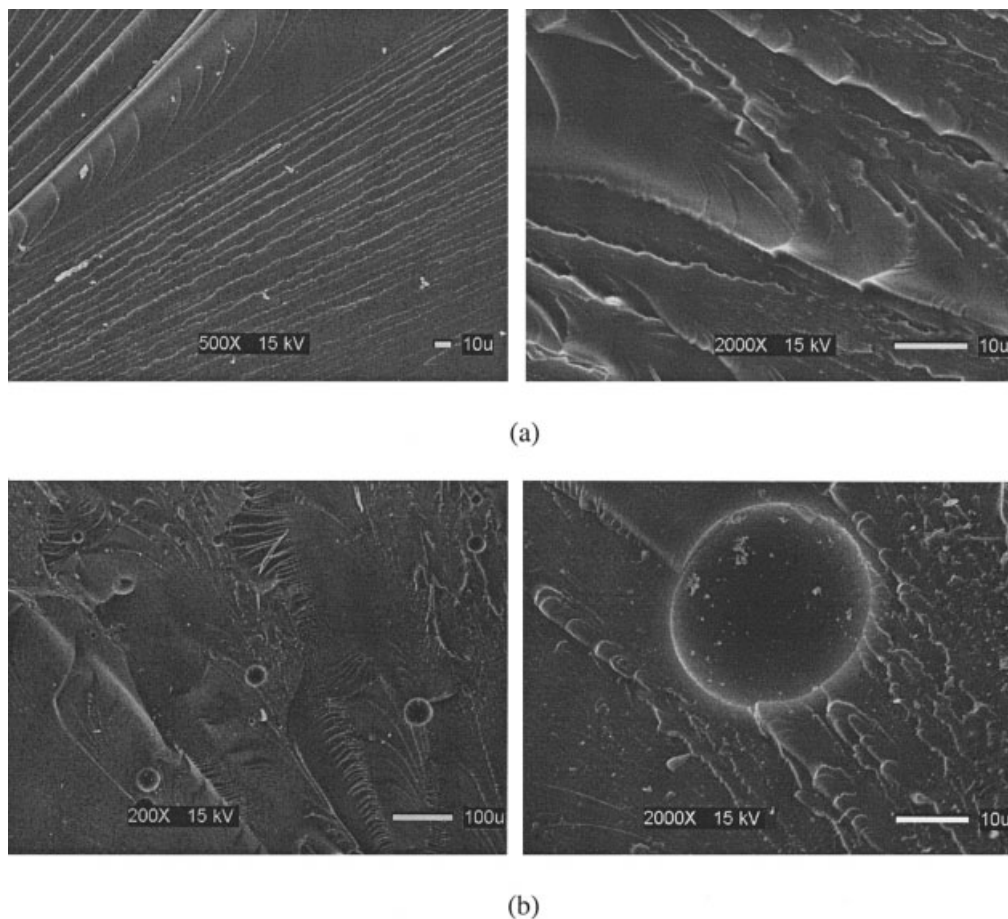


Figure 6 SEM images of representative fracture surfaces of the cured composite resins. (a) Water 1 and (b) Water 6. (In each pair of images, the left one had a lower magnification, and the right one had a higher magnification.)

SEM study. This observation merited further study to establish flaw presence in postcuring vacuum heated composite resins.

CONCLUSION

In this study, dental restorative composite resins of Bis-GMA/TEGDMA (50/50, mass ratio), with different initial water contents in monomer mixture systems (Table I), and subject to various postcuring conditions (Table II), were prepared. The systematic investigations of the water contents and various postcuring conditions on the photopolymerization rate, mechanical properties of the cured composite resins, and the degrees of methacrylate double bond conversions were carried out. Within the scope of this investigation, the water content was found to have less appreciable effects to either the photopolymerization rate or the degree of methacrylate double bond conversion. However, the addition of distilled water into the monomer mixtures resulted in some minor differences, including slightly slowing down the curing process, especially when water was oversaturated.

The postcuring 100°C vacuum heating increased flexural strength and elastic modulus of the composite resins by at least 30%. However, the improvements would quickly diminish upon subsequent water aging. Unlike the samples subjected to the postcuring vacuum heating, the samples without postcuring heating generated less distinguishable variations in mechanical properties (modulus and strength) upon vapor or water aging. In addition, the sample of Water 6 (which was oversaturated with water), under all kinds of postcuring conditions, had lower flexural strength than the other samples (which were undersaturated with water).

NIR spectra revealed that the water contents affected the near-infrared absorption region from 5000 to 5300 cm^{-1} . The results of the methacrylate double bond conversions showed that, under all kinds of postcuring conditions, the higher the initial water content, the higher the degree of double bond conversion; therefore, Water 6 system had the highest conversion among all systems. Besides, for the samples without postcuring vacuum heating (A to G in Fig. 5), the longer the postcuring time, the higher the degree of

double bond conversion. Nevertheless, if the samples received postcuring 100°C vacuum heating (H to K in Fig. 5), the postcuring continuous polymerization did not happen. In addition, for the samples of D, G, H, I, J, and K in Figure 5, the degrees of methacrylate double bond conversions were roughly the same, but the mechanical properties were quite different (Fig. 4). The result suggested that (1) after the photopolymerization, the leftover amount of postcurable methacrylate double bonds could be further cured either by heating or by long-time aging, and (2) the degree of methacrylate double conversion was not the only factor that determined the strength and modulus of the cured resin.

SEM images showed that the fracture surfaces of Water 0, 1, 2, 3, 4, and 5 were essentially indistinguishable, but for the Water 6 sample, numerous water voids could be identified on the fracture surfaces. The formation of these water voids could be the reason for the lower flexural strength of the Water 6 samples compared to the other samples.

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