

Water Sorption, Degree of Conversion, and Hydrophobicity of Resins containing Bis-GMA and TEGDMA

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In this study, water sorption of resins and composites containing Bis-GMA and TEGDMA in various proportions were measured, and the influence of degree of conversion and the hydrophobicity of the material on the water sorption characteristics of Bis-GMA/TEGDMA resins were evaluated. Unfilled resins and composites containing Bis-GMA/TEGDMA, with a ratio of 1/1, 2/1, or 3/1 by weight, were prepared and cured. Water uptake and the degree of conversion of each specimen were determined, and the hydrophobicity was compared by measuring the contact angle of water. Both unfilled resins and composites containing Bis-GMA/TEGDMA in the ratio of 1/1 showed significantly greater water uptake than the others. The degree of conversion of the specimens increased as the proportion of TEGDMA was increased, and no inverse relationship was found between the water sorption and the degree of conversion. In contrast, the contact angle of the 1/1-specimen was less than the others, demonstrating significant correlation with the water uptake. These findings indicate that Bis-GMA/TEGDMA resins showed the greatest water uptake at the ratio of 1/1, and the water sorption characteristic was not influenced by the degree of conversion but mainly by the hydrophobicity of the material.

Key words: Water sorption, Resins, Degree of conversion

INTRODUCTION

There have been several studies investigating the influence of water sorption on physical properties of resin composites¹⁻⁸⁾. Some reports describe beneficial effects; the relaxation of polymerization contraction is obtained by hygroscopic expansion, and marginal adaptability of composite restorations can be improved¹⁻⁴⁾. On the other hand, deleterious effects have also been reported; water sorption deteriorates composites and the mechanical properties of the materials are hampered⁵⁻⁸⁾. Therefore, water sorption is considered to be an important phenomenon relevant to the durability of composite restorations.

It would be beneficial for the prediction of clinical results if the water sorption behavior of composites could be speculated from their composition. Although the influence of silanization and filler types on the water sorption of composites have been well documented^{6,9-13)}, the relationship between the components of the polymer matrix and the water sorption kinetics of composites has not yet been clarified in detail. For Bis-GMA/TEGDMA resins widely used in commercially available composites,

only a few studies have focused on the water sorption characteristics and composition. Kalachandra and Turner¹⁴⁾ demonstrated that the uptake of water by Bis-GMA/TEGDMA co-polymer, which is cured by heat, increased as the proportion of TEGDMA increased. On the contrary, Matsumae *et al.*¹⁵⁾ clarified that light-activated Bis-GMA based resins with 35% TEGDMA showed the smallest water uptake among specimens incorporating 25-45% TEGDMA. The reason for these conflicting results is not known, and it is of interest to elucidate the relationship between the composition of Bis-GMA/TEGDMA resins and other properties relevant to water sorption characteristics.

The purpose of the present investigation was to determine the water sorption, degree of conversion and the hydrophobicity of experimental unfilled resins and composites containing Bis-GMA and TEGDMA in various proportions, and to elucidate the relationships, if any, between these properties.

MATERIALS AND METHODS

Specimens

2, 2-bis [4-(3-methacryloxy-2-hydroxypropoxy) phenyl] propane (Bis-GMA, Shin Nakamura Kagaku, Wakayama, Japan) was purified, and triethyleneglycol dimethacrylate (TEGDMA, Shin Nakamura Kagaku) was used without further purification. Other reagent grade chemicals, dimethylaminoethyl methacrylate (DMAEMA, Wako Pure Chemical Industries, Osaka, Japan), camphorquinone (CQ, Wako Pure Chemical Industries) and butylhydroxytoluene (BHT, Wako Pure Chemical Industries) were used as received from the manufacturer.

Three kinds of Bis-GMA/TEGDMA unfilled resins were prepared by mixing the respective monomers in the ratios of 1/1, 2/1 and 3/1 by weight (Table 1). CQ and DMAEMA were added to each resin as catalysts. To prepare the resin composite, SiO₂ filler treated with silane-coupling agent was loaded at 65 wt% to each unfilled resin.

Table 1 Compositions of the materials used (% w/w)

	Code	Bis-GMA	TEGDMA	DMAEMA	CQ	BHT	filler
Unfilled resin							
Bis-GMA/TEGDMA: 1/1	U1	48.52	48.52	1.94	0.97	0.05	0
2/1	U2	65.02	32.02	1.94	0.97	0.05	0
3/1	U3	72.78	24.26	1.94	0.97	0.05	0
Composites							
Bis-GMA/TEGDMA: 1/1	C1	16.98	16.98	0.68	0.34	0.02	65.0
2/1	C2	22.75	11.21	0.68	0.34	0.02	65.0
3/1	C3	25.47	8.49	0.68	0.34	0.02	65.0

Bis-GMA: 2, 2-bis [4-(3-methacryloxy-2-hydroxypropoxy) phenyl] propane
 TEGDMA: triethyleneglycol dimethacrylate
 DMAEMA: dimethylaminoethyl methacrylate
 CQ: camphorquinone
 BHT: butylhydroxytoluene

Each unfilled resin or composite paste was placed into a stainless steel mold (10 mm diameter, 2 mm high), and the surfaces were covered with a celluloid matrix (GC, Tokyo, Japan) and glass slides. The top and bottom surfaces were irradiated for 160 sec each with a light activation unit (Quick Light VL-1, Morita, Kyoto, Japan), then subjected to further light exposure for 10 min using a light source (α -Light II, Morita) at room temperature to achieve complete curing. The specimens were stored in a desiccator at 37°C for 1 week.

Water sorption

Water sorption and the diffusion coefficient for water of each material were determined according to the method previously reported¹⁶. Before immersion in water, the weight (W_0) of each specimen was measured, and the volume (V_0) was calculated from the diameter and the thickness. The specimen was then placed into 10 ml of distilled water maintained at 37°C. Periodically, the specimen was picked up and reweighed (W_1) after blotting away the surface water with paper until free from visual moisture. This procedure was continued for 5 weeks for unfilled resins and 6 weeks for composites. The values of water sorption (W_{sp}) in $\mu\text{g}/\text{mm}^3$ were calculated using the following equation :

$$W_{sp} = (W_1 - W_0) / V_0$$

The diffusion coefficient was calculated from the slope of the graph plotting M_t/M_∞ and $t^{1/2}/2l$, where M_t and M_∞ represent the water absorbed at times t and at equilibrium, respectively, and $2l$ is the thickness of the specimen¹⁷.

The specimens were stored in a desiccator at 37°C for 1 week after the water sorption experiment, and the solubility of each material in $\mu\text{g}/\text{mm}^3$ was calculated from the weight of the dried specimens after the experiment and W_0 .

Degree of conversion

Uncured paste of each material was smeared on a potassium bromide disc and the absorbance peaks before curing were obtained by transmission mode Fourier transformation infrared spectroscopy (FTIR, 8100M, Shimadzu, Kyoto, Japan). The cured specimen was then pulverized into a fine powder with a mortar and pestle. Fifty μg of powder was mixed with approximately 5 mg of potassium bromide, and the absorbance peaks were recorded by diffuse-reflection mode FTIR. As previously reported¹⁸, the percentage of unreacted double carbon bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638.6 cm^{-1})/aromatic C...C (peak at 1609.4 cm^{-1}) before and after curing of the specimen, and the degree of conversion was calculated by subtracting the % C=C from 100%.

Contact angle

The contact angle of distilled water on each specimen was determined as a parameter of hydrophobicity. One μl of distilled water was placed on each specimen and the contact angle was measured after 60 sec with a contact angle goniometer (Erma, Tokyo, Japan). The measurement was carried out at three points on each of the

specimens at $23 \pm 2^\circ\text{C}$.

Statistical analysis

In all experiments, five specimens were tested for each material, and the data were analyzed by ANOVA, Sheffe's *F*-test and Pearson's correlation test at a significance level of 0.05.

RESULTS

Water sorption

Figs. 1 and 2 show the water uptake of unfilled resins and composites for each immersion period. Water sorption of unfilled resins reached a plateau after 4 weeks of immersion as the weight change was less than 0.05 mg for each specimen (ca. $0.32 \mu\text{g}/\text{mm}^3$) after this time. For composites, the equilibrium of water uptake was obtained at 5 weeks of immersion.

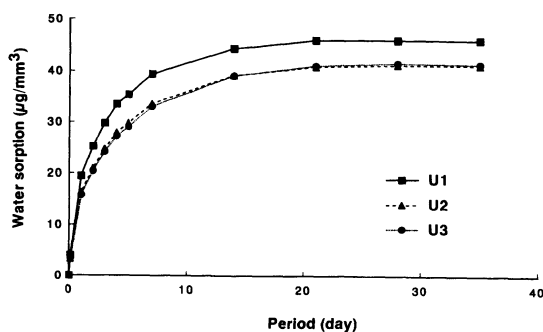


Fig. 1 The amount of water uptake of unfilled resins for each immersion period. The plots indicate mean of five replicates.

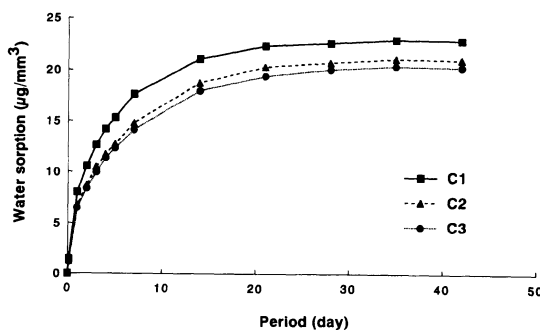


Fig. 2 The amount of water uptake of composites for each immersion period. The plots indicate mean of five replicates.

Table 2 Water uptake, diffusion coefficient, solubility, degree of conversion and contact angle of unfilled resins

	Water uptake ($\mu\text{g}/\text{mm}^3$)	Diffusion coefficient ($D \times 10^{-8} \text{cm}^2\text{sec}^{-1}$)	Solubility ($\mu\text{g}/\text{mm}^3$)	Degree of conversion (%)	Contact angle ($^\circ$)
U1	46.0 (0.2)	1.71 (0.04)	2.57 (0.11)	68.5 (2.1)	61.1 (1.2)
U2	41.2 (0.3)	1.49 (0.05)	2.50 (0.46)	58.9 (2.1)	67.6 (1.4)
U3	41.5 (0.6)	1.26 (0.10)	2.44 (0.40)	53.2 (3.9)	68.6 (1.7)

(): standard deviation of five replicates

vertical lines indicate no significant difference ($p > 0.05$)

Table 3 Water uptake, diffusion coefficient, solubility, degree of conversion and contact angle of composites

	Water uptake ($\mu\text{g}/\text{mm}^3$)	Diffusion coefficient ($D \times 10^{-8} \text{cm}^2\text{sec}^{-1}$)	Solubility ($\mu\text{g}/\text{mm}^3$)	Degree of conversion (%)	Contact angle ($^\circ$)
C1	22.9 (1.7)	1.08 (0.01)	1.63 (0.28)	70.8 (2.2)	61.0 (1.9)
C2	21.1 (0.5)	0.83 (0.04)	1.66 (0.25)	58.9 (2.1)	67.7 (1.1)
C3	20.4 (0.2)	0.81 (0.01)	1.60 (0.11)	52.0 (2.1)	68.9 (1.8)

(): standard deviation of five replicates

vertical lines indicate no significant difference ($p > 0.05$)

The amount of water uptake at equilibrium, the diffusion coefficient for water ($D \times 10^{-8} \text{cm}^2\text{sec}^{-1}$), and the solubility of the samples are summarized in Tables 2 and 3. Unfilled resins showed a water uptake almost twice that of composites containing corresponding resins. The water uptake of U1, consisting of Bis-GMA and TEGDMA at the rate of 1/1, was significantly greater than U2 and U3 ($p < 0.05$, Sheffe's F -test), and there were no significant differences between U2 and U3. The diffusion coefficients of unfilled resins were greater ($p < 0.05$) as the proportion of TEGDMA was increased. As for composites, C1, containing 1/1-Bis-GMA/TEGDMA resin, demonstrated significantly greater water uptake and diffusion coefficient ($p < 0.05$) than C2 and C3, although no differences were found between C2 and C3.

There were no significant differences ($p > 0.05$) in the solubility among the three specimens for either unfilled resins or composites (Tables 2 and 3).

Degree of conversion

The degree of conversion of each specimen of unfilled resins and composites is shown in Tables 2 and 3. For both materials, the specimen containing the greater amount of TEGDMA demonstrated significantly greater conversion ($p < 0.05$).

Contact angle

The relationship between the contact angle and the amount of TEGDMA incorporated were similar for unfilled resins and composites (Tables 2 and 3). The value for U1 was significantly less than the values for U2 and U3 ($p < 0.05$), and C1 showed less value than C2 and C3 ($p < 0.05$). However, there were no significant differences between U2 and U3, or between C2 and C3.

DISCUSSION

The process of water uptake by a resin based material is complicated, and several factors including hydrophilicity of the material^{10,19)} and cross-link density^{19–22)} are involved. In the present study, we focused on the composition of the monomers and the water sorption characteristics of Bis-GMA/TEGDMA resins. Additionally, we determined the degree of conversion and the hydrophobicity of each material, and elucidated the relationship between the water sorption and these properties.

The measurement of the amount of water uptake and the diffusion coefficient for water indicated that unfilled resins containing 1/1–Bis-GMA/TEGDMA absorbed significantly more water than the specimens containing Bis-GMA/TEGDMA at 2/1 or 3/1. The lack of difference in the solubility among the three specimens validates the significance of difference in the amount of absorbed water. The present results are in agreement with the previous findings in that heat-cured co-polymers made of 50% Bis-GMA and 50% TEGDMA showed greater water uptake than the co-polymers of 70% Bis-GMA and 30% TEGDMA¹⁴⁾. Composites specimens showed similar results to unfilled resins, indicating that the water uptake of the specimen containing 1/1–Bis-GMA/TEGDMA was significantly greater than the others. For the composites used in the present study, SiO₂ filler was loaded at 65% by weight, and this filler content was approximately 46% in terms of the volume. The water uptake by composite specimens was almost half that of corresponding resins, and this implies that the water sorption by composites reflects the uptake of water by polymer matrix. Generally, the proportion of Bis-GMA and TEGDMA in proprietary composites ranges from 1/1 to 3/1, and it is possible that composites with Bis-GMA/TEGDMA at the ratio of 1/1 absorb more water than the others if they include similar amounts of filler.

The degree of conversion of both unfilled resins and composites was greater as the proportion of TEGDMA was increased. The addition of diluent monomer to base resin improves not only the handling properties but also the mobility of monomer molecules and enhances the reactivities of the components. Therefore, theoretically, the greater the proportion of TEGDMA, the greater the degree of conversion of Bis-GMA/TEGDMA co-polymers. The present findings support both this theory and previously published information²³⁾. Based on the heat produced from polymerization of Bis-GMA and TEGDMA²⁴⁾, the theoretical amount of heat evolved during complete polymerization of 1 g of each specimen was calculated to be 53.6–46.0 J/g for U1–U3 and 29.1–25.1 J/g for C1–C3, respectively. Accordingly, it is considered that the differences

in the heat evolved among the three specimens were small and the production of heat during curing had little influence on the degree of conversion. The fact that the degree of conversion of cured dimethacrylate resin is greater means that the polymer is more rigid and has a more highly cross-linked network. Kalachandra and Kusy¹⁹⁾ indicated that the diffusion coefficient of a network based on dimethacrylates was generally lower than methyl methacrylates because of their cross-linking nature. Furthermore, Pearson and Longman²⁵⁾ reported that the water sorption of composites was increased due to incomplete conversion of the monomers. However, in the present study, water uptake of both unfilled resins and composites which showed greater degree of conversion (U1, C1) was greater than other materials with lesser conversion, and no inverse relationship was found between the water uptake and the degree of conversion. This implies that the increase in network density of the specimens tested did not show effective inhibition of the diffusion of water. Therefore, it is considered that although the cross-linking nature reduces the water uptake of polymer compared with a single strand configuration, an increase in the conversion of dimethacrylate resins, whose degree of curing is generally large, does not contribute significantly to reducing the water uptake.

The hydrophobicity of the specimens was compared by measuring the contact angle of water on the material. For both unfilled resins and composites, specimens containing Bis-GMA/TEGDMA in the ratio of 1/1 demonstrated smaller contact angles than 2/1 or 3/1 specimens, indicating greater hydrophilia. Since an inverse relationship between the contact angle and water uptake was likely to be found, the values of all specimens were plotted for correlation of these two factors (Figs. 3 and 4). The correlations of the two factors were significant ($p < 0.05$, Pearson's correlation test) for both unfilled resins ($r = -0.907$) and composites ($r = -0.618$).

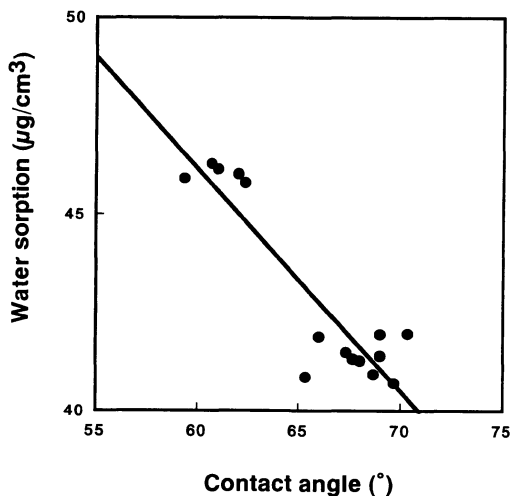


Fig. 3 Correlation between the water uptake and contact angle for unfilled resins.

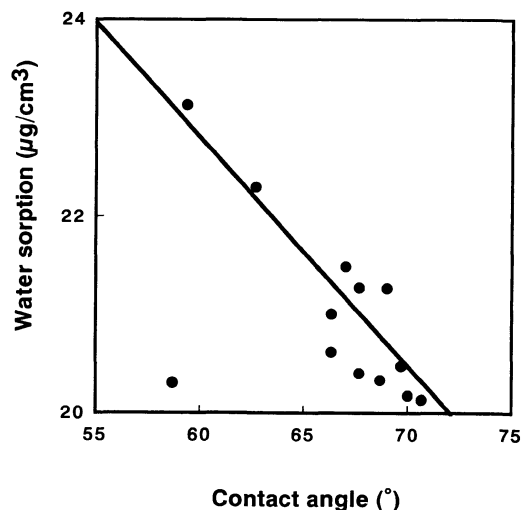


Fig. 4 Correlation between the water uptake and contact angle for composites.

Kalachandra and Kusy¹⁹⁾ demonstrated that the water uptake of TEGDMA homo-polymer was 4.4 times larger for Bis-GMA homo-polymer and that the contact angle of water on TEGDMA and Bis-GMA homo-polymers was 63 and 66 degrees, respectively. It is considered that an increase in the proportion of TEGDMA resulted in the increase of its hydrophilic nature and subsequently provoked greater water uptake. The lack of differences in water uptake and contact angle between the specimens at the rates of 2/1 and 3/1 may be attributable to a too-small disparity in the proportion of TEGDMA. The ratios of Bis-GMA/TEGDMA can be termed as the molar ratio of 1/1.8 for U1 and C1, 1/0.9 for U2 and C2, and 1/0.6 for U3 and C3, respectively. In the estimation of both weight and molar ratio, the 2/1-specimens contain 1.5 times more TEGDMA than the 3/1-specimens. It can be concluded, therefore, that the water sorption of Bis-GMA/TEGDMA resin was influenced mainly by the hydrophobicity of the material, which depends upon the proportion of TEGDMA incorporated, but increasing the proportion of TEGDMA to about two times may provide significantly different water sorption characteristics.

Since the proportion of TEGDMA utilized in this study was within the range of variation for proprietary composites, the findings could be extrapolated to commercial products. However, proprietary composites contain various amounts of filler and other additives, and the influence of these components on the water uptake of Bis-GMA/TEGDMA based composites requires further investigation.

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