Effects of Water on the Long-Term Properties of Bis-GMA and Silylated-(Bis-GMA) Polymers

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ABSTRACT: Bis-GMA (2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane) is a viscous hygroscopic monomer which is used with triethyleneglycol-dimethacrylate (TEGDMA) for dental restorations. Bis-GMA was silylated with dimethyl-isopropyl-siloxane and further polymerized in order to increase water resistance and viscosity. The viscosity of the silylated monomer, Sil·Bis-GMA, was 50 times lower than that of the parent monomer. After 1 month in water, poly(Bis-GMA/TEGDMA) absorbed 2.6% water and the silylated polymer, poly(Sil·Bis-GMA), only 0.56%. During this process water extracted residual monomer from each polymer. The behavior of water sorption and desorption as a function of time in poly(Sil·Bis-GMA) was completely different from that shown by poly(Bis-GMA/TEGDMA). The difference is discussed in terms of diffusion coefficients. Initially, water advancing contact angles (θ_{ADV}) were 75° and 95°, respectively. After 1 month in water both polymers showed a reduction of about 20° in θ_{ADV}. In poly(Bis-GMA/TEGDMA), the reduction in θ_{ADV} obey to water absorption and bulk plasticization; it showed a reduction of 15°C in glass transition temperature, T_g. In contrast, the reduction in θ_{ADV} in poly(Sil·Bis-GMA) obeyed to water adsorption and reorientation of the molecules at the surface in contact with the water phase; it only showed a change of 2°C in T_g. Contact angle hysteresis provided further evidence about plasticization. According to our results poly(Sil·Bis-GMA) is more stable in water than poly(Bis-GMA/TEGDMA). © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1169–1178, 2008

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INTRODUCTION

Modern development in dental resins focuses mainly on increasing the permanence of the initial properties of the implant as well as on its application simplicity during teeth restorations. Resin based materials are used mainly in adult anterior teeth due to the high levels of stress that posterior teeth suffer during mastication compared with anterior teeth. In children, having lower level of stresses may be used in posterior teeth.

Bis-GMA, 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane, or a Bis-GMA analogue, such as ethoxylated Bis-GMA or urethane dimethacrylate is the main organic component of most dental resins, such as composites and compomers.[1–5] These dental resins also contain a cross-linking dimethacrylate agent, inorganic fillers, made of glass and/or ceramic, the same as a photo-initiator system. These resins are cured (polymerized) by following methacrylate chemistry through irradiation with UV-light.

Generally a dimethacrylate agent such as triethyleneglycol-dimethacrylate, TEGDMA, or urethane diethyleneglycol methacrylate, UDEMA, is added with a double purpose: to reduce the initial viscosity of the resin and to cross-link the polymer. The reduced viscosity facilitates wetting during resin application and chemical cross-linking improves physical properties such as modulus of elasticity, mechanical strength, hardness, and solvent resistance. The usual concentration of TEGDMA ranges between 15 and 30% w/w, otherwise water absorption and other properties of the resin fall below proper limits.[6–8] Interfacial physical–chemical interactions play an important role when the implanted material is in contact with water or saliva.

It has been observed that these Bis-GMA based materials show better physical properties with respect to glass ionomer cements.[9] After polymerization these materials initially show good physical properties and resistance to water, common liquids, and food.[10] However, they still have drawbacks during and after implantation, mainly related to water absorption and the development of interfacial stresses. Dentists face two critical aspects during restoration, in addition to repairing teeth under dry conditions: to ensure complete wetting of the tooth surface under treatment by the resin is one and the

other is to apply the resin in thin layers in order to reduce the stresses at the tooth/resin interfaces caused by polymerization shrinkage.[11,12]

Wetting is complicated because of the paste consistency of the resin which must be forced to make complete and intimate contact with the treated tooth zone before curing. Imperfect wetting leaves defects (interstices) at the tooth/resin interface. These defects are dangerous because, after restoration, they act as points of stress concentration during mastication that, in turn, promote microcracks where saliva and other liquids diffuse, i.e., microleakage. The shrinkage stresses arise due to the establishment of adhesion at the gel point (stage of the curing reaction where the resin becomes solid). Hence, further curing produces a shrinkage which generates stresses at the tooth/resin interfaces (the resin, unable to flow, cannot release these stresses). These shrinkage stresses during mastication could lead to an adhesive failure, also promoting microleakage.[13] Dental restorations are also exposed to cyclic stresses, due to daily mastication and temperature changes, caused by beverages and food, which produce thermomechanical fatigue, in particular at the tooth/resin interface.[14] Therefore properties of dental restorations decay before it is expected.

Poor resin wetting, shrinkage stresses, and fatigue usually promote cracking and eventually caries.[15] Absorbed water also reduces the glass transition temperature, T_g, therefore the dimensional stability of the material. It is then considered that the durability of restorations is a most critical point in dentistry. Interfacial cracking being the most critical aspect of restorations with dental resins, it is highly recommended to improve the permanence of the adhesive joint between the tooth and the dental resin.

Other related aspects that must be considered in improving long-term permanence of dental restorations is the curing reaction efficiency (degree of conversion into polymer) and resin water absorption after curing. In general, properties increase with conversion, including water resistance.[16,17]

Absorbed water could deteriorate the performance of these dental materials. Because Bis-GMA and TEGDMA are relatively hydrophilic, there is a growing need to replace them by other less hydrophilic monomers that exhibit lower water up-take, as is the case of the silylated Bis-GMA monomer.[1]

Kalachandra et al. studied a silylated Bis-GMA in which Bis-GMA hydroxyl groups were substituted by dimethyl-isopropyl-siloxy groups in order to reduce both viscosity and water absorption.[18] Here, the effects of water up-take on the properties of both a silylated Bis-GMA and the resultant polymer in comparison with those of Bis-GMA are discussed.

MATERIALS AND METHODS

Materials

All materials used in this work were reactive grade: 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]ropane (Polysciences), TEGDMA, [6]-ditert-butyl-*p*-cresol (DTBPC) 4-dimethyl-amine-pirydine (DAMP), Benzene, hydrochloric acid, (1s)-(+) camphorquinone (CQ) as photo-initiator, *N*,*N*,3,5-tetramethyl-aniline as promoter (Sigma), triethyl-amine (TEA), chloro-dimethyl-isopropil silane (Cl-DMIPS) (Aldrich) sodium chloride, magnesium sulfate, anhydrous (J.T. Baker), and deionized water (resistivity 18 MΩ/cm).

Synthesis of sylilated Bis-GMA

The synthetic route for silylating Bis-GMA with Cl-DMIPS (Fig. 1) was carefully studied and the reaction conditions were optimized. The silylated monomer, Sil·Bis-GMA, was purified by chromatography in silica gel packed columns using a mixture of hexane/ethyl acetate (90/10%, v/v) as eluent. The structure of the obtained monomer was determined by ^{1}H-, ^{13}C-, and ^{29}Si-NMR (Bruker Advance 400 MHz). The monomer was dissolved in acetone-d_6 using TMS as reference for the ^{1}H and ^{13}C spectra.[19]

One mole of Bis-GMA, used as received, was mixed in the reactor vessel with 100 ppm/mol of DTBPC as inhibitor, and then 1 mole of DAMP was added with 80 mL of benzene. After stirring the mixture, 1 mole of TEA, was injected with a syringe through a septum. After 5 min, 2 moles of Cl-DMIPS per mol of Bis-GMA were also injected. The reacting mixture was heated to 80°C and kept under stirring in dry N$_2$ flow for 12 h.
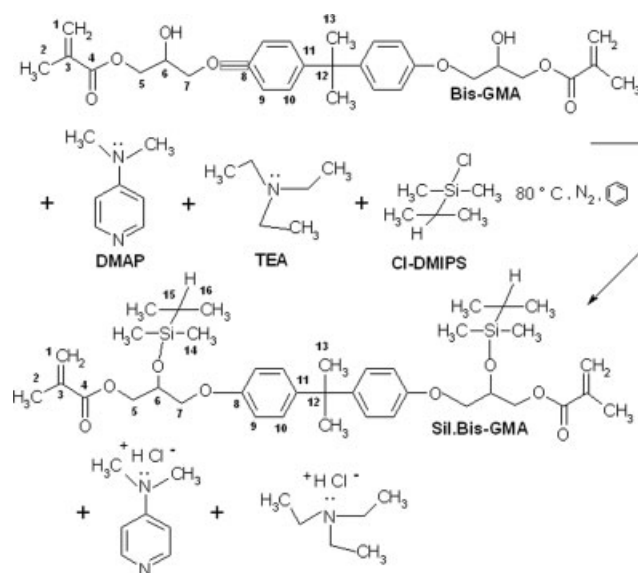

Figure 1 Silylation reaction scheme of Bis-GMA.

To ensure a high degree of conversion during the polymerization of Sil·Bis-GMA it was purified as follows: First, the side products of the reaction were eliminated by diluting the polymer solution in benzene and promoting precipitation of residual DAMP and TEA with concentrated NaCl solution and HCl 1.5M, under strong stirring. The aqueous phase containing the chlorohydrated amine salts was then separated from the organic phase containing the monomer. The procedure was repeated three times to eliminate the amine salts. The residual water in the organic phase was eliminated with anhydrous MgSO$_4$ and the solids were filtered. The Sil·Bis-GMA dissolved in the benzene was recovered by distillation at reduced pressure. The monomer was redissolved in a hexane/ethyl acetate mixture, 90/10% v/v under stirring. The solid impurities found were precipitated from the solution and separated by filtration. The clear solution was injected into a chromatographic separation column, packed with silica using the same eluent. The DTBPC came out first from the column, and then the Sil·Bis-GMA mixed with traces of Bis-GMA; this process was monitored by thin layer chromatography. Finally, the monomer solution was distillated under vacuum to recover the purified Sil·Bis-GMA. After purification, the monomer was kept in the dark at 4°C for its subsequent use.

Polymerization

Sil·Bis-GMA was mixed with the photo-initiator CQ (0.2%, w/w) and the promoter TMA (0.3%, w/w) at room temperature and the reacting mixture was degassed.

For comparison, a Bis-GMA/TEGDMA monomer mixture was also prepared. The Bis-GMA monomer was mixed with CQ (0.2%, w/w) in a vessel. In another vessel, TEGDMA, washed previously in NaOH solution and dried over anhydrous CaSO$_4$, was mixed with TMA (0.3%, w/w). Afterward the so prepared comonomers were mixed in 70/30% w/w proportion and degassed.

The polymerization procedure for both monomer systems was the same: The chemical reaction was photo-activated by irradiating with monochromatic light, 468–480 nm for 60 s (using a Starlux plus, Corix Medical Systems dental lamp equipped with an optical fiber). The output flux was 200 mW/cm^2. The real output intensity and the dissipated heat were monitored with a radiometer (Heat/Glare Radiometer, model 200, Demetron Research Co.).

For the polymer tests, the reacting mixture was poured in open circular molds, 15 mm in diameter and 2 mm thick. The two open faces of the molds were covered with transparent Mylar and glass slides. The photo-polymerization was initiated by irradiating seven evenly distributed zones of the upper face of the mold, considering the diameter of the beam (4.6 mm). After a post-curing time of 24 h the polymer samples were degassed under -50 kPa vacuum for 2 h. At least five polymer discs were prepared for each test.

Water tests

The solubility of the monomer in water was measured as follows: the monomer was mixed with water (1/1 w/w) and stirred, after 72 h in rest at 37°C the excess water was removed. The water absorbed by the monomer, $(M_S^m)_t$, at time t, was calculated using the following equation:

$$(M_S^m)_t = \frac{(M_t - M_0)}{M_0} 100 \qquad (1)$$

where M_t is the monomer mass after a time t in water and M_0 is the monomer mass at time zero (dry sample).

The solubility of residual monomer in the polymers was also measured. A polymer disc was placed in a vial after measuring its weight and dimensions. Subsequently, water was added to the sample and kept closed at 37°C. The change of weight at different times was determined after taking the sample out from the water and removing the liquid. Afterward the sample was placed in a desiccator with CaSO$_4$ at 37°C and the change of weight was monitored at different times up to constant weight.

The sorption in the polymer per unit volume, $(M_S^p)_t$, at time t, was calculated according to eq. (2)[10]:

$$(M_S^p)_t = \frac{M_t - M_0}{V} \qquad (2)$$

where M_t is the polymer mass after a time t in water, M_0 is the polymer mass at time zero (dry sample), and V is the initial volume of the sample.

The water sorption percent, %WS, at the equilibrium time can be expressed as follows:

$$(\%\text{WS}) = \frac{M_\infty^S - M_0}{M_0} 100 \qquad (3)$$

where M_∞^S is the mass at equilibrium time after sorption.

The following expression was devised to calculate the extracted monomer and obeys to the kinetic behavior observed for the sorption/desorption tests as shown below in Figure 2.

$$(\%\text{MS}) = \frac{M_0 - M_\infty^{DS}}{M_0} 100 \qquad (4)$$

As shown below in the Results and Discussion section, poly(Sil·Bis-GMA) lost weight during the
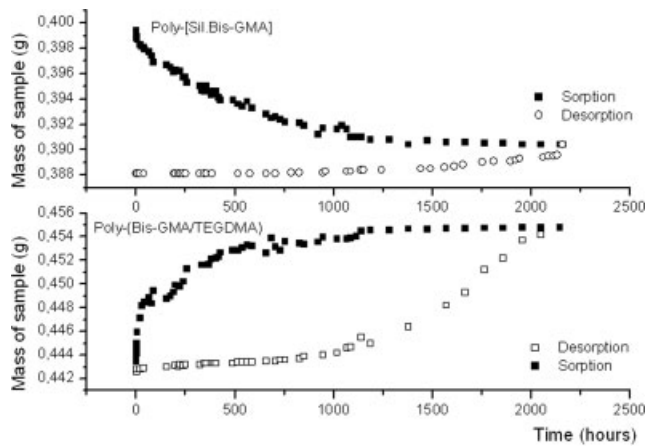
Figure 2 Mass as a function of time during water sorption and desorption on poly(Sil·Bis-GMA) and poly(Bis-GMA/TEGDMA) at 37°C.

sorption tests. To determine the net absorption of water, desorption tests were made. In this case, the adsorbed water was calculated using the following equation:

$$(M_S^p)_t = \frac{M_t - M_\infty^{DS}}{V} \tag{5}$$

where M_∞^{DS} is the mass of the sample after total water absorption and desorption test up to constant weight (2160 h).

For this case (%WS) can be expressed:

$$(\%WS) = \frac{M_\infty^S - M_\infty^{DS}}{M_0} 100 \tag{6}$$

The residual monomer percent, (%MS), extracted with water was calculated as follows:

$$(\%MS) = \frac{M_0 - M_\infty^S}{M_0} 100 \tag{7}$$

Considering a polymer disc as a plane sheet bounded by two parallel planes, the diffusion coefficient, D, could be estimated by Fick's Second Law assuming diffusion in one dimension. This approximation is valid only at the early stages of sorption or desorption, and liquid concentration distributions cannot be obtained.

In general, the equation of mass transfer (diffusion) is expressed as follows[20]:

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial C}{\partial x^2} + \frac{\partial C}{\partial y^2} + \frac{\partial C}{\partial z^2}\right] \tag{8}$$

Assuming diffusion in one dimension (x direction) the linear flow of liquid mass in the solid is:

$$\frac{\partial C}{\partial t} = D\left[\frac{\partial C}{\partial x^2}\right] \tag{9}$$

Equation (9) is solved for the region $-1 < x > +1$ at zero initial water concentration and constant concentration at the surfaces for $t > 0$.

The rates of sorption and desorption were determined by using the conventional solution of Fick's Second Law for a plane sheet[20]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\left[\frac{1}{(2n+1)^2}\right]\exp\left[\frac{-\pi^2 Dt(2n+1)^2}{4l^2}\right] \tag{10}$$

Classical diffusion theory predicts linearity during the early stages of sorption, usually when $M_t/M_\infty \leq 0.5$[21,22]:

$$\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{1/2} \tag{11}$$

where M_t is the mass absorbed (or lost) at time, t, M_∞ is the mass at equilibrium, and $2l$ is the thickness of the sample. By plotting M_t/M_∞ vs. $t^{1/2}$ a straight line should be obtained at the early stages of diffusion [eq. (12)] and D is calculated directly from the slope, m, [eq. (13)].[1,2,22,23]

$$\frac{M_t}{M_\infty} = 4\left(\frac{D}{\pi}\right)^{1/2}\cdot\frac{t^{1/2}}{2l} \tag{12}$$

$$D = m^2\left(\frac{\pi}{16}\right) \tag{13}$$

The chemical potential of pure water being greater than that of saline water or saliva, the diffusion coefficient D, of the former should also be greater.[24]

Glass transition temperature

The effect of absorbed water on the T_g of each polymer was determined by thermal analysis (DSC, Dupont, model 910) at a ramp of 10°C/min. The T_gs of [Bis-GMA] and [TEGDMA] homopolymers were also obtained as references.

Contact angles and surface roughness

Polymer samples 22 × 22 × 1 mm^3 were also prepared as described above. The dynamic advancing (θ_{ADV}) and receding (θ_{REC}) contact angles of water were determined by the Wilhelmy method (KSV, model Sigma 70 Wilhelmy balance) at 37°C.

The contact angle hysteresis, θ_H, was used to estimate roughness and surface homogeneity according to the following equation:

$$\theta_H = \theta_{ADV} - \theta_{REC} \tag{14}$$

The polymer surfaces were studied with the aid of an atomic force microscope (Jeol scanning probe

microscope, model JSPM-4210). Images of the dry surfaces were obtained in air on different disc regions.

The mean roughness can de expressed as follows[25]:

$$R_{\text{rms}} = \left[\frac{\sum\limits_{n=1}^{n} \left(Z_n - \bar{Z} \right)^2}{n-1} \right]^{1/2} \qquad (15)$$

where Z_n is the height in a zone, Z is the mean height, and n is the number of zones.

RESULTS AND DISCUSSION

Chemical structure

The chemical structure of Sil·Bis-GMA monomer was solved by ^{1}H-, ^{13}C-, and ^{29}Si-NMR. The signals are shown below. The first number corresponds to the carbon atom of the structure (see Fig. 1) and the second number to the chemical shift in ppm:

^{1}H NMR signals: (1-t: 6.16), (1-c: 5.59), (2: 1.97), (5: 4.37), (6: 4.27), (7: 3.95), (9: 7.15), (10: 6.84), (13: 1.65), (14: 1.426), (15: 0.401), (16: 1.404).

^{13}C NMR signals: (1: 18.34), (2: 126.26), (3: 135.74), (4: 167.28), (5: 68.69), (6: 68.29), (7: 65.58), (8: 156.40), (9: 114.00), (10: 127.99), (11: 143.91), (12: 41.89), (13: 31.21), (14: 14.27), (15: 14.63), (16: 17.05).

^{29}Si NMR signals: (6: −39.26), (14: 8.68), (15: 76.5), (15: −64). The chemical shift at −39.26 ppm corresponds to the Si atom attached to carbon 6 through the oxygen.[26] These signals evidence the silylation reaction of Bis-GMA depicted in Figure 1.

The chemical structure of Bis-GMA was also solved by ^{1}H- and ^{13}C-NMR and matched well with those reported elsewhere[19]:

^{1}H NMR signals: (1-t: 6.19), (1-c: 5.62), (2: 1.97), (5: 4.36), (6: 4.28), (7: 4.04), (9: 7.17), (10: 6.84), (13: 1.65).

^{13}C NMR signals: (1: 183.4), (2: 126.26), (3: 135.74), (4: 167.28), (5: 68.69), (6: 68.29), (7: 65.58), (8: 156.01), (9: 114.10), (10: 127.93), (11: 143.59), (12: 41.93), (13: 31.24).

Polymerization

Bis-GMA, TEGDMA, and Sil·Bis-GMA were polymerized by a chain reaction mechanism initiated by free radicals. Upon UV irradiation the reaction rate was very fast, photo-polymerization occurred between 5 and 10 min. These conditions are usually needed in dental restorations.[27–29] Optimum reaction conditions such as photo-activation time, light intensity, effective depth of photo-activation, and previously absorbed water were described above in the

TABLE I
Absorbed Water, M_S^m, and Weight Percent Oxygen (WPO) of Monomers

Monomer	Absorbed water M_S^m (%, w/w)	WPO (%)
TEGDMA	5.20	33.5
Bis-GMA	1.55	25.0
Bis-GMA/TEGDMA (70/30%, w/w)	3.40	28.0
Sil·Bis-GMA	1.05	18.0

experimental section. According to the sorption/desorption results, discussed below, residual monomer concentrations were below 2.5%, suggesting that conversions were well above 90%. Conversions of 75% have been reported for typical polymeric dental resins. However, it has also been reported that the acrylic groups of residual monomer may react slowly after the polymerization period ends (post-curing).[30,31]

Water absorption and diffusion coefficients

The studied monomers are hygroscopic and dissolve partially in water. Thus, when water is in contact with the polymers, residual monomer tend to diffuse to the water phase as shown below.[10]

Monomer water absorption and the weight percent of oxygen (WPO) bound chemically to the molecule are shown in Table I.[18,32]

The absorbed water, M_S^m, for the first three monomers shown in Table I agrees well with data reported elsewhere.[32] As expected, absorbed water increased with the WPO. Among the studied monomers TEGDMA shows the greatest values of M_S^m and WPO.

Affinity to water has been related to the oxygen atoms able to form hydrogen bonds in the case of TEGDMA.[18,33] In the Bis-GMA/TEGDMA mixture, the absorbed water and the WPO are almost proportional to the content of TEGDMA. In contrast, Sil·Bis-GMA shows the lowest values of absorbed water because of its lowest WPO. The chemical composition, temperature, and exposure time are important factors on the water sorption process. Water absorption is important because water makes it difficult for the photo-polymerization reactions of Bis-GMA monomers, including cross-linking.[34,35]

The polymers show a partial hydrophilic character because both have groups susceptible to hydrolysis, such as ester and ether linkages, and hydroxyl groups in Bis-GMA.[35] However, according to our results poly(Sil·Bis-GMA) has a hydrophobic character.

Sorption data are shown in Figure 2 as the change of mass with immersion time in water for both polymers together with desorption. As it has been reported elsewhere, water extracts residual monomer
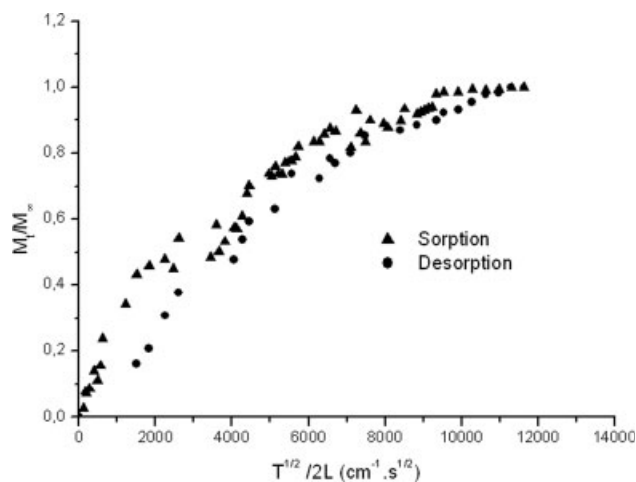
Figure 3 Relative weight change of poly(Bis-GMA/TEGDMA) during immersion time in water, at 37°C (▲) and during desorption (●).

out of the poly(Bis-GMA/TEGDMA).[23] It can be noticed that the behavior during the water sorption and desorption tests in poly(Sil·Bis-GMA) is completely different from that in poly(Bis-GMA/TEGDMA).

The water absorbed by poly(Bis-GMA/TEGDMA) up to equilibrium time (2160 h) at 37°C was 2.6% w/w (equivalent to 0.0336 μg/mm³), while the extracted residual monomer was much lower: 0.14% w/w (0.0017 μg/mm³). As expected, this polymer absorbed 77% w/w less water than the respective monomer mixture. It could be inferred that the ability of the monomer to absorb water is reduced in the copolymer by both interactions between hydroxyl and carbonyl groups and cross-linking.

As seen in Figure 2, poly(Sil·Bis-GMA) lost weight during the water sorption test. After the desorption test, the weight of the polymer (M_∞^{DS}) was lower than the initial weight (M_0). The difference ($M_\infty^{DS} - M_0$) corresponds the amount of extracted monomer by water.

The mass of water absorbed by poly(Sil·Bis-GMA), 0.576% w/w, (equivalent to 0.0070 μg/mm³) is much lower than the mass of extracted residual monomer, 2.3023% w/w, (0.0282 μg/mm³). As expected, this polymer absorbed 55% w/w less water than the respective monomer. These results show that poly(Sil·Bis-GMA) is almost nonpermeable to water. As shown below, water is mainly adsorbed at the surface region of the polymer and it is more hydrophobic than poly(Bis-GMA/TEGDMA).

As reported elsewhere, water may produce deleterious effects on the structure of the polymeric material (swelling, plasticization and softening, and chemical changes such as oxidation and hydrolysis).[35]

The fact that poly(Bis-GMA/TEGDMA) absorbed 4.5 times more water than poly(Sil·Bis-GMA) is

explained by the hydrophilic ester and ether linkages present in both TEGDMA and Bis-GMA and also by the hydroxyl groups in Bis-GMA. Poly(Sil·Bis-GMA) is more hydrophobic because it has neither TEGDMA nor hydroxyl groups. Water up-take depends mainly on the potential for hydrogen bonding and polar interactions and can be related to the solubility parameter in water.[35] Thus, the solubility parameter of poly(Bis-GMA/TEGDMA) should be greater than that of poly(Sil·Bis-GMA).

The plots of relative change of mass as a function of time, M_t/M_∞, Figures 3 and 4, adjust to Fick's Second Law in one dimension, eq. (13), for values of $M_t/M_\infty < 0.5$. Above this point the linearity is lost.[24,32] From these results the diffusion coefficients of sorption and desorption were obtained. For poly(Bis-GMA/TEGDMA), Figure 3, the diffusion coefficient for sorption, $D_s = 0.7854 \times 10^{-8}$ cm²/s, is four times greater than for desorption, $D_d = 0.1964 \times 10^{-8}$ cm²/s. These results also indicate that the diffusion rates for sorption and desorption are different.

In contrast, for the silylated polymer, Figure 4, the rates for sorption and desorption are similar: diffusion coefficients are $D_s = 0.1964 \times 10^{-8}$ cm²/s and $D_d = 0.1590 \times 10^{-8}$ cm²/s, respectively, Table II. In this case linearity extends to $M_t/M_\infty \leq 0.8$.[22]

The diffusion coefficient of sorption of poly(Bis-GMA/TEGDMA) is greater than that of poly(Sil·Bis-GMA) because of its greater water affinity. As shown below, water absorption promotes plasticization of the copolymer.[36]

It can be observed in Figure 4 that the sorption and desorption curves for poly(Sil·Bis-GMA) are quite similar, suggesting that desorbed monomer rate is higher than absorbed water rate because the amount of extracted monomer is much higher than the absorbed water.
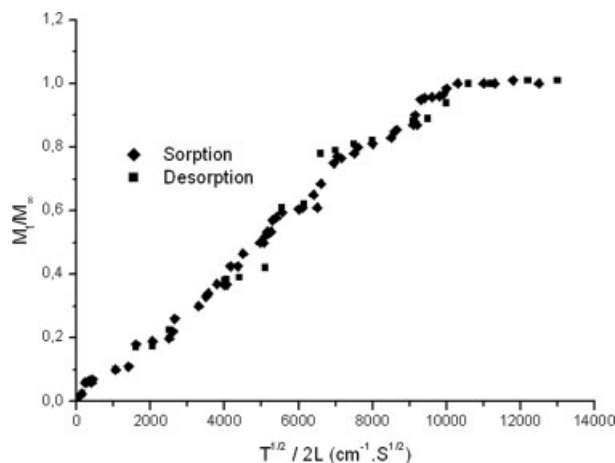
Figure 4 Relative weight change of poly(Si·Bis-GMA) during immersion time in water at 37°C (◆) and during desorption (■).

TABLE II
Diffusion Coefficients for Water Sorption and Desorption of Polymers

Polymer resins	Temperature (°C)	Curing time (s)	Sorption at equilibrium (%, w/w)	Diffusion coefficient, (cm^2/s)	
				Sorption (10^{-8})	Desorption (10^{-8})
TEGDMA[a,b]	37	–	1.86	1.14	1.14
Bis-GMA[a,b]	37	–	2.8	0.617	0.563
Bis-GMA/TEGDMA (70/30%, w/w)	37	30	2.32	0.8 ± 0.05	0.2 ± 0.01
Sil·Bis-GMA	37	30	−2.6	0.2 ± 0.01	0.16 ± 0.01

[a] Ref. 2.
[b] Ref. 32.

Water sorption has been related to the WPO and the presence of groups susceptible of hydrolysis.[35] The WPO of the repeating unit of the polymers is as follows: poly(Bis-GMA) > poly(Bis-GMA/TEGDMA) > poly(TEGDMA) > poly(Sil·Bis-GMA). However, the diffusion coefficient for sorption, D_s, decreases as follows: poly(TEGDMA) > poly(Bis-GMA/TEGDMA) > poly(Bis-GMA) > poly(Sil·Bis-GMA). The diffusion coefficient is therefore more reliable than the WPO to explain water absorption.

Monomer viscosities

The viscosities of Sil·Bis-GMA and Bis-GMA monomers, measured by rehometry, were 2.7 Pa s and 1200 Pa s, respectively, at 37°C. Such significant difference indicates that there is no need to add TEGDMA to Sil·Bis-GMA in order to reduce the viscosity of the resin as in Bis-GMA. Apparently, silylation increased internal rotation by a reduction in hydrogen bonding yielding a much more flexible molecule.[18]

Polymer surfaces

The character of the polymer surfaces was determined by the contact angle of water as a function of time, Figure 5. For poly(Bis-GMA/TEGDMA) the advancing contact angle, θ_{ADV}, was initially 75°, indicating that its surface is hydrophobic. However, θ_{ADV} decayed with immersion time in water. During the first 60 h the θ_{ADV} decayed slowly then it dropped at a higher rate to 65°, due to plasticization, but after 170 h it decreased slowly to 55°.

For poly(Sil·Bis-GMA) the initial advancing contact angle was 95°, indicating that the virgin surface was highly hydrophobic. Again, θ_{ADV} also decayed as the immersion time in water increased to 75°. As discussed above, poly(Sil·Bis-GMA) practically did not absorb water, suggesting that the decay in contact angle obeys to molecular reorientation of the hydrophilic groups of the polymer at the surface region, hence reducing its hydrophobic character.

In general, the advancing contact angle of water is highly reproducible on hydrophobic surfaces (low energy surfaces).[37] Our results suggest that the initial decay in θ_{ADV} is the result of water adsorption at the surface region. The interchange between residual monomer and water at the interface is a secondary process. Both being amorphous polymers, the spaces between polymer segments (free volume) facilitate molecular diffusion.[10] An additional evidence for the interchange of water with residual monomer is provided by thermal analysis, as shown below.[37,38]

It is known that above a mean roughness of 0.5 μm differences contact angle hysteresis is observed, eq. (14). Chemical heterogeneity at the surface also leads to hysteresis because each chemical species has a different specific surface energy.[37,39]

Roughness and surface homogeneity were analyzed by atomic force microscopy. In both polymers the surfaces appeared to be homogenous and the mean roughness was below 0.05 μm, providing evidence that the surfaces of both polymers are smooth,
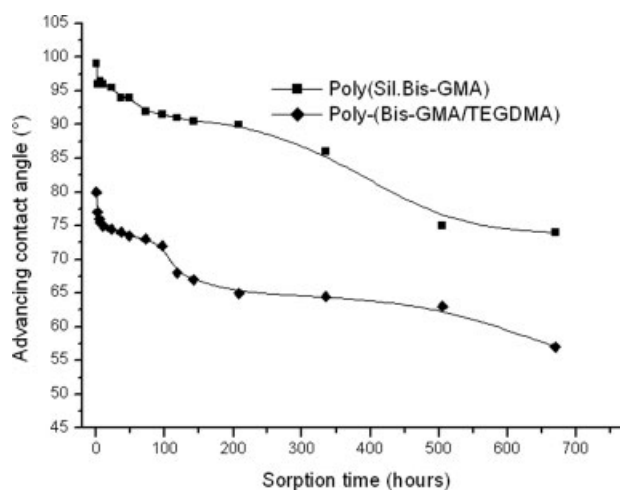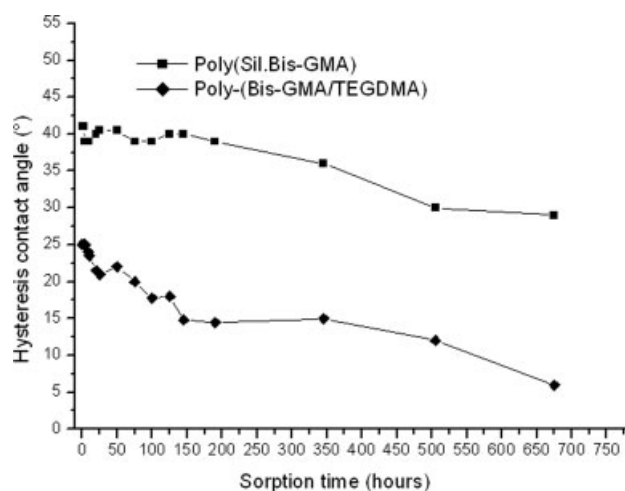

Figure 5 Advancing contact angle as a function of immersion time in water on poly(Bis-GMA/TEGDMA) and poly(Sil·Bis-GMA) at 37°C.
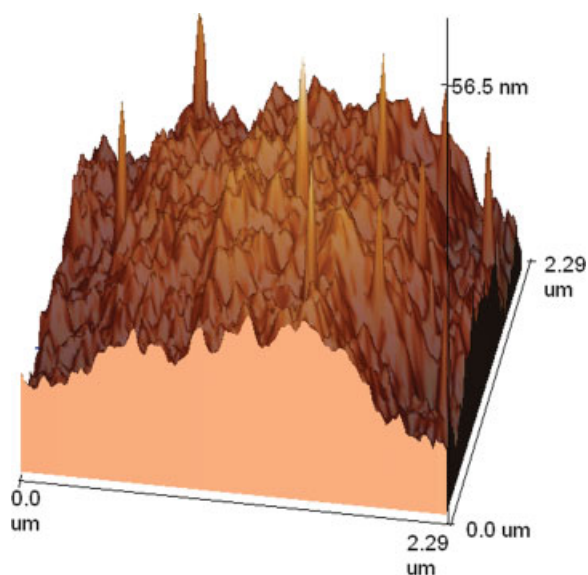
Figure 6 Surface image of poly(Bis-GMA/TEGDMA). Area 5.3 (μm)^2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

but also chemically homogeneous as determined previously by NMR and FTIR.[19,37] Figure 6 shows an image of the poly[[Bis-GMA/TEGDMA)] surface. The maximum roughness (difference between peaks and depths) is below 0.09 μm and the mean roughness was 0.05 μm.

According to our measurements both polymer surfaces showed significant contact angle hysteresis, θ_H, Figure 7. This effect is attributed here to reorientation of the hydrophilic groups in contact with water because in both polymers the surfaces are homogeneous and smooth, as shown above. The observed initial hysteresis shows that the polymer surfaces in

TABLE III
Glass Transition Temperatures of Monomers and Polymers

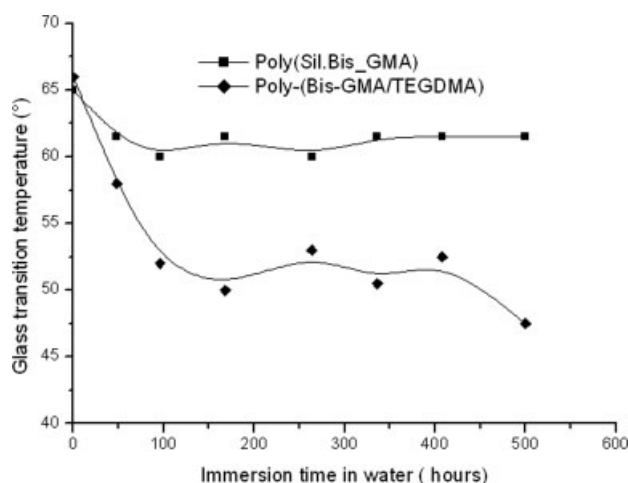| Material	T_g (°C)	
	Monomer	Polymer
TEGDMA	−81.7[a]	65.0[b]
Bis-GMA	−6.6[a]	67.0[b]
Bis-GMA/TEGDMA	−46.0 ± 2	66.0 ± 2
Sil·Bis-GMA	−44.0 ± 2	65.0 ± 2

[a] Ref. 5.
[b] Ref. 33.

contact with water are far from equilibrium. However, it can be observed that θ_H decreases with immersion time in both cases.

Furthermore, for poly(Bis-GMA/TEGDMA) θ_H approximates to zero after 650 h, in this case there is molecular relaxation at the surface but also in the bulk because of plasticization (as shown below), therefore, the system approximates to the equilibrium. However, in poly(Sil·Bis-GMA) molecular relaxation occurs only at the solid–liquid interface (adsorption) but not in the bulk, thus, the surface is far from equilibrium.

Thermal properties

The DSC thermograms show the presence of glass transition temperature, T_g in both polymers, but not melting points revealing they are completely amorphous. The T_g of poly(Bis-GMA/TEGDMA) is, as expected, very similar to those reported for poly[TEGDMA] and poly[Bis-GMA], 65 and 67°C, respectively, Table III. It can be noticed also that the T_g of

Figure 7 Contact angle hysteresis as a function of immersion time in water for poly(Bis-GMA/TEGDMA) and poly(Sil·Bis-GMA) at 37°C.

Figure 8 Glass transition temperature (°C) of poly(Sil·Bis-GMA) and poly(Bis-GMA/TEGDMA) versus immersion time in water.

poly(Sil·Bis-GMA) is very similar. This similarity could be attributed to a plasticizing effect of the residual monomer but also to different degrees of polymerization.[28,29,40]

The effect of absorbed water on the T_g as a function of time is shown in Figure 8. It can be observed an asymptotic decay in the T_g of poly(Bis-GMA/TEGDMA) of about 15°C. The observed decay in T_g by absorbed water is in the same range as other acrylic polymers.[2] As water diffused into the bulk there was a plasticizing effect in the copolymer. It is known that this effect reduces the mechanical and thermal stability.[2,10,36] In poly(Sil·Bis-GMA) T_g only changed to 3°C. Since water did not diffuse into the bulk there was no bulk plasticization.

Other authors explain this effect by the presence of structural heterogeneities, multiple thermal transitions, trapped free radicals, and residual monomer in the final structures.[28,41]

CONCLUSIONS

Our results confirm that silylation of the Bis-GMA monomer reduces the viscosity to about 50 times at human body temperature. The mixture Bis-GMA/TEGDMA is three times more hygroscopic than the Sil·Bis-GMA monomer. After polymerization both materials absorbed less water than the respective monomers. The poly(Sil·Bis-GMA) is hydrophobic; it absorbed 4.5 times less water than the parent polymer. Water extracted more monomer from poly(Sil·Bis-GMA) than from poly(Bis-GMA/TEGDMA) because of both: First, the concentration of residual monomer in poly(Bis-GMA/TEGDMA) is lower than in poly(Sil·Bis-GMA) and second, the former polymer is less hydrophobic as well as the parent monomer. Therefore, water sorption and desorption behavior as a function of time is completely different in poly(Bis-GMA/TEGDMA) form than that shown by poly(Sil·Bis-GMA). And, the diffusion coefficient for water sorption of poly(Bis-GMA/TEGDMA) is greater than that shown by poly(Sil·Bis-GMA).

Water sorption induced bulk plasticization in poly(Bis-GMA/TEGDMA) thus reducing its T_g. In contrast, water absorption in poly(Sil·Bis-GMA) was very low, therefore, no change in T_g was observed. From this point of view the thermal stability of poly(Sil·Bis-GMA) is greater. However, although the poly(Sil·Bis-GMA) surface initially showed a highly hydrophobic character ($\theta_A > 90°$), after being in contact with water its surface was relaxed and the contact angle decayed about 20%. Apparently water adsorption induced surface relaxation and reorientation of the hydrophilic groups being at the surface region toward the water phase. According to our results, the stability of poly(Sil·Bis-GMA) in water as a function of time is greater than that shown by the copolymer poly(Bis-GMA/TEGDMA).

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