Characteristics of the Sorption of Water and an Ethanol/Water Solution by Light-Cured Copolymers of 2-Hydroxyethyl Methacrylate with Dental Dimethacrylates

Irini D. Sideridou, Maria M. Karabela

Laboratory of Organic Chemical Technology, Department of Chemistry,
Aristotle University of Thessaloniki, Hellas, Greece GR-54124

ABSTRACT: This work concerns the synthesis of copolymers of 2-hydroxyethyl methacrylate (HEMA) and the dimethacrylates bisphenol A glycol dimethacrylate, bisphenol ethoxylated dimethacrylate, urethane dimethacrylate, and triethylene glycol dimethacrylate (50/50 mol/mol) because of their potential use in contemporary dentine adhesives. Copolymerization was carried out at room temperature with visible light (λ_{max} = 470 nm), with the system camphorquinone/N,N-dimethylaminoethyl methacrylate being used as the photoinitiator. The behavior of these copolymers under oral conditions is of great concern. Thus, the sorption/desorption kinetics of water and a 75 vol % ethanol/water solution (which is an oral/food simulating liquid) by these copolymers were studied. The maximum amount of sorbed/desorbed liquid, solubility, and diffusion coefficient of each liquid were determined. The amount of sorbed liquid and solubility of the copolymers depended on both the structure of the copolymer and the nature of the solvent. The amount of water sorbed by the copolymers and their diffusion coefficients were much lower than those of the HEMA homopolymer but closer to those of the homopolymers of the dimethacrylate comonomers. All the copolymers sorbed a higher amount of the ethanol/water solution than water. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2503–2512, 2008

Key words: adsorption; biomaterials; dental polymers; diffusion; photopolymerization

INTRODUCTION

In contemporary dentine adhesives, hydrophilic monomers are customarily mixed with hydrophobic dimethacrylates to facilitate bonding to an intrinsically wet dentine substrate. Among the hydrophilic monomers used is 2-hydroxyethyl methacrylate (HEMA), which has a very high affinity for water and good compatibility with biological systems. The most commonly used dimethacrylates, known as dental dimethacrylates, are bisphenol A glycol dimethacrylate (Bis-GMA), bisphenol ethoxylated dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA; Fig. 1).[1–3] Although these monomers are considered hydrophobic, they contain hydrophilic linkages, such as ester, urethane, and ether linkages, as well as hydroxyl groups. Copolymer networks prepared from these monomers are considered to be largely insoluble structures with relatively high chemical and thermal stability. However, when they are exposed externally to salivary fluids and internally to the underlying hydrated dentine, they may absorb water and chemicals. As the copolymer's hydrophilicity increases, a considerable amount of water can be sorbed.

Water molecules sorbed by hydrophilic polymers can exist in three distinct forms: (1) free water, (2) freezable bound water, and (3) nonfreezable bound water. Free and freezable water are characterized by high mobility and low plasticizing efficiency. In contrast, nonfreezable water has much lower mobility and exhibits high plasticizing efficiency. Because of this plasticizing effect, the water induces swelling and causes dimensional changes in the copolymer network.[4] The sorbed water may also induce chemical oxidation and hydrolysis of copolymer chains.[5] It has been found that the modulus of elasticity[6] and the mechanical strength[7] of copolymers are reduced after storage in water, and this reduction is increased with the hydrophilicity of the copolymer. The swollen copolymer may also release residual unreacted monomers through the dentinal tubules into the pulp and elicit adverse biological reactions.[8,9] Thus, the behavior of dental copolymers under oral conditions is obviously of great concern.

Studies of the sorption and solubility of various dental polymeric materials in a wet *in vitro* environment have been mainly conducted in water[10,11] and oral/food simulating liquids.[12–15] Among the latter is the 75 vol % ethanol/water solution. This solution
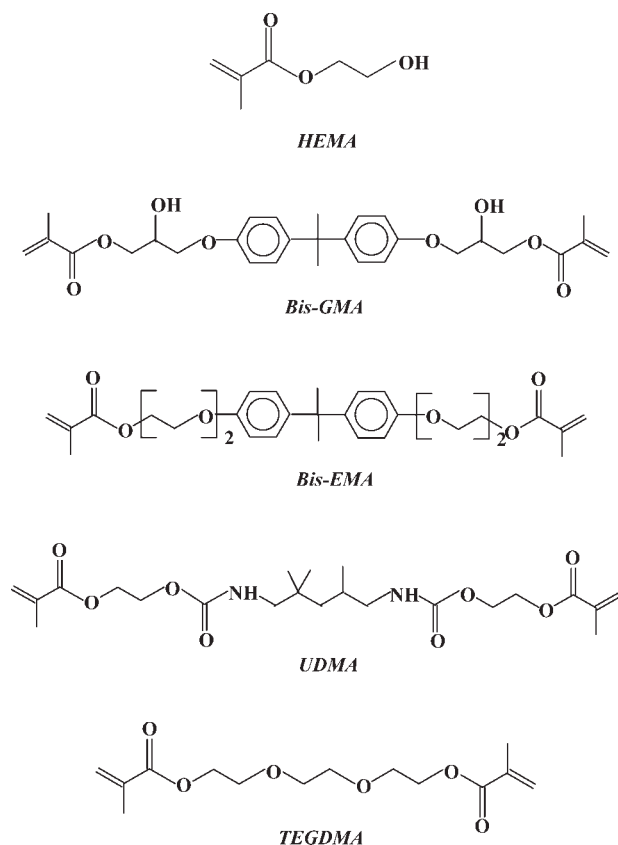
Figure 1   Chemical structures of the monomers.

is recommended by U.S. Food and Drug Administration guidelines (1976 and 1988) as a food simulator and might be considered clinically relevant.

The mechanism of the transport of liquids into polymers may be determined by a variety of experimental techniques, the simplest and most common of which is the sorption technique. In a sorption experiment, including both the sorption and desorption of the liquid, the gain in the mass of the polymer is monitored as a function of time t. This study gives the possibility of determining liquid sorption characteristics and the diffusion coefficient, which expresses the rate of liquid diffusion into the polymer network. It is envisaged in this study that the amount of unreacted monomers extracted by the liquid, which is known as solubility, can be determined.

The main thrust of this work is therefore focused on the sorption kinetics of water and an ethanol/water solution (75 vol %) by HEMA/Bis-GMA, HEMA/Bis-EMA, HEMA/UDMA, and HEMA/TEGDMA copolymers with a 50/50 mol/mol composition because of their potential use in dentine adhesives. It is aimed at the study of the effect of the copolymer composition and nature of the solvent on the equilibrium liquid uptake, diffusion coefficient, and solubility. Our results could be useful for

the interpretation of the sorption behavior of dentine adhesives containing these copolymers.

In previous works, the sorption of water by a light-cured homopolymer of HEMA[16] and the sorption of water or ethanol[17] or an ethanol/water solution (75 vol %)[14] by light-cured dental dimethacrylates have been studied.

EXPERIMENTAL

Materials

The monomers were Bis-GMA (Aldrich Chemical Co.; lot no.07210BB (Seelze, Germany)), UDMA (Ivoclar-Vivadent; lot no. B00338 (Scaan, Liechtenstein)), TEGDMA (Aldrich Chemical; lot no. 17529EA-503), HEMA (Aldrich Chemical; lot. no. 01128MU), and Bis-EMA (Aldrich Chemical; lot no. 03514 HF). They were used as received without further purification. Four mixtures of these monomers were prepared with HEMA/Bis-GMA, HEMA/Bis-EMA, HEMA/UDMA, or HEMA/TEGDMA in a ratio of 50/50 mol/mol. To light-cure the samples, 2 mol % camphorquinone (CQ; Aldrich Chemical; lot no. S12442-053) and 2 mol % N,N-dimethylaminoethyl methacrylate (Riedel-de Haën; lot no. 20770 (Seelze Germany)) were added to act as the photosensitizer and reducing agent, respectively. CQ and N,N-dimethylaminoethyl methacrylate were first dissolved in 50 mL of dichloromethane. Then, 10 mL of this solution was added to 20 g of the monomer(s), and the solvent was subsequently evaporated *in vacuo*.

Preparation of the specimens

Sorption and solubility tests were determined according to the method described in ANSI/ADA Specification 27-1993 (ISO 4049-1988). Specimen discs were prepared by a Teflon mold (15 mm in diameter and 1 mm thick) being filled with the unpolymerized material, with care taken to minimize entrapped air. The upper and lower surfaces of the mold were covered with glass slides. The completed assembly was held together with spring clips and irradiated with an XL 3000 dental photocuring unit (3M Co., St. Paul, MN). This source consisted of a 75-W tungsten halogen lamp, which emitted radiation between 420 and 500 nm and had its maximum peak at 470 nm (CQ: λ_{max} = 470 nm, ε = 3.8 × 10^4 cm^2/mol). The light and heat (IR) intensities were monitored regularly with a Hilux curing light meter. Because of the large size of our specimen, this unit was used without the light guide at a distance of approximately 0.8 cm from the sample. The samples were irradiated for 200 s on each side. This irradiation time was found to be adequate for the completion of polymerization. Thereafter, the mold was dismantled, and the disc was carefully removed by the flex-
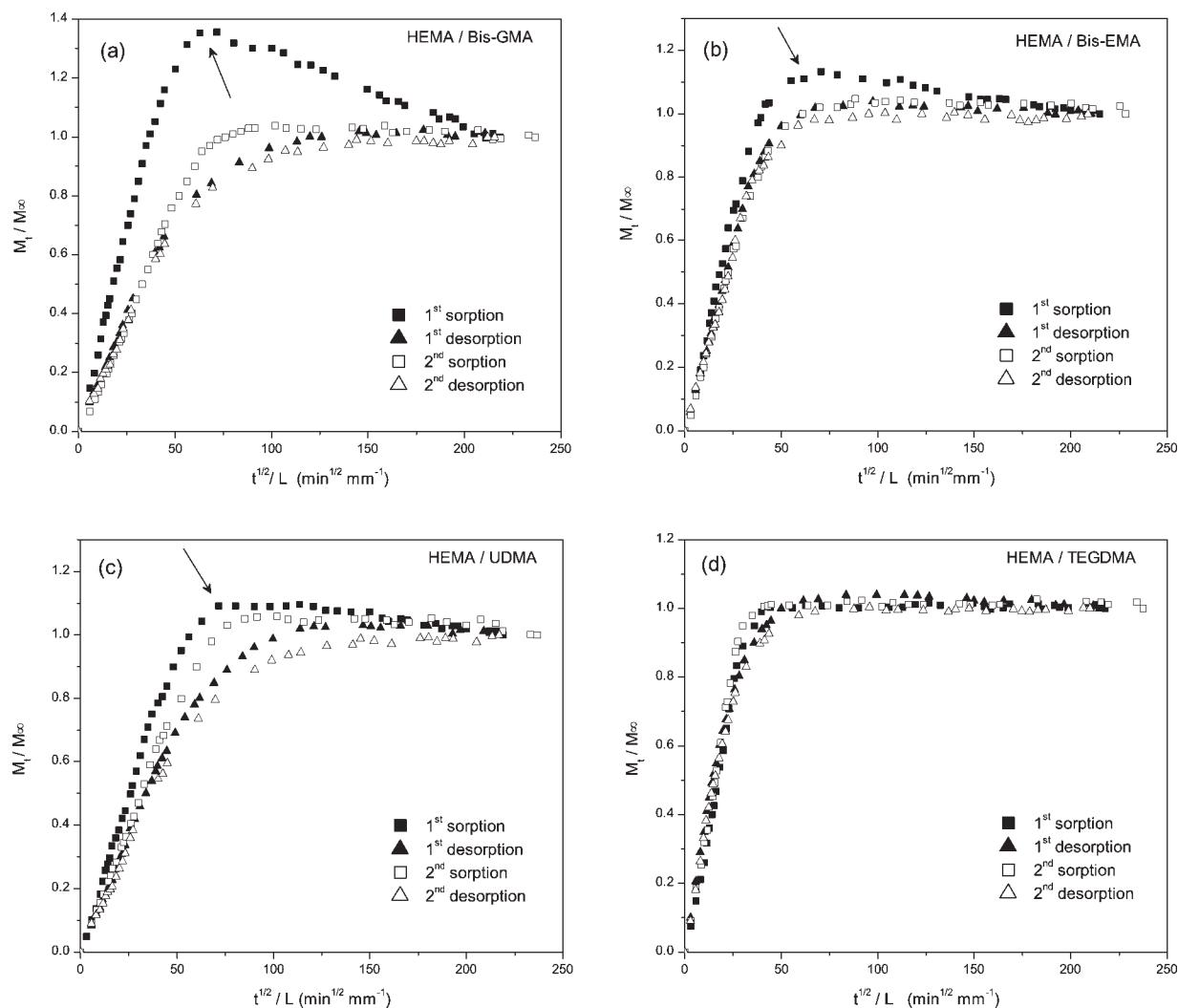
Figure 2 Dependence of M_t/M_∞ on $t^{1/2}/L$ for the sorption and desorption of water 37°C by the copolymers: (a) HEMA/Bis-GMA, (b) HEMA/Bis-EMA, (c) HEMA/UDMA, and (d) HEMA/TEGDMA. The arrows show the maxima.

ing of the Teflon mold. The thickness and diameter of the discs were measured accurately at five points with a micrometer (0–25 mm; Moore & Wright, Sheffield, United Kingdom) and a no. 599 vernier caliper (0–17 cm; Rabone Chesterman, Ltd.), respectively.

Sorption of water or the ethanol/water solution and solubility

All the specimens were placed in a desiccator and transferred to a preconditioning oven at 37°C. After 24 h, they were removed, stored in the desiccator for 1 h, and weighed with a Mettler H54AR (Columbus, OH) balance. This cycle was repeated until a constant mass [initial mass (m_i)] was obtained. Then, the discs were immersed in water or a 75 vol % ethanol/water solution at 37 ± 1°C. At fixed time intervals, they were removed, blotted dry to remove excess liquid, weighed, and returned to the liquid. As the rate of uptake slowed, the time interval was

increased from half an hour for the first 4 h to 1 h for the next 4 h and to 2 h for the next 4 h. The uptake of the liquid was then recorded each day over a period of 30 days. The weight increase of the specimens [WI (%)] was calculated with the following formula:

$$\text{WI } (\%) = 100 \times \frac{m_s - m_i}{m_i} \tag{1}$$

where m_s represents the weight of the saturated specimen after 30 days of immersion and m_i represents the initial mass of the specimen before immersion. This is an apparent value for the liquid sorbed because the unreacted monomer is simultaneously extracted and this results in a decrease in the specimen weight.

For the determination of the extracted monomer, the samples were transferred to a drying oven maintained at 37°C, and a process similar to that used for sorption was repeated during desorption. The

TABLE I
First Sorption of Water by the Copolymers at 37°C

Copolymer	WS (%)[a]	$D_s \times 10^8$ (cm^2/s)[b]	VI (%)[c]	f[d]
HEMA/Bis-GMA	6.15 ± 0.05	2.53 ± 0.23[A,B]	6.46 ± 0.52	0.85 ± 0.07[D]
HEMA/Bis-EMA	4.42 ± 0.20	2.32 ± 0.06[A]	4.74 ± 0.47[c]	0.88 ± 0.07[D]
HEMA/UDMA	5.27 ± 0.07	1.21 ± 0.08	4.89 ± 0.36[C]	0.76 ± 0.06[D]
HEMA/TEGDMA	11.42 ± 0.20	2.75 ± 0.18[B]	11.3 ± 0.28	0.80 ± 0.03[D]

The mean values plus or minus the standard deviation of four replicates are shown. Common corresponding letters (A, B, C, or D) in a given column indicate no significant difference ($p > 0.05$).
[a] Water sorption [calculated with eq. (4)].
[b] Diffusion coefficient for water sorption.
[c] Volume increase due to water sorption [calculated with eq. (8)].
[d] Fraction of water contributing to an increase in swelling [calculated with eq. (9)].

amount of water [WD (%)] or the ethanol/water solution [EWD (%)] that was desorbed by the specimens was calculated with the following formula:

$$WD\ (\%)\ \text{or}\ EWD\ (\%) = 100 \times \frac{m_s - m_d}{m_s} \quad (2)$$

where m_d represents the weight of the specimen after desorption for 30 days. The amount of unreacted monomer that was extracted by water or the ethanol solution during the 30 days of immersion, known as the solubility (SL) of the composite, was calculated with the following formula:

$$SL\ (\%) = 100 \times \frac{m_i - m_d}{m_i} \quad (3)$$

The weight of water or the ethanol/water solution sorbed is then given by the following formula:

$$WS\ (\%)\ \text{or}\ EWS\ (\%) = WI\ (\%) + SL\ (\%) \quad (4)$$

where WS is the water sorbed and EWS is the ethanol/water solution sorbed. Finally, the samples were placed back into the water or ethanol/water solution

at 37°C, and a second sorption–desorption cycle was recorded with approximately the same time intervals.

Diffusion coefficients

According to Fick's Law, the equation for diffusion is one-dimensional (x) when the diffusion coefficient (D) is constant, and it is expressed as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (5)$$

where C denotes the concentration of the diffusing species at time t.

The solution of eq. (5) for the sorption of a liquid in a thin plane sheet, in which diffusion through the edges can be neglected, is given by the following equation:[18,19]

$$\frac{M_t}{M_\infty} = \frac{m_t - m_o}{m_\infty - m_o}$$
$$= 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2}{L^2} Dt\right) \quad (6)$$

where M_t is the accumulated mass of the diffusing liquid at time t, M_∞ is the mass of the sorbed liquid at equilibrium (after infinite time), m_o is the mass of the dry disc, m_t is the mass of the disc at time t, m_∞ is the mass of the specimen at equilibrium, L is the thickness of the disc, and D is the diffusion coefficient of the liquid during the sorption process.

It was shown empirically that for very small values of the parameter Dt/L^2, eq. (6) can be successfully replaced with the following equation:[19]

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{1/2} \quad (7)$$

Figure 3 Dependence of the volume percentage increase on the water sorption percentage of the studied specimens.

On the basis of eq. (7), if one plots M_t/M_∞ against $t^{1/2}/L$, the diffusion coefficient can be calculated from the initial slope of the curve.
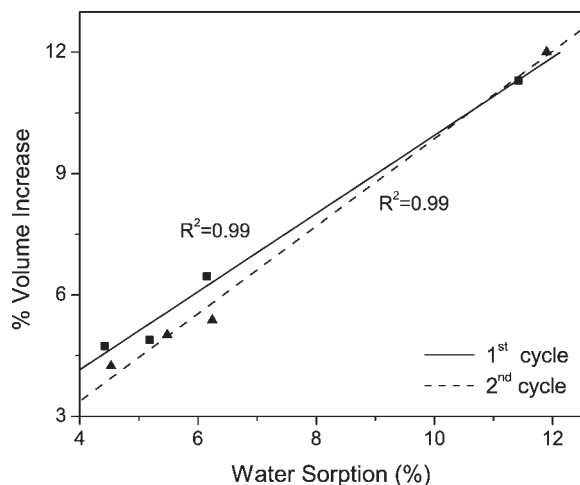
TABLE II
First Desorption of Water by the Copolymers at 37°C

Copolymer	Desorption (%)	$D_d \times 10^8$ (cm²/s)[a]	Solubility (%)
HEMA/Bis-GMA	5.56 ± 0.10	0.77 ± 0.06[A]	2.74 ± 0.16
HEMA/Bis-EMA	4.15 ± 0.16	1.69 ± 0.06	1.01 ± 0.22[B]
HEMA/UDMA	4.79 ± 0.08	0.68 ± 0.04[A]	1.01 ± 0.09[B]
HEMA/TEGDMA	10.1 ± 0.21	3.74 ± 0.15	0.60 ± 0.05

The mean values plus or minus the standard deviation of four replicates are shown. Common corresponding letters (A or B) in a given column indicate no significant difference ($P > 0.05$).
[a] Diffusion coefficient for water desorption.

Fickian sorption equations for liquids can be applied also to desorption.

Density measurements

The densities of all the samples were measured under dry or saturated conditions with a Mettler–Toledo AG 64 balance, and they were calculated on the basis of Archimedes' principle. Furthermore, the volume increase [VI (%)] was calculated with the available data on the densities of the dry (ρ_d) and saturated (ρ_s) specimens:[20]

$$\text{VI (\%)} = \frac{100 \, (\rho_d - \rho_s) + w\rho_d}{\rho_s} \quad (8)$$

where w represents the percentage of the water or ethanol/water solution sorbed [WS (%) or EWS (%), respectively]. With the previous expression, the fraction of the liquid contributing to an increase in swelling (f) in a dimensionless form can be expressed as follows:

$$f = \frac{\text{VI}}{w\rho_d} \rho_l \quad (9)$$

where ρ_l is used to denote the density of the absorbed liquid.

Values of f range between extreme cases of $f = 1$, where the liquid contributes all its volume to the resin, and $f = 0$, where there is no contribution. According to Kalahandra and Turner,[20] the provi-

sional significance given to $1 - f$ is that it corresponds to the fraction of absorbed liquid that is accommodated in microvoids without causing swelling.

Statistical analysis

The values reported in the following tables and figures represent mean values plus or minus the standard deviation of four replicates. A one-way analysis of variance test, followed by Tukey's test, for multiple comparisons between means to determine significant differences was used at a significance level set at $P \leq 0.05$.

RESULTS AND DISCUSSION

Sorption and desorption of water

The curves of M_t/M_∞ versus $t^{1/2}/L$ obtained for the first sorption of water by the HEMA/Bis-GMA, HEMA/Bis-EMA, and HEMA/UDMA copolymers showed a maximum, which was most intensive in the case of the HEMA/Bis-GMA copolymer, followed by a decrease in the water uptake [Fig. 2(a–c)]. Such a maximum in the sorption curve was also observed[17] in first water sorption by the homopolymers poly-Bis-GMA, poly-Bis-EMA, and poly-UDMA. The maxima were attributed to the simultaneous extraction of the unreacted monomer with the water sorption.[17] It is well known that light-cured dental resins contain some quantity of the unreacted monomer that can be extracted by water.[21,22] Maxima were also observed in the corresponding curves

TABLE III
Second Sorption of Water by the Copolymers at 37°C

Copolymer	Sorption (%)	$D_s \times 10^8$ (cm²/s)[a]	VI (%)[b]	f[c]
HEMA/Bis-GMA	6.24 ± 0.10	0.66 ± 0.02	5.38 ± 0.76[A]	0.70 ± 0.09[B]
HEMA/Bis-EMA	4.53 ± 0.15	1.56 ± 0.11	4.24 ± 0.30	0.77 ± 0.03[B]
HEMA/UDMA	5.48 ± 0.06	0.79 ± 0.04	5.01 ± 0.18[A]	0.75 ± 0.02[B]
HEMA/TEGDMA	11.9 ± 0.38	3.50 ± 0.05	12.01 ± 0.72	0.81 ± 0.06[B]

The mean values plus or minus the standard deviation of four replicates are shown. Common corresponding letters (A or B) in a given column indicate no significant difference ($P > 0.05$).
[a] Diffusion coefficient for water sorption.
[b] Volume increase due to water sorption.
[c] Fraction of water contributing to an increase in swelling.

TABLE IV
Second Desorption of Water by the Copolymers at 37°C

Copolymer	Desorption (%)	$D_d \times 10^8$ (cm^2/s)[a]	Solubility (%)
HEMA/Bis-GMA	5.87 ± 0.09	0.71 ± 0.05	0.55 ± 0.02[A]
HEMA/Bis-EMA	4.39 ± 0.04	1.54 ± 0.14	0.32 ± 0.07
HEMA/UDMA	5.24 ± 0.05	0.59 ± 0.03	0.61 ± 0.06[A,B]
HEMA/TEGDMA	10.7 ± 0.15	3.38 ± 0.16	0.64 ± 0.03[B]

The mean values plus or minus the standard deviation of four replicates are shown. Common corresponding letters (A or B) in a given column indicate no significant difference ($P > 0.05$).
[a] Diffusion coefficient for water desorption.

of the homopolymer poly-HEMA and were also attributed to the existence of a sufficient amount of unreacted monomer in the specimen during the first sorption process.[16]

Maxima in sorption curves have been observed for several liquid–polymer systems, and it has been suggested that they are due to the relaxation phenomena of polymer chains.[23–25] The solvent can be sorbed by the sample before the polymer chains have a chance to completely relax, and the structural rearrangements, which the sample experiences as the chains eventually reorient themselves, lead to the rejection of some of the solvent from the sample. This partial exclusion of the penetrant will be more pronounced in instances when the diffusion rate is faster than the rate of chain relaxation because most of the solvent is sorbed into an unrelaxed network.[24] This behavior, however, does not occur in our case
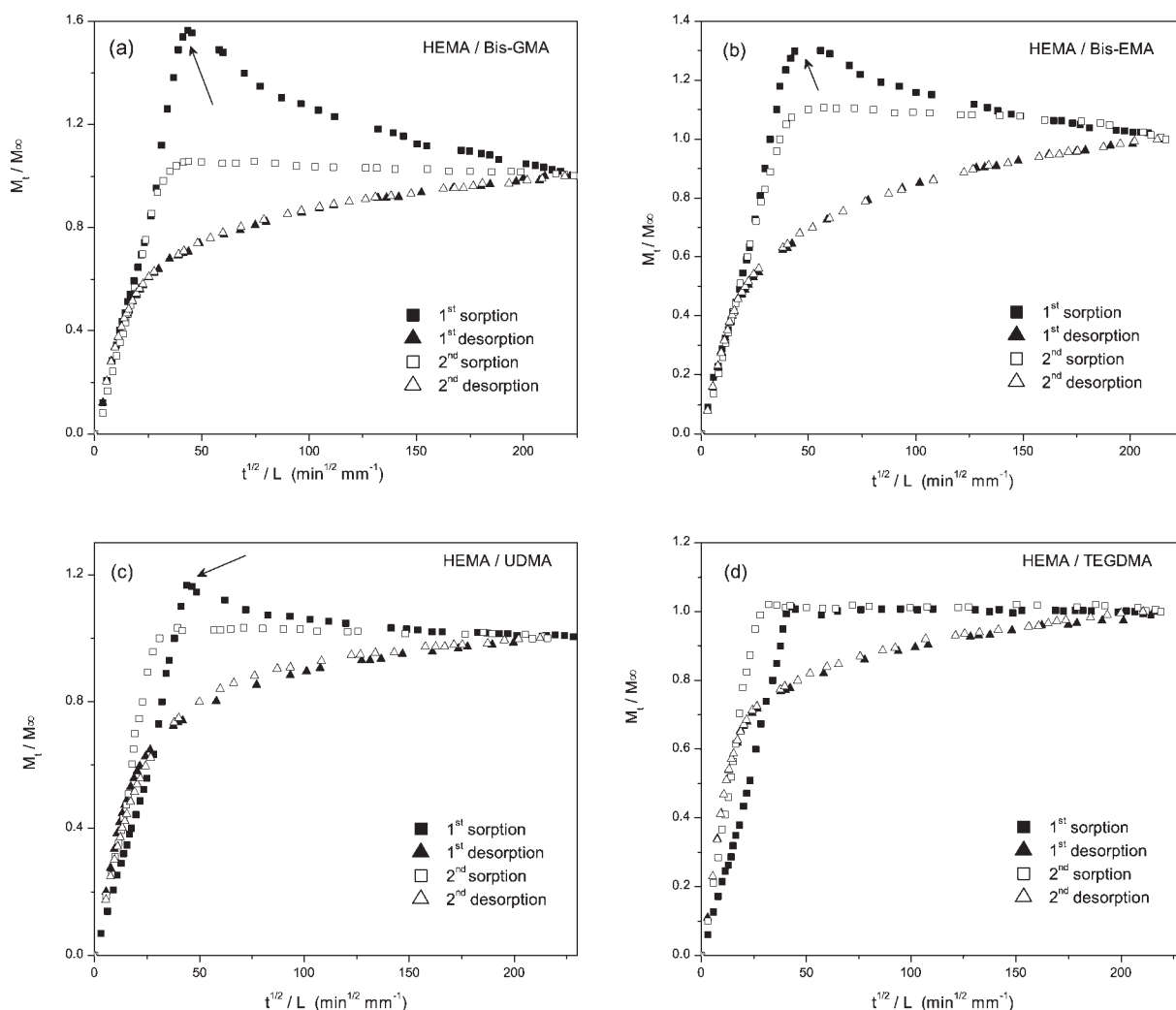

Figure 4 Dependence of M_t/M_∞ on $t^{1/2}/L$ for the sorption and desorption of the ethanol/water solution (75 vol %) at 37°C by the copolymers: (a) HEMA/Bis-GMA, (b) HEMA/Bis-EMA, (c) HEMA/UDMA, and (d) HEMA/TEGDMA.

TABLE V
First Sorption of the Ethanol/Water Solution by the Copolymers at 37°C

Copolymer	Sorption (%)	$D_s \times 10^8$ (cm^2/s)[a]	VI (%)[b]	f[c]
HEMA/Bis-GMA	17.12 ± 0.15[A]	3.44 ± 0.50	25.3 ± 1.35[C]	1.00 ± 0.05[D]
HEMA/Bis-EMA	13.81 ± 0.18	2.58 ± 0.08	19.9 ± 0.21	1.00 ± 0.01[D]
HEMA/UDMA	19.72 ± 0.35	1.72 ± 0.36[B]	29.3 ± 1.71	1.02 ± 0.05[D]
HEMA/TEGDMA	17.40 ± 0.33[A]	1.49 ± 0.11[B]	24.3 ± 2.59[C]	0.94 ± 0.09[D]

The mean values plus or minus the standard deviation of four replicates are shown. Common corresponding letters (A, B, C, or D) in a given column indicate no significant difference ($P > 0.05$).
[a] Diffusion coefficient for the sorption of the ethanol/water solution.
[b] Volume increase due to the sorption of the ethanol/water solution.
[c] Fraction of the solution contributing to an increase in swelling.

because our experimental curves of M_t/M_∞ versus $t^{1/2}/L$ obtained for the second water sorption process show not a maximum but instead Fickian behavior; Fickian sorption occurs when the rate of diffusion is significantly slower than the rate of relaxation of polymer chains.[23] Nevertheless, the experimental curves of $m_t = f(t)$ obtained[17] for the first water sorption process of homopolymers poly-Bis-GMA, poly-Bis-EMA, and poly-UDMA perfectly fit the following equation, which gives the sample mass during sorption at time t:

$$m_t = m_o + \text{mass gain} - \text{mass loss} =$$

$$= a + d\left\{1 - \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2i+1)^2}\exp\left(-(2i+1)^2 b \cdot t\right)\right\}$$
$$-f\left\{1 - \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2i+1)^2}\exp\left(-(2i+1)^2 c \cdot t\right)\right\} \quad (10)$$

where

$$a = m_o$$
$$b = \frac{\pi^2 D_l}{L^2}$$
$$c = \frac{\pi^2 D_m}{L^2}$$
$$d = M_l^\infty$$
$$f = M_m^\infty$$

This equation predicts the presence of a maximum due to the simultaneous extraction of the unreacted monomer (mass loss) with the water sorption (mass gain).

Even though the curves of M_t/M_∞ versus $t^{1/2}/L$ for the HEMA/Bis-GMA, HEMA/Bis-EMA, and HEMA/UDMA copolymers showed maxima, the initial parts of these curves showed Fickian behavior. Therefore, by the application of eq. (7), the values of the diffusion coefficient for water sorption were obtained, and they are presented in Table I. These values are apparent values that are related to the diffusion coefficient of water during its sorption process and to the diffusion coefficient of the monomer extraction.[17]

The experimental curve of M_t/M_∞ versus $t^{1/2}/L$ for the HEMA/TEGDMA copolymer showed Fickian behavior [shown later in Fig. 4(d)]. However, this curve is also a composite curve consisting of water sorption and monomer extraction curves,[17] so an apparent value of the diffusion coefficient for water sorption is also obtained in this case, which is presented in Table I. The diffusion coefficients for water sorption for all the copolymers are much lower than that found[23] for the homopolymer of HEMA (15.5–20 × 10^{-8} cm^2/s) and close to those found by us[17] for the homopolymers of Bis-GMA (1.40 × 10^{-8} cm^2/s), Bis-EMA (3.13 × 10^{-8} cm^2/s), UDMA (1.10 × 10^{-8} cm^2/s), and TEGDMA (1.72 × 10^{-8} cm^2/s).

Table I shows the percentage of the sorbed water during the first sorption. This amount is much lower than that of the HEMA homopolymer (59%)[16,26] and close to those of the homopolymers of the dimetha-

TABLE VI
First Desorption of the Ethanol/Water Solution by the Copolymers at 37°C

Copolymer	Desorption (%)	$D_d \times 10^8$ (cm^2/s)[a]	Solubility (%)
HEMA/Bis-GMA	13.73 ± 0.53[A]	3.36 ± 0.15[B]	6.27 ± 0.34
HEMA/Bis-EMA	11.60 ± 0.18	2.59 ± 0.12	2.19 ± 0.21
HEMA/UDMA	15.97 ± 0.11	3.74 ± 0.31[B]	1.14 ± 0.28
HEMA/TEGDMA	14.17 ± 0.24[A]	5.59 ± 0.36	0.54 ± 0.13

The mean values plus or minus the standard deviation of four replicates are shown. Common corresponding letters (A or B) in a given column indicate no significant difference ($P > 0.05$).
[a] Diffusion coefficient for ethanol/water solution desorption.

TABLE VII
Second Sorption of the Ethanol/Water Solution by the Copolymers at 37°C

Copolymer	Sorption (%)	$D_s \times 10^8$ (cm^2/s)[a]	VI (%)[b]	f[c]
HEMA/Bis-GMA	17.27 ± 0.50[A]	3.14 ± 0.25	22.1 ± 0.21[B]	0.89 ± 0.02[C]
HEMA/Bis-EMA	13.42 ± 0.10	2.27 ± 0.04	16.8 ± 1.49	0.88 ± 0.08[C]
HEMA/UDMA	18.17 ± 0.53	3.65 ± 0.05	24.5 ± 1.15	0.92 ± 0.02[C]
HEMA/TEGDMA	16.66 ± 0.18[A]	4.56 ± 0.22	20.9 ± 0.71[B]	0.86 ± 0.02[C]

The mean values plus or minus the standard deviation of four replicates are shown. Common corresponding letters (A, B, or C) in a given column indicate no significant difference ($P > 0.05$).
[a] Diffusion coefficient for the sorption of the ethanol/water solution.
[b] Volume increase due to the sorption of the ethanol/water solution.
[c] Fraction of the ethanol/water solution contributing to an increase in swelling.

crylates, which range from 2 to 6%.[10,17] The water sorption efficiency of the studied copolymers is in the following order: HEMA/TEGDMA > HEMA/Bis-GMA > HEMA/UDMA > HEMA/Bis-EMA. This is similar to that obtained for the homopolymers of the dimethacrylates.[10,17]

The water sorption caused a volume percentage increase that was found to be linearly dependent on the water sorption percentage (Fig. 3). This volume increase was caused by 76–88% of the sorbed water (Table I). The rest of the sorbed water was accommodated in voids of the copolymer network without causing swelling.

The experimental curves of M_t/M_∞ versus $t^{1/2}/L$ for the water desorption for all the copolymers showed Fickian behavior (Fig. 2). The calculated percentage of the desorbed water, the percentage of the extracted monomer during the first sorption process, and the desorption diffusion coefficient of water are shown in Table II. A comparison of the values of Tables I and II shows that the amount of desorbed water is slightly lower than that sorbed, and this means that a small amount of water was retained in the copolymer matrix after desorption. The HEMA/Bis-GMA copolymer showed the highest solubility in water, which, however, was lower than that of the homopolymer of HEMA (6.37).[16]

The results obtained from the second cycle of sorption and desorption are tabulated in Tables III and IV, respectively. The amount of water sorbed during the second sorption was not statistically different from that sorbed during the first sorption.

Similar results were also observed for the water desorption half-cycle. The solubility of the copolymers was lower during the second sorption, so the unreacted monomers were extracted mainly during the first sorption.

Sorption and desorption of the ethanol/water solution

The experimental curves of M_t/M_∞ versus $t^{1/2}/L$ obtained for the sorption of the ethanol/water solution by the HEMA/Bis-GMA, HEMA/Bis-EMA, and HEMA/UDMA copolymers also showed maxima as in the case of water sorption [Fig. 4(a–c)], whereas that of the HEMA/TEGDMA copolymer showed Fickian behavior [Fig. 4(d)]. Such maxima were also observed in the first sorption of an ethanol/water solution (75 vol %) by homopolymers of Bis-GMA, Bis-EMA, and UDMA and were attributed to the extraction of the unreacted monomer.[14]

The results obtained for the sorption and desorption of the ethanol/water solution during the first and second cycles are presented in Tables V–VIII. The sorption of the ethanol/water solution by copolymers was in the following order: HEMA/UDMA > HEMA/Bis-GMA ≈ HEMA/TEGDMA > HEMA/Bis-EMA. The sorbed amount of the ethanol/water solution by these copolymers was higher than the amount of the ethanol/water solution sorbed by the corresponding homopolymers of the dimethacrylates[14] and higher also than the amount of pure ethanol sorbed by the homopolymers of the dimethacrylates.[17]

TABLE VIII
Second Desorption of the Ethanol/Water Solution by the Copolymers at 37°C

Copolymer	Desorption (%)	$D_d \times 10^8$ (cm^2/s)[a]	Solubility (%)
HEMA/Bis-GMA	14.68 ± 0.44[A]	3.39 ± 0.16	0.65 ± 0.18[A]
HEMA/Bis-EMA	11.83 ± 0.09	2.53 ± 0.13	0.38 ± 0.11[A]
HEMA/UDMA	15.92 ± 0.41	3.88 ± 0.27	−0.01 ± 0.04
HEMA/TEGDMA	14.38 ± 0.16[A]	5.66 ± 0.29	−0.10 ± 0.12

The mean values plus or minus the standard deviation of four replicates are shown. Common corresponding letters (A) in a given column indicate no significant difference ($P > 0.05$).
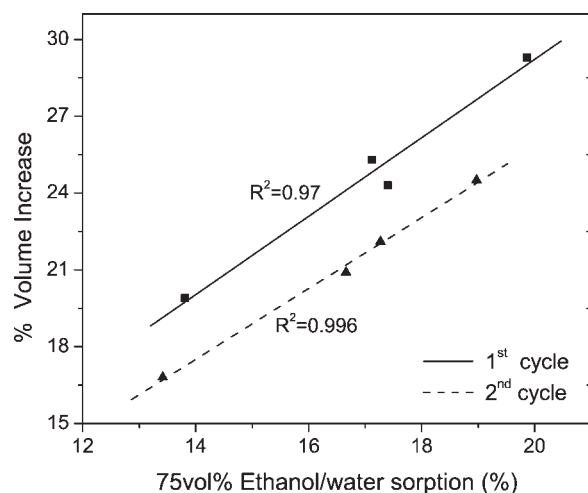[a] Diffusion coefficient for the desorption of the ethanol/water solution.

Figure 5 Dependence of the volume percentage increase on the ethanol/water solution sorption percentage of the studied specimens.

The sorbed amounts of the ethanol/water solution during the first and second cycles were very close, and the desorbed amounts of the ethanol/water solution during the first and second cycles were also very close (Table V–VIII). However, the amount of the desorbed solution was lower than the sorbed amount, and this indicated that some of the solution remained in the samples after desorption.

The sorption of the ethanol/water solution caused a volume increase that linearly depended on the absorbed amount (Fig. 5).

Figure 6 presents the effect of the copolymer structure on the sorption percentage of different solvents. All the copolymers sorbed more of the ethanol/water solution than water. The HEMA/TEGDMA and HEMA/UDMA copolymers showed the highest sorption of water and the ethanol/water solution, respectively, whereas the HEMA/Bis-EMA copoly-
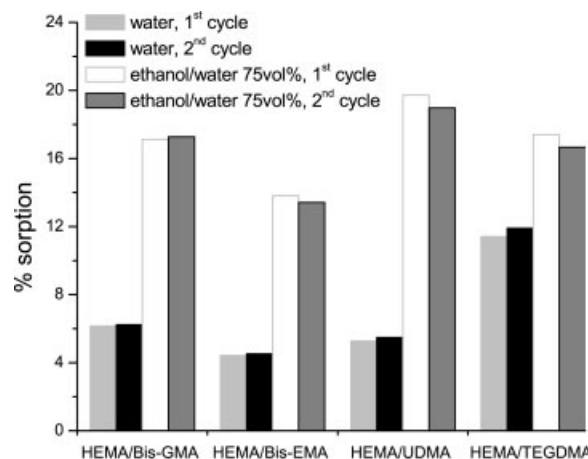

Figure 6 Effect of the copolymer structure and nature of the solvent on the amount of solvent sorbed [water or ethanol/water (75 vol %) at 37°C].
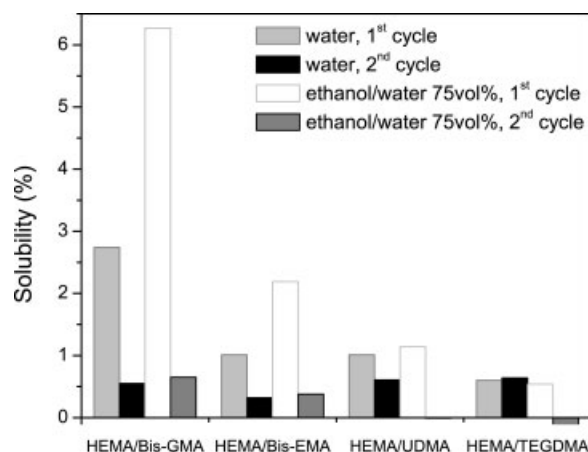

Figure 7 Solubility of the copolymers studied in water or ethanol/water (75 vol %) at 37°C.

mer showed the least sorption capacity for water and the ethanol/water solution.

Figure 7 shows the solubility of the copolymers in both water and the ethanol/water solution. The HEMA/Bis-GMA copolymer showed the highest solubility in both, and this behavior could be due to the lowest degree of conversion of Bis-GMA molecules in comparison with the other dimethacrylates, as observed in a previous work.[21]

CONCLUSIONS

The experimental curves of M_t/M_∞ versus $t^{1/2}/L$ of the first sorption of water or a 75 vol % ethanol/water solution by the HEMA/Bis-GMA, HEMA/Bis-EMA, and HEMA/UDMA copolymers showed maxima due to the simultaneous extraction of the unreacted monomers with the solvent sorption. The curves for the second sorption and first and second desorption showed Fickian behavior. Fickian behavior for sorption and desorption was shown by the HEMA/TEGDMA copolymer.

The amount of solvent sorbed and the solubility of the copolymers depended on both the structure of the copolymers and the nature of the solvent. All copolymers sorbed more of the ethanol/water solution than water. The volume increase caused by the solvent sorption was found to linearly depend on the amount of the sorbed solvent.

The amount of water sorbed by the HEMA copolymers and their diffusion coefficients were much lower than those of the HEMA homopolymer but closer to those of the homopolymers of the dimethacrylate comonomers.

The results of this work could be useful in the interpretation of the sorption characteristics of dental materials containing these copolymers.

References

1. Yiu, C. K. Y.; King, N. M.; Carrilho, M. R. O.; Sauro, S.; Rueggeberg, F. A.; Prati, C.; Carvalho, R. M.; Pashley, D. H.; Tay, F. R. Biomaterials 2006, 27, 1695.

2. Linden, L. A. In Radiation Curing in Polymer Science and Technology; Fouassier, J. P.; Rabek, J. E., Eds.; Elsevier: Essex, England, 1993; Vol. IV, p 387.

3. Van Landuyt, K. L.; Snauwaert, J.; De Munk, J.; Peumans, M.; Yoshida, Y.; Poitevin, A.; Coutinho, E.; Suzuki, K.; Lambrechts, P.; Van Meebeek, B. Biomaterials 2007, 28, 3757.

4. Musto, P.; Ragosta, G.; Scarinza, G.; Mascia, L. J Polym Sci Part B: Polym Phys 2002, 40, 922.

5. Ferracane, J. L. Dent Mater 2006, 22, 211.

6. Ito, S.; Hashimoto, M.; Wadgaonkar, B.; Svizero, N.; Carvalho, R. M.; Yiu, C.; Rueggeberg, F. A.; Fougler, S.; Saito, T.; Nishitani, Y.; Yoshiyama, M.; Tay, F. R.; Pashley, D. H. Biomaterials 2005, 26, 6449.

7. Yiu, C. K.; King, N. M.; Pashley, D. H.; Suh, B. I.; Carvalho, R. M.; Carrilho, M. R. O.; Tay, F. R. Biomaterials 2004, 25, 5789.

8. Gerzina, T. M.; Hume, W. R. J Dent 1996, 24, 125.

9. Bouillaguet, S.; Wataha, J. C.; Hanks, C. T.; Ciucchi, B.; Holz, J. J Endod 1996, 22, 244.

10. Sideridou, I.; Tserki, V.; Papanastasiou, G. Biomaterials 2003, 24, 655.

11. Sideridou, I.; Achilias, D. S.; Spyroudi, C.; Karabela, M. Biomaterials 2003, 25, 367.

12. McKinney, J. E.; Wu, W. J Dent Res 1985, 64, 1326.

13. Lee, S. Y.; Greener, E. H.; Menis, D. L. Dent Mater 1995, 11, 348.

14. Sideridou, I. D.; Achilias, D. S.; Karabela, M. M. J Biomed Mater Res B 2006, 81, 207.

15. Sideridou, I. D.; Karabela, M. M.; Bikiaris, D. N. Dent Mater 2006, 23, 1142.

16. Sideridou, I. D.; Papanastasiou, G. E. J Appl Polym Sci 2007, 106, 2380.

17. Sideridou, I. D.; Karabela, M. M.; Vouvoudi, E. C.; Papanastasiou, G. E. J Appl Polym Sci 2008, 107, 463.

18. Crank, J. The Mathematics of Diffusion; Clarendon: Oxford, 1975.

19. Kovacs, A. J Chem Phys 1948, 45, 258.

20. Kalahandra, S.; Taylor, D. T. J Biomed Mater Res 1987, 21, 329.

21. Sideridou, I.; Tserki, V.; Papanastasiou, G. Biomaterials 2002, 23, 1819.

22. Sideridou, I. D.; Achilias, D. S. J Biomed Mater Res B 2005, 74, 617.

23. Ghi, P.; Hill, D. J. T.; Whittaker, A. K. J Polym Sci Part B: Polym Phys 2000, 38, 1939.

24. Vrentas, J. S.; Duda, J. L.; Hou, A. C. J Appl Polym Sci 1984, 29, 399.

25. Smith, M. J.; Peppas, N. A. Polymer 1985, 26, 569.

26. Franson, N. M.; Peppas, N. A. J Appl Polym Sci 1983, 28, 1299.