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Water sorption and diffusion coefficient through an experimental dental resin

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Abstract Polymeric composites have been widely used as dental restorative materials. A fundamental knowledge and understanding of the behavior of these materials in the oral cavity is essential to improve their properties and performance. In this paper we computed the data set of water absorption through an experimental dental resin blend using specimen discs of different thicknesses to estimate the diffusion coefficient. The resins were produced using Bisphenol A glycol dimethacrylate, Bisphenol A ethoxylated dimethacrylate and Triethylene glycol dimethacrylate monomers. The water sorption test method was based on International Standard ISO 4049 "Dentistry-Polymer-based filling materials". Results show a diffusion coefficient around 6.38×10^{-8} cm^2/s, within a variance of 0.01%, which is in good agreement with the values reported in the literature and represents a very suitable value.

1 Introduction

One of the advantages of resin dental materials is excellent aesthetics. Since their commercial introduction in the mid-1960s [1, 2] resin composites have undergone significant development. Furthermore, new monomers [3] have been developed to obtain materials with suitable degree of conversion, shrinkage and marginal leakage. However, despite researchers' efforts, aspects such as water sorption and solubility still limit application of these materials. Solvent uptake impair mechanical properties [4–6] and modulus of elasticity [7, 8], causes adverse effects [9] to the composites, including swelling [10, 11], hydrolysis [12], solubility [13], elution of unreacted monomers [14–17], leaking of fillers [12, 18], and release of methacrylic acid [19], and causes decrease in glass-transition temperature (T_g) [8], reducing thermal stability and polymer plasticization. According to ISO 4049 Standard [20], for dental resin-based filling material to be deemed suitable for use, its maximum water sorption must be less than (40 μg/mm^3) after seven days of immersion.

Water sorption and the diffusion coefficient depend on the structure of the copolymer and the nature of the solvent [21, 22], monomer [23–26] and filler [27] composition, interaction between polymeric matrix and filler [28], degree of polymerization, crosslinking [29], environmental temperature [30, 31], concentration of catalyst and initiator systems, cycle of water sorption [32] and presence of air-filled voids within the matrix [33]. Furthermore, the diffusion phenomenon is complex and the presence of crystallites in a polymer reduces the effective cross-section area of diffusion [34].

The mathematical theory of diffusion rests on the hypothesis that the rate of transfer of the diffusing substance is proportional to the concentration gradient measured normal to the cross section. The partial differential equation for mass transfer (diffusion) is determined by immersion time and sample dimensions as represented by Eq. 1:

$$\frac{\partial C}{\partial t} = D\left(\nabla^2 C\right) \tag{1}$$

where D is the diffusion coefficient, C the concentration of diffusing substance, ∇ the concentration gradient and t the immersion time

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Frequently, diffusion occurs effectively in one direction only, and there is a concentration gradient along the x-axis only. In such cases Eq. 1 reduces to Eq. 2:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{2}$$

In this paper, we calculate the diffusion coefficient of an experimental neat dental resin blend to quantify the polymer contribution to sorption and water uptake without the influence of filler content. In commercial resins this is difficult to measure due to the presence of filler and other components, such as pigments, silane coupling agents, inhibitor agents and other substances involved in the complex formulation of these composites.

2 Materials and methods

The experimental neat dental resin blend was obtained by mixing Bisphenol A glycol dimethacrylate (Bis-GMA) from DENTSPLY®, Bisphenol A ethoxylated dimethacrylate (BisEMA) and Triethylene glycol dimethacrylate (TEGDMA) from Sartomer Company Inc. All materials in this study were used as received without further purification.

The resins were prepared using Bis GMA:Bis EMA:TEGDMA in wt/wt ratios of 50:20:30, respectively.

This composition was selected on the basis of our preliminary studies of hardness and degree of conversion data. The monomers were mixed by hand spatulation. After homogenization of the resin, the 2,4,6-trimethylbenzoyl-diphenyl phosphine (TPO), 0.25 wt%, from New Sun Chemical Co. was incorporated into the formulation as a photoinitiator. The manipulation was performed in a dark room to prevent light interfering in the polymerization (setting).

In order to eliminate entrapped air, the blend was maintained under vacuum (50 mmHg) for 2 h.

Specimen discs approximately (14.81 mm ± 0.15) in diameter and (0.5, 1.0, 1.5, 2.0, 2.5 mm) thick were fabricated in a PTFE mould. The discs were then irradiated for 40 s on each side with an Optlight Plus dental photocuring unit from Gnatus®. This unit emitted radiation predominantly in the 420–500 nm range and the source consisted of a 75 W tungsten halogen lamp, a series of optical filters and lenses, and an (11 mm) diameter fused fiber optic light guide. Five specimen discs of each thickness were prepared. The specimens were hand-polished with a series of sandpapers up to #1200, and finished to an accuracy of (±0.05 mm) thickness. Sample thickness was measured accurately at five points using an electronic digital caliper (Max–Cal, Fowler & NSK, (0.01 mm) resolution, USA). For specimens up to (2.0 mm) thick, the side surface was covered with wax to prevent water uptake from the sidewall. Preliminaries tests to the wax were carried out using identical conditions from discs immersion and no significative variation mass was observed. The wax is composed by hydrocarbons, mineral oil and pigment. Due to its composition, the wax is a highly hydrophobic material. For this reason, the water sorption through wax can be disregard.

Subsequently, the specimens were washed with deionized water in ultrasonic cleaning equipment for 15 min and transferred to a desiccator with silica gel maintained at 37°C, where they were kept for seven days until weight loss change stabilized. Constant mass (m_i) was obtained with an accuracy of (±0.001 g) using an analytical balance (AND HM-202, CE, Japan). The ultrasonic cleaning has no influence on the absorption test because in despite of the short duration of procedure (the ultrasonic cleaning takes just fifteen minutes), the conditioned mass is established after the cleaning and the mass water, which could be absorbed in this short interval, is certainly desorbed during the mass stabilization period.

2.1 Water sorption and solubility

Sorption uptake tests were performed according to the method described in international Standard ISO 4049 [20]. All specimens were immersed in deionized water bath at 37°C ± 0.5°C. At fixed time intervals they were removed, blotted dry to remove excess water, weighed and returned to the water. The time intervals were shorter over 2 days and extended as uptake slowed. Water uptake was recorded until quasi-equilibrium was attained and a constant mass (m_t) was obtained. This process took about three months (2016 h). Specimen percentage weight increase, Wi (%), was calculated as follows:

$$Wi(\%) = 100\left(\frac{m_t - m_i}{m_i}\right) \tag{3}$$

$$Wi = \left(\frac{m_t - m_i}{V}\right) \tag{4}$$

This is an apparent value for water uptake, because unreacted monomer is simultaneously leached, resulting in weight loss.

Following the sorption cycle, the specimens were dried inside a desiccator containing fresh silica gel and weighed to obtain a constant mass mt', with an accuracy of ±0.001 g.

The solubility values were obtained, in micrograms per cubic millimeter, using the following equation:

$$W_{sl} = \left(\frac{m_i - m_{t'}}{V}\right) \tag{5}$$

Here m_i is the conditioned mass, in micrograms, prior to immersion in water as previously described and V is the volume of the specimen, in cubic millimeters.

The values obtained for the sum of (4) and (5) equations represent the overall water sorption.

2.2 Diffusion coefficients

Equation 2 for Fick's Law for diffusion in one dimension (x), when the diffusion coefficient D is constant in plane sheet geometry and Co is the surface concentration, can be solved as follows (6):

$$\frac{C(\xi)}{C_O} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\, e^{-(2n+1)^2}\pi^2 T/_4 \cos\frac{(2n+1)\pi\xi}{2} \tag{6}$$

where $T = \frac{Dt}{h^2}$ and $\xi = \frac{x}{h}$ are dimensionless parameters, h is the thickness of the specimen in cm and x, the diffusion front of maximum concentration of water in the cross section direction.

The numerical solution of Eq. 2 was obtained and the resulting distribution functions were integrated numerically in order to obtain an integrated Fickian diffusion function, which could be numerically fitted against the experimental parameter for the diffusion coefficient estimation.

The experimental values of reduced concentration (*C/Co*) for each specimen disc thickness were fitted into the integrated diffusion function using non-linear multivariate regression, and the overall diffusion coefficient D calculated within a variance of 0.01%.

2.3 Statistics

The mean and standard deviation of water uptake were calculated for each group of equal-thickness discs. All data were then analyzed by ANOVA and the groups were compared. Multiple comparisons were also performed using the Tukey–Kramer test. Statistical significance was preset at $\alpha = 0.05$.

3 Results

The maximum percentage water sorption values at 37°C: *Wi* (%) and *Wi* (μg/mm^3) and the solubility value W_{sl} (μg/mm^3) were calculated for each copolymer disc using Eqs. 3–5, respectively. The mean values and standard deviations are shown in Table 1. Note that water sorption *Wi* (%) is slightly lower for the thicker discs (1.5–2.5 mm) than the thinner ones (0.5 and 1.0 mm).

Table 1 Maximum water sorption *Wi* (%) and *Wi* (μg/mm^3), and solubility W_{sl} (μg/mm^3) of the neat resin discs

Specimen thickness (mm)	W_i (%) max	W_i (μg/mm^3)	W_{sl} (μg/mm^3)
0.5	2.998 ± 0.06	34.668 ± 0.15	11.600 ± 0.26
1.0	2.928 ± 0.11	35.296 ± 0.04	10.735 ± 1.61
1.5	2.656 ± 0.07	35.300 ± 0.02	14.844 ± 2.14
2.0	2.653 ± 0.06	32.220 ± 0.03	11.180 ± 2.21
2.5	2.669 ± 0.06	32.736 ± 0.03	7.010 ± 1.60

As shown in Table 1, the sorption values *Wi* (μg/mm^3) obtained in this study are in the (32.22–35.30 μg/mm^3) range. Consequently, the blend is deemed to have passed the sorption test in conformity with Standard 4049 that establishes (40 μg/mm^3) as the maximum water uptake value. However, taking into account the leaching out of residual unreacted monomers obtained, W_{sl} (μg/mm^3) parameter, the overall water sorption *Wi* (μg/mm^3) is around 45 μg/mm^3. Consequently, to blend studied to be deemed suitable to use by sorption requirement is necessary to improve this composition blend.

Figure 1 shows the kinetics of water sorption through each thickness group. The kinetic water sorption data exhibit high sorption rates until around 53 h of storage, with the rates subsequently beginning to decrease. The kinetic water sorption data in the initial stage, reflecting peak uptake in the period is shown in detail in Fig. 2. Early in storage time, the various disc thickness groups returned almost the same values. The diffusion coefficients (D) were obtained by superimposing the experimental curve on the theoretical diffusion Eq. 6, resulting in an average value of (6.38×10^{-8} cm^2/s) with a variance of 0.01%. The superimposed curves are displayed in Fig. 3.

4 Discussion

The slightly lower water sorption *Wi* (%) for the thicker discs (1.5–2.5 mm) was inferred to be related with the

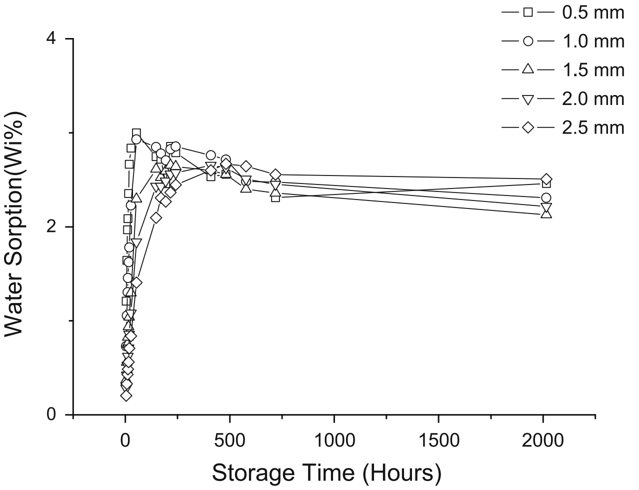

Fig. 1 Water sorption in specimens of different thicknesses (☐ 0.5 mm, ○ 1.0 mm, Δ 1.5 mm, ▽ 2.0 mm, ◇ 2.5 mm) over storage time. Values are means for $n = 5$

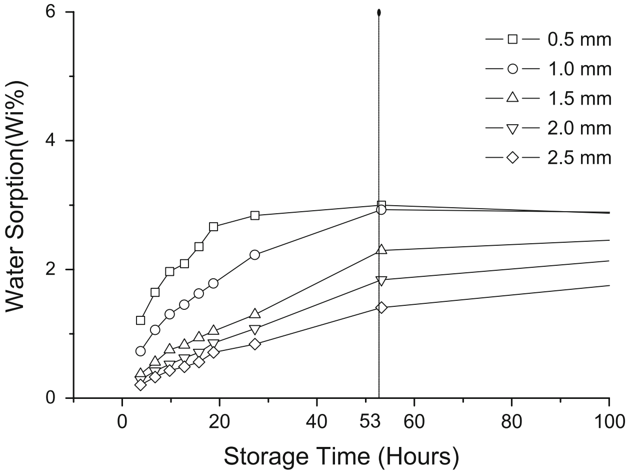

Fig. 2 Kinetic water sorption in specimens of different thicknesses (□ 0.5 mm, ○ 1.0 mm, Δ 1.5 mm, ∇ 2.0 mm, ⋄ 2.5 mm) in the initial stage. Values are means for $n = 5$

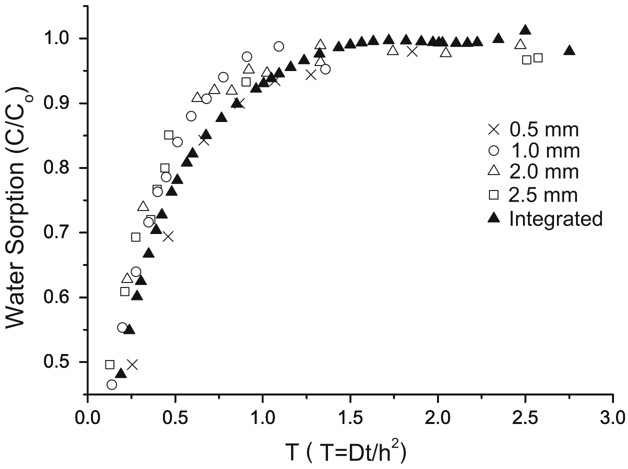

Fig. 3 Water sorption ratio C/Co versus T (dimensionless parameter) and the superimposed theoretical diffusion equation curve. Integrated Fick's PDE solution experimental data C/C$_o$ (%) (▲). 0.5 mm (X), 1.0 mm (○), 2.0 mm (Δ) and 2.5 mm (□), for the diffusion coefficient estimation

calculations, which did not include leaching of the resin components. This phenomenon is more pronounced in the thicker discs, decreasing slightly the water sorption values. Similar behavior was observed in a previous report [35] on varying thicknesses of a commercial filling resin.

As shown in Table 1, the sorption values obtained in this study are in the (32.22–35.30 μg/mm^3) range. The sorption values data *Wi* (%) are obtained without considering solubility.

Water uptake by a copolymer blend depends on the hydrophilic characteristics of the individual components and the structure of the polymer network.

Several reports [7, 30, 36, 37] have observed that water absorbed into hydrophilic polymers can exist in different forms: free water, freezable bound water and non-freezable water. The different kinds of linkage between the water molecules and the polymer network causes differing effects, such as plasticizing, swelling and dimensional changes. Moreover, exposure to water at high temperature may produce irreversible effects, such as chemical degradation and cracking. Investigations into water states in polymers give valuable information on diffusion in hydrophilic polymers and elucidate the different types of interaction between water molecules and the macromolecular network. However, it is beyond the scope of this paper to include such considerations of water states in the blend studied.

Some studies [7, 30, 38] have reported that the extent of water sorption can be explained using Hoy's solubility parameter (δ) calculated by adding the molar attraction constants of each repeating functional group in the polymers, according to the method of Van Krevelen [39]. In the current study, the monomers BisGMA, BisEMA and TEGDMA were used in the ratio 50:20:30 wt/wt intending to get a blend with a suitable sorption value in view of the hydrophilicity of each neat polymer used.

A previous study [25] reports water sorption values of 6.3 wt% for TEGDMA, 1.8 wt% for BisEMA and 2.6 wt% for BisGMA. The high water sorption by TEGDMA can be attributed to the polymer's high network flexibility and heterogeneity creating spaces which accommodate a larger amount of water.

One approach to improving dental resin properties involves suitable polymer combinations. The synergistic effect of BisEMA, BisGMA and TEGDMA, in appropriate proportions, raises the polymerization degree and decreases water sorption. The improvement in polymerization degree almost always, justifies their use, despite the high sorption value for TEGDMA. A previous report [25] has also observed that all copolymers containing TEGDMA monomer units exhibit lower water sorption and solubility values than predicted for the neat polymers. This behavior could be attributed to hydrogen bond formation between the unreacted BisGMA (−OH) and TEGDMA (C=O, –O–) monomers preventing leaching of the monomer by water.

As can be seen in Table 1, the results show satisfactory characteristics of sorption. For comparison purpose, it is worth noting that recent reports show water uptake in the range of 0.55–12.83% [7] and 9.9–19.8 μg/mm^3 in dental composite formulations [23].

It is worth pointing out that in the current study unfilled resins were used, however the incorporation of some specific filler can decrease water sorption and diffusion coefficient values [24] and improve the mechanical properties of the composite material.

The thicker specimens (1.5; 2.0; 2.5 mm) show slightly lower sorption rates (*Wi*%). This fact relates to initial mass values, which increase with specimen thickness, decreasing

Wi (%) according to Eq. 3. Thicker specimens thus take longer to reach quasi-equilibrium. A gradual weight decrease, attributed to leaching of residual unreacted monomers, was computed after prolonged immersion. Nonetheless, as can be seen in the plots, these weight losses are small when compared with overall mass gain.

The diffusion coefficient was obtained and resulting in an average value of (6.38×10^{-8} cm^2/s). This value is comparable with diffusion coefficients obtained previously [24, 28, 38] for similar copolymer resins. It is interesting to note that the theoretical simulations are in very good agreement with the experimental data over the whole sorption curve. This finding confirms that Fickian diffusion can be assumed for this copolymer blend during the overall sorption period. Similar outcomes obtained previously [35] corroborate the results of this study.

5 Conclusions

The sorption data set obtained in this study is in the range (32.22–35.30 μg/mm^3), revealing that the blend studied is deemed to have passed sorption testing to standard 4049, which establishes (40 μg/mm^3) as the maximum value.

However, taking into account the leaching out of residual unreacted monomers, W_{sl} (μg/mm^3) parameter, the overall water sorption *Wi* (μg/mm^3) obtained is around 45 μg/mm^3. Consequently, to the blend studied to be deemed suitable to use by sorption requirement is necessary to improve this composition blend.

The thicker discs (1.5–2.5 mm) exhibit slightly lower water sorption *Wi* (%) than the thinner ones (0.5 and 1.0 mm). This fact relates to initial mass values, which increase with specimen thickness, decreasing *Wi* (%). An experiment is currently being designed in order to confirm the above leaching effect for this blend as well as in filled blends of this resin.

The diffusion coefficient estimated at around ($D = 6.38 \times 10^{-8}$ cm^2/s), within a variance of 0.01%, is in good agreement with the values reported in the literature and represents a very suitable value.

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