Sorption Kinetics of Restorative Dental Composites Immersed in Different Solutions

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ABSTRACT
The long life of any dental composites in oral cavity depended on the environment to which it is exposed. Dental composites have water sorption in oral cavity this sorption may have negative effects on dental composites. Forty-eight Disc specimens were prepared with three different composites. Sorption and solubility were measured after immersion in four different solutions: distilled water, artificial saliva, ethanol/water, and mouthwashes (Chlorhexidine) for 100 days at 37°C. Sorption and solubility (µg/mm³) were calculated based on ISO 4049, while diffusion coefficient (m²/s) was calculated according to Fick’s second law. The experimental data obtained from sorption and solubility were found depending on the immersion media. Ethanol/water and Chlorhexidine had the most significant effects, and these values were depending on the components of dental composite. On the other hand, Stability and equilibrium were measured by immersing in water and artificial saliva occurred within 2 weeks for all the three composites, while it took about 4 to 5 weeks to stability in ethanol/water and Chlorhexidine. Highest sorption after immersion in water, and artificial saliva 16.96 and 20.95 µg/mm³ respectively, and solubility (7.98 and 7.7 µg/mm³) respectively, while the highest values of diffusion coefficients were found to be (19.08−1.09×10⁻¹³ m²/s).

Keywords: sorption; solubility; diffusion coefficient; alcohol; mouth wishes; composite resins.

Introduction
The dental restorative materials are required to have long term durability in the oral cavity. Composites are most important and more popular as dental restorative materials because of their strength, rapid polymerization, and esthetic appearance (1).

In general, the composition of resin composites is constituted of a polymeric matrix, filler particles, and a coupling agent (silane), which links the matrix to the fillers. The durability and long life of dental composites resin are basically influenced by the
characteristics of the oral environment \(^{(2, 3)}\).

Water sorption in the dental composite was a controlled diffusion that causes several times dependent effects, such as effect on physical properties \(^{(4)}\), impair mechanical properties \(^{(5-7)}\) and modulus of elasticity \(^{(8, 9)}\), increase the wear of composite resins \(^{(10)}\), hydrolysis and solubility \(^{(11, 12)}\), leaking of fillers \(^{(13)}\), elution of leachable species \(^{(14)}\), causes decrease in glass-transition temperature \((T_g)\) \(^{(9)}\) and the toxicity testing results of dental composite resins are variable according to immersion media \(^{(15)}\).

Water sorption characteristics depend on many factors, such as the structure of the composites and the nature of the solution \(^{(16)}\), monomer \(^{(17-19)}\) and filler composition \(^{(20, 21)}\), interaction between matrix and filler \(^{(21)}\), cross linking and degree of polymerization \(^{(22)}\). The commonly method used by researchers to determine water sorption and solubility of restorative dental composites is the ISO 4049 method. The standard limits for the water sorption and solubility are 40 µg/mm\(^3\) and 7.5 µg/mm\(^3\) respectively \(^{(23)(23)}\).

Media of immersion include culture media, distilled water \(^{(24)}\), artificial saliva, solution of ethanol/water \(^{(17, 25)}\) and Chlorhexidine \(^{(26)}\). Distilled water simulates the wet oral environment provided by saliva and water, and the ethanol solution simulates certain beverages, including alcohol, vegetables, fruits, candies and syrups.

Alcohol is a good polymer chain solvent, and solutions with high alcohol concentrations can degrade the mechanical properties. Mouthwashes are usually recommended for consumers to reduce halitosis, prevent and control dental caries and periodontal diseases \(^{(2)}\). It is estimated that the higher power oxidative of bleaching agents in contact with organic molecules change the polymeric bonds and make the composites more perishable \(^{(26)}\). Many researches proposed that diffusion coefficient is important effect in determining the time dependent mechanical properties and time dependent hydroscopic expansion of resins for clinical use \(^{(27)}\).

The aim of this study was to evaluate sorption, solubility and kinetic process of water diffusion of dental composites resin when immersed in four different solutions; distilled water, artificial saliva, 40% ethanol/water, and mouthwash Chlorhexidine. Distilled water was used as control.

**Materials and methods**

The composites used in this study were described in Table 1. The materials were chosen because of the different matrix composition and filler type. All the resin composites are light-cured. Four solutions were used in the study of: distilled water, the artificial saliva had an electrolyte composition similar to human saliva. It was composed of (Sodium chloride NaCl 125.64, Potassium chloride KCl 963.9,
Potassium thiocyanate KSCN 189.2, Potassium Dihydrogen orthophosphate KH$_2$PO$_4$ 654.5, Urea CO(NH$_2$)$_2$ 200, Calcium chloride dehydrate CaCl$_2$.2H$_2$O 227.8, Sodium sulphate Na$_2$SO$_4$.10H$_2$O 763.2, Sodium Hydrogen Carbonate NaHCO$_3$ 630.8 and Ammonium chloride NH$_4$Cl 178 mg/L) (28), Carboxymethyl cellulose are responsible for the viscoelastic character (29). Ethanol/water solution 40% ethanol, and mouthwashes Chlorhexidine 0.2% Philadelphia Pharmaceuticals / Jordon. Distilled water was used as the control. The pH measured with a pH meter (TRANS BP 3001). The pH value and composition of each tested solution is shown in Table 2.

Table 1. Composite resin used in the study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Main composition</th>
<th>Filler content Weight% (Vol%)</th>
<th>manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Competence universal</td>
<td>CU</td>
<td>Bis_GMA*, TEGDMA**, inorganic filler parties of (0.02-1.5 µm)</td>
<td>76% (57%)</td>
<td>Willmann &amp; Pein GmbH Hamburg, Germany</td>
</tr>
<tr>
<td>Bright light</td>
<td>BL</td>
<td>Bis_GMA, TEGDMA, inorganic filler parties of (0.05-1.5 µm)</td>
<td>80% (65%)</td>
<td>DMF LTD, E. U.</td>
</tr>
<tr>
<td>Spectrum</td>
<td>SP</td>
<td>Bis-GMA adduct Bis-EMA*** TEGDMA, Ba-Al-borosilicate glass/colloidal silica</td>
<td>76% (57%)</td>
<td>DENSPLY, Konstanz, Germany</td>
</tr>
</tbody>
</table>

*Bis_GMA: Bisphenol A-glycerololate dimethacrylat, **TEGDMA: TriethyleneGlycol Dimethacrylate , ***Bis_EMA: Ethoxylated Bisphenol A Glycol Dimethacrylate .

Table 2. Solution used in the study.

<table>
<thead>
<tr>
<th>Erosion solution</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water (DW)</td>
<td>7.2</td>
</tr>
<tr>
<td>Artificial saliva (AS)</td>
<td>6.92</td>
</tr>
<tr>
<td>Ethanol/water (EW)</td>
<td>7.99</td>
</tr>
<tr>
<td>Chlorhexidine (MW)</td>
<td>5.25</td>
</tr>
</tbody>
</table>
Preparation of specimens
16 disc specimens were prepared for each composite, according to the specification standard for composite dental resins (ISO 4049: 2008), specimen discs approximately 15±0.2 mm in diameter and 1±0.1 mm in thickness were fabricated in a stainless steel mold held between two glass slabs, they were irradiated 40sec with a LED light source (visible light λ=480nm) (Woodpecker China) with intensity of 600 W/m² and with exit window diameter of 6 mm, the curing tip placed in 1 mm from the glass plate. After polymerization was completed, the specimens were removed from the mold and ground wet with silicon carbide paper 1200-grit, then randomly divided into four test groups.

Water sorption and solubility
All the specimens were kept in a desiccator containing silica gel maintained at 37°C for 1 week. After that, they were removed and weighted, and this cycle was repeated until the mass change is stabilized at constant mass (M₀) with an accuracy of ±0.1mg using a (KERN ACS 220-4 Germany). Following, the discs were immersed in four solutions at 37°C, at fixed time intervals. They were removed, blotted dry to remove excess water, weighted and returned to the water. The time intervals were more during the first day, preceding daily as the uptake slowed at more extended intervals. The sorption was recorded until there was no significant change in weight, i.e. stabilized was attained (mass variation less than ±0.1 mg) (M₁). This process lasted for 100 days. After this, the discs were removed from solution and placed in a desiccator containing silica gel after one week was weighed (M₂).

Water sorption (WA) and solubility (WS) values were obtained according to ISO 4049, using the following equation (23):  
\[
WA = \frac{M₁ - M₂}{V} \quad (1) 
\]
\[
WS = \frac{M₀ - M₂}{V} \quad (2) 
\]

Diffusion coefficients
Stefan’s approximation of the appropriate solution of Fick’s second law used for obtaining a diffusion coefficient (30) is expressed as:
\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \quad (3) 
\]
Here, c (%) is the concentration where of the diffusing species at time, t (s) is the time, and D (m/s) is the diffusion coefficient. For the one-dimensional model of linear flow of mass in the solid bounded by two parallel planes, the differential equation is expressed as follows (31):
\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} \right) 
\]
The solution to the Fick’s second law for longer times of diffusion, the solution to this differential equation is:
\[
\frac{M_t}{M_\infty} = -\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{(2n+1)^2\pi^2Dt}{L^2}\right] 
\]
However, for the initial stages of uptake (when $M_t/M_\infty \leq 0.6$), the above equation is reduced to:

$$\frac{M_t}{M_\infty} = \frac{4}{L} \left( \frac{D \pi}{\Gamma} \right)^{1/2}, \quad (5)$$

where $D$ is the diffusion coefficient of the liquid (mm/s) during the sorption process, $M_t$ was the mass uptake (g) at time $t$ (s), $M_\infty$ was the mass uptake (g) at equilibrium, $L$ is the specimen thickness. Eq. (4) is for longer time of diffusion, while (Eq. (5)) for earlier stages of uptake (when $M_t/M_\infty < 0.6$) sorption.

If the uptake $M_t$ is measured at convenient intervals of time until equilibrium is reached, then a plot of $M_t/M_\infty$ against $t^{1/2}$ should provide a straight line for the earlier stages with the slope, $S$:

$$S = 4 \left( \frac{D}{\pi L^2} \right)^{1/2}, \quad (6)$$

**Results**

The water sorption (WA) and solubility (WS) values at 37°C ($\mu g/mm^3$) were calculated for each specimen, using Eq. (1 and 2) respectively for composites after being immersed for 100 days. Table 3 shows the mean values and standard deviations for sorption, Highest sorption achieved in composites immersion in ethanol/water (18.83-39.41 $\mu g/mm^3$), while the lowest sorption shown in composites immersion in distal water, and Artificial Saliva solution. Table 4 shows solubility for all composites, the result was found that BL was significantly higher after immersion in water/alcohol, the lowest solubility recorded in distal water (2.65-6.98 $\mu g/mm^3$).

From an observation of Figures 1-3, it can be noticed that the three composites studied during sorption, an equilibrium state was achieved for water, and Artificial Saliva solution equilibrium state is achieved in less than 14 days for all composites, for the water/alcohol and Chlorhexidine need more time to achieve equilibrium that is 30 and 40 days respectively, also presented the lowest diffusion coefficient when immersed in ethanol/water, the initial part of the rate of sorption desorption curves (i.e. until $M_t/M_\infty < 0.6$) is always linear.

Table 5 shows mean value and standard division of the diffusion coefficient $D$ for all composites studied, which applies Eq. (6) from the slope of these lines (liner relation between $M_t/M_\infty$ and $t^{1/2}$ for all specimens). The values of $D$ estimated shown in all resin composites immersed in distal water presented the highest diffusion coefficient, follow artificial saliva, while all composites immersion in ethanol/water recorded lowest $D$. 
Table 3. Means± standard deviations of the Sorption (µg/mm³).

<table>
<thead>
<tr>
<th>Material</th>
<th>DW</th>
<th>AS</th>
<th>EW</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Competence universal</td>
<td>16.34±0.94</td>
<td>17.89±0.32</td>
<td>39.41±1.45</td>
<td>19.2±0.92</td>
</tr>
<tr>
<td>Bright Light</td>
<td>16.96±0.62</td>
<td>20.95±7.33</td>
<td>34.05±0.95</td>
<td>21.03±0.3</td>
</tr>
<tr>
<td>Spectrum</td>
<td>16.06±0.42</td>
<td>14.37±0.97</td>
<td>18.83±1.91</td>
<td>14.18±0.29</td>
</tr>
</tbody>
</table>

Table 4. Means± standard deviations of the Solubility (µg/mm³).

<table>
<thead>
<tr>
<th>Material</th>
<th>DW</th>
<th>AS</th>
<th>EW</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Competence universal</td>
<td>4.07±0.68</td>
<td>6.69±0.68</td>
<td>8.46±2.81</td>
<td>5.24±0.47</td>
</tr>
<tr>
<td>Bright Light</td>
<td>6.98±0.77</td>
<td>7.70 ±0.64</td>
<td>18.10±14.55</td>
<td>6.80±0.16</td>
</tr>
<tr>
<td>Spectrum</td>
<td>2.65±0.27</td>
<td>3.49±0.15</td>
<td>5.21±1.46</td>
<td>4.02±0.09</td>
</tr>
</tbody>
</table>

Table 5. Means± standard deviations of the diffusion coefficient (×10⁻¹³ m²/s)

<table>
<thead>
<tr>
<th>Material</th>
<th>DW</th>
<th>AS</th>
<th>EW</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Competence universal</td>
<td>17.80±3.41</td>
<td>14.21±1.95</td>
<td>1.09±0.33</td>
<td>2.51±0.76</td>
</tr>
<tr>
<td>(R²=0.817)</td>
<td>(R²=0.774)</td>
<td>(R²=0.907)</td>
<td>(R²=0.765)</td>
<td></td>
</tr>
<tr>
<td>Bright Light</td>
<td>19.08±4.56</td>
<td>16.56±2.33</td>
<td>1.30±0.61</td>
<td>3.01±1.03</td>
</tr>
<tr>
<td>(R²=0.925)</td>
<td>(R²=0.759)</td>
<td>(R²=0.933)</td>
<td>(R²=0.867)</td>
<td></td>
</tr>
<tr>
<td>Spectrum</td>
<td>12.1±1.64</td>
<td>8.8±0.32</td>
<td>1.35±0.56</td>
<td>2.08±1.34</td>
</tr>
<tr>
<td>(R²=0.935)</td>
<td>(R²=0.977)</td>
<td>(R²=0.868)</td>
<td>(R²=0.827)</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1 Plot of $M_t/M_\infty$ against the $t^{1/2}$ for Spectrum resin composite.

![Competence (CU)](image1)

Fig. 2 Plot of $M_t/M_\infty$ against the $t^{1/2}$ for Competence resin composite.

![Brigh Light (BL)](image2)

Fig. 3 Plot of $M_t/M_\infty$ against the $t^{1/2}$ for Bright Light resin composite.

**Discussion**
There are many factors that influence sorption of dental composites, depending on the composition matrix resin, type of the filler and the content in the composites, and the coupling agent. The factors affecting water sorption are time of immersion, temperature, surface condition, stress and concentration of water that is hitherto absorbed (22, 30, 32).

When the composite resin is immersed in water, two different mechanisms occur. First, water sorption produces a
mass increase via the accumulation of water molecules in micro-spaces at the interface between the filler and the resin causing small morphological defects. This accumulation of water molecules can cause hygroscopic expansion, reduction in the mechanical properties such as color changes, degradation of the filler/matrix combination, reduction of hardness, and wear resistance. Second, the leaching of components, such as particles or residual monomers, small polymer chains and particle ions, result in loss of mass and characterize the phenomenon of solubility (33, 34).

The water molecules also tend to degrade the siloxane bonds (i.e. bonds between the filler and silane coupling agent) via hydrolyses reaction, causing filler deboning. On the other hand, alcohol is a good polymer chain solvent, and solutions with high alcohol concentrations can degrade the mechanical properties and increase the wear of composite resins (10, 35). Therefore, alcohol has a clear influence on the hardness properties, sorption and solubility of composite resins, but its effect does not happen by its own; rather, there must be a simultaneous interaction of other factors that affect the physical properties of composite resins. In addition, ethanol can reduce bonding between resin matrix and inorganic fillers, which might decrease erosion resistance and cause staining of resin matrix (10).

Water sorption is strongly dependent upon the composition of the resin monomers of polymer composite (34). ISO standard test for dental composites stipulate to the amount of water sorption can be measured only for the materials that have a diffusion coefficient higher than 1×10^{-14} \text{ m}^2/\text{s} (27). In this study, three different dental composites (Competence universal (CU), Bright Light (BL) and Spectrum (SP)) were used to ensure the measurement of diffusion sorption of composites; when immersed into four different solutions in the composition and different pH values, only the relationship among the immersion time, the specimens immersed in water and artificial saliva showed a similar behavior. The sorption increases rapidly up to 7 days, but after that, at a much lower rate or in some cases not at all. In ethanol/water and Chlorhexidine, more time was needed to reach the maximum sorption. The maximum sorption value in ethanol/water is much higher than those in distilled water and artificial saliva, which should be due to the easier penetration of ethanol into the resin matrix.

Table 3 shows the means and standard deviations of water sorption for all composites. The water sorption values ranged from 16.34 to 16.96 µg/mm³, which is lower than those required by ISO 4049 standard of 40 µg/mm³. Overall, water sorption for all composites was significantly higher.
after immersion in alcohol/water and Chlorhexidine.

When comparing water sorption among composites, the results follow this order: SP < CU < BL. These results were interesting although BL contained the highest percentage.

In the present study, the highest solubility was presented by BL (18.1 µg/mm³) Table 4, also have higher value of solubility in distal water 7.98 µg/mm³, which is higher than those required by ISO 4049 standard of 7.5 µg/mm³, however SP and CU composites have lower value. In addition, the solubility of the resin composites in ethanol/water and Chlorhexidine was higher than those in distilled water and artificial saliva. The components from composites may be unreacted monomer units and filler degraded within the matrix which have a higher solubility in ethanol/water compared to another solution.

According to Figures. 3–5, plots had linear rise in early stages of the process for all the solutions, the plots of $M_t/M_\infty$ against $t^{1/2}$, which showed that the process for composites was diffusion controlled. The plots became stabilized at the end of the process when the composites were completely saturated, meaning that no more solution can be absorbed or desorbed by the composites. This stability depends on the composition of solution. In Table 5, the goodness of fit parameter for the linear approximation ($R^2$ parameter) is shown for each linear fit, it can be observed that all values are higher than 0.75, plots for composites immersed in water and artificial saliva are closely fitted in early stage of process when $M_t/M_\infty < 0.6$, which indicated the plots followed by Fickian behavior.

Composites immersed in ethanol/water and Chlorhexidine are closely fitted in 5 week of process when $M_t/M_\infty < 0.6$. The diffusion coefficients obtained in this study for composites immersed in water and artificial saliva in the range of $12.1 – 19.08 \times 10^{-13} \text{m}^2/\text{s}$ and $8.8 – 16.56 \times 10^{-13} \text{m}^2/\text{s}$ (Table 5), in good agreement with other works for similar copolymer resins (12, 20, 36). Among other aspects, ethanol /water have a more intensive effect on the diffusion coefficients than water and artificial saliva, because of its organophilic nature which cause surface degradation of dental composites. Its ranged $(1.09 - 1.35 \times 10^{-13} \text{m}^2/\text{s})$ to reach this result of the findings of approach. Even mouthwashes Chlorhexidine without alcohol in composition have shown higher diffusion coefficients than ethanol /water in all composites (Table 5).

**Conclusion**
This study demonstrated that:
1. Sorption and solubility values were found to depend on the type of immersion media and time of immersion.
2. The effect of ethanol/water solutions exhibited higher sorption and solubility on composites more than
distal water, artificial saliva and mouthwishes.

3. Diffusion coefficient was found higher in distal water than other media.

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

Reference


23. ISO4049., *Dentistry-resin-based filling materials: 7.9*
حركية الامتصاص في متراكبات الأسنان الضوئية المغمورة في محاليل مختلفة

رافد مصطفى البدر
 كلية طب الأسنان جامعة البصرة

dيمومة متراكبات الأسنان الضوئية في تجويف الفم يعتمد على البيئة التي تتعرض لها متراكبات الأسنان من الامتصاص للسوائل في تجويف الفم ناتجة من تناول الأشربة والاطعمة، هذا الامتصاص قد تكون له آثار سلبية على مركبة الأسنان، لذا اعتمدت الدراسة أنغمار انغماس متراكبات الأسنان في سوائل مختلفة يمكن للفم تناولها. تم تحضير ثمانية واربعين عينة من ثلاثة متراكبات اسنان مختلفة وقيست مقدار الامتصاصية والذوبانية لها في اربعة محاليل مغمورة: الماء واللعاب القياسي وخلط كحولي وغسول فم كلورهيكسيدين بعد غمرها لحد 11 يوم وبدرجة حرارة 37 مئوي. قياس الامتصاصية والذوبانية ضمن المعايير الدولية 4049 الخاصة بمتراكبات الأسنان. فيما قيس معامل الانتشار طبقا لقانون Fick الثانوي، الدراسة بينت اعتماد الذوبانية والامتصاصية على الحلول المغمورة، في محلول الائيثانول/ الماء وغسول الفم أكثر تأثير والقيم تعتمد على نوعية متراكبات الأسنان. من جانب آخر تحققت التعادل والاشباع للمتراكبات التي غمرت في الماء واللعاب القياسي في أسبوعين في حين حصل التعادل والاشباع في الكحول وغسول الفم في 4 إلى 5 أسابيع، أعلى الامتصاصية حصلت في الماء واللعاب القياسي 16.96 (µg/mm³) على التوالي والذوبانية 7.98 إلى 7.7 (µg/mm³) على التوالي في حين تراوح معامل الانتشار بين 19.08 - 10.99 × 10⁻¹³ (m²/s)