Water absorption, dimensional change and radial pressure in resin matrix dental restorative materials

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Abstract

The purpose of this work was to study the relationship between water absorption, dimensional change (swelling) under cavity constraint and radial stress generation in resin matrix dental restorative materials. Water absorption was determined on disc specimens whilst swelling was determined on samples of materials restrained within cavities cut in cast polymethylmethacrylate and pressure generated was determined using a ‘push-out’ test. Four commercially available resin matrix materials were used. A giomer material gave significantly greater water absorption than two compomers and a fluoride releasing composite ($p < 0.05$). The giomer material was the only material which produced a significant degree of swelling ($p < 0.05$) when restrained within a cavity. The giomer product produced the greatest radial pressure (over 20 MPa in 1 month) following water storage, however a significant pressure generation was also observed for other materials despite their much lower water absorption values.

The mechanism of water absorption and the amount of water absorbed determine the dimensional changes and radial pressure generated by resin matrix materials in a moist environment.

Keywords: Dental materials; Dental composites; Water absorption; Radial pressure; Hygroscopic expansion

1. Introduction

Materials which are placed for long periods in the oral environment will undergo an interaction with oral fluids. In some cases the interaction may involve dissolution or degradation of surface layers whilst in others the interaction may involve a leaching out of unbound or loosely bound components or an uptake of fluids into the structure of the material. Such fluid absorption may affect the mechanical properties of the material and cause damaging dimensional changes. The precise effect of fluid absorption depends on many factors including not only the rate and amount of fluid (normally water) absorbed but also on the mechanism of absorption. Any absorption, which causes a dimensional change, has potentially important clinical consequences. Furthermore, if the absorption also results in a significant generation of pressure it can be damaging to the material [1,2] and if the material is constrained within a cavity or is being used as a luting agent can also be damaging to the associated tooth structures and restorative materials [3,4].

One positive effect of water absorption for filling materials is that it provides a mechanism for the potential compensation of polymerisation shrinkage and the relaxation of stress [5–7], although measurements of marginal adaptation have revealed that hygroscopic expansion does not always cause complete closure of contraction gaps around composite filling materials [8].

Some materials are required to promote the diffusion of water or aqueous solutions in order to achieve certain performance requirements. For example, dental restorative materials which are designed to release fluoride do so by diffusion of fluoride ions within an absorbed aqueous medium. The release of fluoride is therefore mediated by an ability to allow diffusion of water. The mechanism of release is a significant factor in determining whether the material is able to sustain a beneficial release whilst maintaining a structural integrity which enables the material to function in a satisfactory manner. Central to the ability to release fluoride is an
ability of a material to support diffusion of water whilst not having an excessively large value of water absorption. A large value of water absorption may cause swelling of the resin matrix and the generation of a damaging pressure within the material or a radial pressure which may damage the surrounding tooth substance. The resin matrix materials which are designed for fluoride release can be classified as being:

(a) composites with added fluoride, either within the resin matrix or as filler.
(b) Compomers, in which fluoride is incorporated within the glass filler and becomes available as a result of a delayed reaction between acid groups within the resin and the glass, following water absorption.
(c) Giomers, a new class of materials in which the glass is pre-reacted with poly acid then blended with resin to form a composite-type structure. The pre-reacted zone may affect only the surface of the glass or may consume almost the whole of the glass particles and this difference creates a further sub-division of products within this group.

Manufacturers of fluoride releasing materials sometimes use hydrophilic monomers such as HEMA in order to promote rapid diffusion of water and accelerate fluoride release. Furthermore, the reacted zones on the surfaces of filler particles may not only act as reservoirs for fluoride re-charging but may also contribute to an increased water absorption and diffusion. Such absorption can be tolerated provided that it does not lead to any deterioration in mechanical properties or produce excessive swelling or result in internal or radial pressure being generated when the material is confined, either within a cavity, or when being used as a luting agent [9,10].

The hypothesis tested in this paper was that increased water absorption would be associated with swelling and increased radial pressure.

Commercial materials were chosen to represent a selection of resin-matrix dental restorative materials in which a degree of water absorption is required in order to enable fluoride diffusion, and release, to occur. Whereas swelling can be determined by making measurements of the dimensions of simple disc type specimens stored in aqueous media [11], it was thought to be more appropriate in the present work to measure swelling in the presence of the restraining influence of a cavity wall.

2. Materials and methods

The materials used in the study are described in Table 1. The giomer product Reactmer is a ‘fully reacted’ giomer, i.e. the glass has been ‘fully reacted’ with acid before blending with resin to form a composite type structure.

2.1. Water absorption/desorption

Water absorption was determined on disc specimens, 15 mm diameter and 1 mm thick, for up to 168 days using the method outlined in ISO 4049. The discs were prepared between glass plates and were cured by exposure to a Visilux II curing lamp for 60 s on each side. Samples were measured, weighed and placed in individual sealed containers of water maintained at 37°C. The specimens were removed from the storage water at regular intervals, blotted dry and re-weighed. After 168 days specimens were placed in a desiccator containing dry silica gel and re-weighed at regular intervals over a period of 2 weeks.

2.2. Swelling

Samples of each material were packed into cavities 5 mm diameter and 4 mm deep cut into sheets of cast PMMA. After curing using a Visilux II curing lamp (60 s exposure), the surface of each specimen was lapped using #1200 grit abrasive paper and then profiled in order to establish a baseline relationship between the surface of the PMMA sheet which forms the mould and the surface of the test material. The specimen was then placed into water at 37°C and was removed after 3 months for further profiling. Profiling was carried out using both a contact stylus method (Surfometer SF220 Planar Products, Surrey, UK) and a non-contacting optical scanning method (Uniscan 100P, AG Electro Optics, UK).

2.3. Radial pressure

The method used to measure the development of radial pressure was that described by Momoi et al. [4]. Slightly tapering holes (3 mm long) were cut in brass such that the diameter at one end of the hole was 4.4 mm and that at the other end was 4.3 mm. The pressure exerted by the material on the mould walls was determined by measuring the force required to eject the set material.

Test specimens were prepared by filling the brass moulds and curing by exposure to a Visilux II light for 60 s from each end. Cured samples were lightly lapped on both exposed surfaces. The force to ‘push-out’ the set material from the brass mould was determined using a mechanical testing device (Instron Inc, High Wycombe, UK) at baseline and following periods of water storage in order to determine whether water absorption resulted in the generation of radial pressure by the material. In order to convert the displacement force into normal...
3. Results

Water absorption over 168 days followed by desiccation is shown in Fig. 1. The results at days 1, 7 and 168 are given in Table 2 in order to provide an indication of the variance of the data. The water absorption of the giomer product was greater than that of the other materials ($p < 0.05$, ANOVA). The water absorption was diffusion controlled over the first week of water storage for all materials as shown by the plots of absorption against $t^{1/2}$ in Fig. 2.

The diffusion coefficient for absorption $D_a$ was calculated for each material using Eq. (1):

$$M_i / M_e = 2(D_a t / \pi L^2)^{1/2},$$

where $M_i$ is the water absorbed at time $t$, $M_e$ is the water absorption at equilibrium and $L$ is half the thickness of the specimen.

The values of $D_a$ for each material are given in Table 3. One of the compomers (F2000) had the greatest diffusion coefficient for absorption with a value 2–3 times that of the other materials.

The diffusion coefficients for desorption $D_d$, calculated using the same equation but where $M_i$ is water lost are also given in Table 3 along with the value of the ratio of $D_d / D_a$. Plots showing water desorption as a function of $t^{1/2}$ are given in Fig. 3.

The diffusion characteristics of F2000 appear to be different from the other materials. The value of $D_a$ is greater whilst the value of $D_d$ and the ratio of $D_d / D_a$ is smaller than for other materials.

Swelling was determined from profiles of specimens in cavities cut into PMMA sheet. An example of a three- and two-dimensional optical profile for one material is shown in Fig. 4. The extent to which each material

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Table 1
Details of materials used in the study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Manufacturer</th>
<th>Composition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyract AP, Compomer</td>
<td>Dentsply, Konstanz, Germany</td>
<td>Dimethacrylate resin, polyacid containing methacrylate resin, Strontium fluoro silicate glass, strontium fluoride</td>
</tr>
<tr>
<td>F2000, Compomer</td>
<td>3 M ESPE, Seefeld, Germany</td>
<td>Dimethacrylate oligomer, glyceryl dimethacrylate, ‘hydrophilic polymer’ fluoro alumino silicate glass</td>
</tr>
<tr>
<td>Reactmer Paste, Giomer</td>
<td>Shofu Inc., Kyoto, Japan</td>
<td>Pre-reacted fluoro alumino silicate glass and polyacid, dimethacrylate resin, HEMA</td>
</tr>
<tr>
<td>Xeno CF, Composite</td>
<td>Sankin Dentsply, Japan</td>
<td>Dimethacrylate resin, HEMA, fluoro alumino silicate glass</td>
</tr>
</tbody>
</table>

*HEMA = Hydroxyethylmethacrylate.

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Table 2
Water absorption at specified times of water storage

<table>
<thead>
<tr>
<th>Material</th>
<th>Day 1</th>
<th>Day 7</th>
<th>Day 168</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>s.d.</td>
<td>Mean</td>
</tr>
<tr>
<td>Dyract AP</td>
<td>11.94</td>
<td>0.47</td>
<td>25.66</td>
</tr>
<tr>
<td>F2000</td>
<td>12.40</td>
<td>0.87</td>
<td>29.46</td>
</tr>
<tr>
<td>Reactmer</td>
<td>33.62</td>
<td>2.58</td>
<td>85.66</td>
</tr>
<tr>
<td>Xeno CF</td>
<td>8.58</td>
<td>0.23</td>
<td>17.80</td>
</tr>
</tbody>
</table>

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Fig. 1. Water absorption up to 168 days storage for four commercially available resin matrix dental restorative materials followed by desorption during desiccation. Points are means of five specimens. Absorption and loss at specified times are given in Tables 2 and 4.

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The net loss in weight compared to the original specimen after 8 days of desiccation is given in Table 4. The giomer material showed a small net gain in weight even after desiccation.

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Swelling was determined from profiles of specimens in cavities cut into PMMA sheet. An example of a three- and two-dimensional optical profile for one material is shown in Fig. 4. The extent to which each material
expands above the surface of the cavity in which it is placed is summarised in Table 5.

The displacement force and radial pressure developed within each material as a result of water storage for 1 month is indicated in Table 6. Five additional Reactmer specimens were made and stored in water for 3 months. The average push-out force for these specimens was 665 N (sd = 156). This translates to a radial pressure of 49.2 MPa (sd = 11.5). Mean push-out forces for baseline specimens or control specimens which had been stored dry for 1 month are given in Table 7. For baseline specimens, push-out forces were not significantly different from zero. Similarly, at 1 month, control specimens (dry) of all materials gave push-out forces which were not significantly different from zero. All materials gave push-out force values after 1 month water storage which were significantly greater than baseline or 1 month control (dry) specimens.

The relationship between water absorption, swelling and radial pressure was investigated by regression analysis. This showed that swelling was strongly correlated with water absorption ($R^2 = 0.98$, $p < 0.01$), although the data are heavily influenced by one data point corresponding to the giomer. However, the correlation between radial pressure generation and water absorption ($R^2 = 0.65$, $p > 0.05$) and between pressure generation and swelling ($R^2 = 0.65$, $p > 0.05$) was not as convincing and was not quite significant in both cases.

4. Discussion

The methods used to study water absorption and related dimensional changes have proved to be simple but meaningful. Water absorption is a relatively easy phenomenon to study and the method used here is similar to that outlined in the ISO standard for resin-based restorative materials (ISO 4049). However, the ease of measurement can hide a complexity of mechanism and a variety of consequences which depend upon the mechanism. Small dimensional changes occurring as a result of water absorption can be difficult to measure but the confinement of the test material within a cavity aids the detection of dimensional change by profilometry and arguably makes the measurement more meaningful as the configuration is similar to that used clinically. The generation of radial pressure as a

Table 3
Diffusion coefficients—absorption $D_a$ and desorption $D_d$ ($10^{-13} \text{m}^2 \text{s}^{-1}$)

<table>
<thead>
<tr>
<th>Material</th>
<th>$D_a$</th>
<th>$D_d$</th>
<th>$D_d/D_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactmer</td>
<td>1.67</td>
<td>20.70</td>
<td>12.40</td>
</tr>
<tr>
<td>Dyract AP</td>
<td>1.13</td>
<td>16.38</td>
<td>14.50</td>
</tr>
<tr>
<td>F2000</td>
<td>3.10</td>
<td>11.09</td>
<td>3.58</td>
</tr>
<tr>
<td>Xeno CF</td>
<td>1.36</td>
<td>17.13</td>
<td>12.60</td>
</tr>
</tbody>
</table>

*Absorbed water not completely eliminated during desiccation for this material.
consequence of water absorption has conveniently been measured by monitoring the force to push-out a specimen from a slightly tapering brass mould as reported previously [4]. Increasing push-out force can be due to one of two things; an expansion within the material or the development of adhesive forces between the material and the material of the mould walls. The latter phenomenon is unlikely to be a major factor as the push-out force at baseline (2h) was not significantly different from zero and at one month remained insignificant on dry storage for all test materials. Any adhesive forces between material and mould were expected to be well developed at this stage. It is therefore reasonable to assume that increases in push-out force are primarily due to increases in radial pressure.

This study has shown that water absorption of resin matrix materials can have a significant effect on dimensions and can result in the generation of a significant radial pressure. The results do confirm however that for some materials it is possible for water absorption to occur in a manner which does not result in significant change in dimensions or in the generation of

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**Table 5**

<table>
<thead>
<tr>
<th>Material</th>
<th>Swelling μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>Dyract AP</td>
<td>2.4a</td>
</tr>
<tr>
<td>F2000</td>
<td>1.1a</td>
</tr>
<tr>
<td>Reactmer</td>
<td>56.1</td>
</tr>
<tr>
<td>Xeno CF</td>
<td>0.1a</td>
</tr>
</tbody>
</table>

a Values do not significantly differ from 0, p > 0.05.

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**Table 6**

<table>
<thead>
<tr>
<th>Material</th>
<th>Force (N) to displace specimen from 3 mm deep hole cut in brass</th>
<th>Calculated pressure MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean*</td>
<td>s.d.</td>
</tr>
<tr>
<td>Dyract AP</td>
<td>22.6b</td>
<td>9.3</td>
</tr>
<tr>
<td>F2000</td>
<td>210.9a</td>
<td>76.3</td>
</tr>
<tr>
<td>Reactmer</td>
<td>353.8a</td>
<td>69.9</td>
</tr>
<tr>
<td>Xeno CF</td>
<td>65.0b</td>
<td>52.9</td>
</tr>
</tbody>
</table>

Coefficient of friction μ, Reactmer 0.33; Dyract AP 0.28; F2000 0.31; Xeno CF 0.31.

*One way ANOVA on log converted data. Same superscript indicates no significant difference p > 0.05 between means.

**Significant differences indicated in force column.
a large pressure. A material which is rigid and porous may absorb fluids into porosities (particularly if they are inter-connecting) through capillary action and such an action may produce little, or no, dimensional change nor an increase in radial pressure. In the current work, both water absorption and desorption were diffusion-controlled processes as shown in Figs. 2 and 3.

When a material is constrained within a cavity the extent of water sorption and swelling may be limited by the restraining forces imposed by the cavity walls or in the case of luting agents by the restoration–luting agent–tooth sandwich. Such factors cannot be realised from observations on water absorption and swelling made on simple unconstrained disc specimens where there is no restriction on the volumetric expansion of the material. It is to be expected that an equilibrium position can be reached in which the pressure generated by water absorption matches the restraining pressure or the pressure generated by the elastic response of the material. Just as the stress caused by setting shrinkage is related to the cavity configuration [12] it has been proposed that the hygroscopic expansion stress is similarly related to cavity configuration [13].

The nature of the resin matrix is a fundamental parameter which may control not only the rate of diffusion of water but also the extent of water sorption into that part of the material structure. Hydrophilic monomers such as Hydroxyethylmethacrylate (Reactmer, Xeno CF), Glycerylidimethacrylate (F2000) and acid containing methacrylates (Dyrract AP) are all expected to increase water absorption above what would be expected from a more hydrophobic dimethacrylate matrix. Although the presence of hydrophilic monomers may influence the rate and degree of water absorption it is not the only factor; nor necessarily the dominant factor. Furthermore, a consideration of Tables 2, 3 and 5 indicates that even a substantial degree of water absorption does not necessarily result in swelling if the material is constrained within a cavity. Only the giomer gave a substantial degree of swelling which suggests that the mechanism of water absorption for this material was able to overcome the restraining influence of the cavity. If the water absorption is influenced principally by the hydrophilic components of the resin matrix and if this matrix is relatively flexible it is likely that swelling is readily prevented by the resisting forces of the cavity walls. One factor which could potentially influence water absorption, swelling and radial pressure significantly is an osmotic effect caused by the presence of discrete zones within the material structure in which absorbed water may become concentrated with residual components of the filler, resin matrix, coupling agent or other reaction products. This may drive a continued absorption of water and the osmotic pressure generated may be great enough to overcome the restraining effect of a cavity resulting in swelling and a significant pressure on the cavity walls. Such a mechanism has been proposed to explain the water absorption and ion release from doped silicone polymers where the internal pressure may become great enough to cause internal tearing of the polymeric matrix surrounding expanded water droplets [14]. A reverse of this osmotic effect has been proposed by Saito et al. [15] to explain weight and dimensional changes in alginate impression materials soaked in disinfecting solutions. In the current work there is some evidence that cluster formation may occur in all four materials as indicated by $D_D > D_a$ in each case (Table 3). This is a common finding in polymeric systems in which water diffusion occurs [16,17]. In these circumstances it is expected that the water absorption and pressure generated would vary significantly with the nature and concentration of the aqueous storage solution. The use of saliva instead of water may, for example alter the pattern of behaviour significantly. For composite filling materials it has been proposed that the hydrolytic degradation of filler particles can create sufficient osmotic pressure to cause crack formation [2]. In practice it is likely that the water absorption for any material is controlled by a variety of mechanisms, but the presence of an osmotic effect, is likely to lead to increased radial pressure. Since the giomer material was the only product which demonstrated significant swelling out of a cavity and also the greatest radial pressure it is reasonable to assume that this material more than any other studied is able to generate a significant osmotic effect. The main difference in microstructure between the giomer and compomer materials is the presence of pre-reacted glass-polycid zones which become part of the filler in the giomer structure. It seems likely that these zones are responsible for generating the osmotic effect which leads to swelling and pressure. Similar zones can potentially be formed at the surface of compomer glass particles following the delayed acid-base reaction which occurs following water absorption. The latter reaction is very limited in extent however compared with the almost total consumption of glass which occurs in the giomer product. One of the compomers (F2000) does in fact

### Table 7

<table>
<thead>
<tr>
<th>Material</th>
<th>Baseline Mean*</th>
<th>s.d.</th>
<th>1 month control Mean*</th>
<th>s.d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyrract AP</td>
<td>7.94</td>
<td>4.89</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>F2000</td>
<td>4.76</td>
<td>4.53</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Reactmer</td>
<td>5.09</td>
<td>5.18</td>
<td>1.96</td>
<td>2.26</td>
</tr>
<tr>
<td>Xeno CF</td>
<td>3.68</td>
<td>3.41</td>
<td>2.70</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Mean values are not significantly different from zero, $p > 0.05$, $t$-test.
produce significant radial pressure after a month in water. Water absorption values for composites indicated a potential for swelling and/or pressure generation but did not guarantee that such an effect would be observed. The latter phenomenon suggests that the effects of water absorption depend not only on the amount of water absorbed but also on the mechanism of absorption. Hence we can see that Dyract AP gave a greater level of water uptake compared with F2000 but there was little or no dimensional change recorded for either material and the pressure generated within F2000 was significantly greater than that in Dyract AP. Hence, despite similarities in the structure of these materials there are clearly important differences in the mechanism of water uptake.

Clearly, the mechanism and degree of absorption differs amongst the various test materials. The giomer product appeared to be able to generate osmotic pressure during water storage and this may be due to the pre-reacted zones on the surface of glass filler particles. The pressure generated after 1 month was in excess of 20 MPa, which corresponds approximately with the tensile bond strength of a resin matrix material to enamel or dentine. After 3 months the pressure had risen to almost 50 MPa. Hence, it can be claimed that the pressure is at a level which can be clinically significant. Whether or not the pressure is great enough to cause tooth fractures is uncertain as this will depend upon the cavity dimensions, residual tooth structure thickness, etc. Furthermore, it is likely that osmotic effects may also be influenced by the nature of the aqueous environment in which the material is placed. Hence, the large driving force which appears to exist in developing osmotic pressures within some materials (e.g. giomers and some compomers) may be modified if water is replaced with saliva. This very important factor clearly needs further detailed study. Water absorption of denture soft lining materials was found to be markedly reduced when osmotic solutions were used for specimen storage instead of distilled water [18] and ion release from composites containing glass fillers was greater in artificial saliva than in distilled water [19]. A moderate pressure may actually be beneficial as this could result in an improved cavity sealing capability and reduced cuspal deflection caused by polymerisation shrinkage [5,6]. The level of expansion and pressure generation which would be required to compensate for polymerization shrinkage is unknown and is likely to depend upon the cavity configuration. Hence, the different degrees of swelling and pressure generation may be advantageous or dangerous depending on the extent of the effect and the cavity configuration. This important finding clearly needs further study in order to determine the clinical significance.

Acknowledgements

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References