

**INFLUENCE OF FILLER AMOUNT ON WATER
SORPTION AND SOLUBILITY OF THREE
EXPERIMENTAL FLOWABLE
COMPOSITE RESINS**

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Abstract

Aim: The purpose of the study was to determine the water sorption and solubility of three experimental flowable composite resins (EXP1, EXP2, and EXP3), which differed only in their filler amount (65, 55, and 45wt%, respectively) with a view to assessing the relevance of this parameter.

Materials and methods: The ISO 4049 protocol was followed. Ten discs ($15 \times 1\text{mm}$) of each material were submitted to a drying cycle at 37°C for 35 days, after which the constant mass (m_1) and volume (V) of each were measured. The samples were then immersed in distilled water at 37°C for 168 hours and weighed to determine the constant mass (m_2). A final drying cycle, identical to the first one, allowed to record constant mass (m_3). Water sorption and solubility were calculated by using these measurements.

Results: EXP1, which had the highest filler amount, absorbed significantly less than the other two materials. EXP1 was also significantly less solubilised. EXP3, which had the lowest filler amount, absorbed significantly more than the other two materials and was also significantly more solubilised.

Conclusion: Within the limitations of this experimental study, it was shown that a high filler amount, without affecting the spreading capacity of a flowable resin composite, could reduce water sorption and solubility.

Clinical significances: Given the clinical importance of water sorption and solubility on the behaviour and sustainability of dental restorations, a high filler amount could be a major criterion to be taken into account by dentists when they are selecting flowable composite resins.

1. Introduction

Preventive, adhesive, ultra-conservative, and aesthetic dentistry are closely related and are now an integral part of the dentist's therapeutic arsenal. The flowable composite resins developed over the last 15 years or so are now essential to modern dentistry [1, 2]. These low-viscosity resins of low elastic modulus are indicated for preventive sealing of pits and fissures and for filling small occlusal and cervical cavities [3-5]. Adhesive dentistry is demanding in terms of technique and time and many dentists now choose flowable resins, because they are relatively easy to use thanks to their ability to spread and fit small cavities and to penetrate pits and fissures effectively.

Once in the mouth, these materials are in constant contact with saliva, rich in organic and inorganic substances and with a complex bacterial flora. When placed on a cervical site, they are in contact with sulcular fluid. Therefore, water sorption capacity and solubility must be evaluated from a clinical viewpoint. Water sorption within the polymer causes expansion stress that will have a deleterious effect on tightness of the interface between dental tissue and the restorative material [6]. Furthermore, fluid penetrating the resin has a plasticizing effect and will influence its mechanical properties, particularly, reducing its resistance to wear and flexion, as well as its elastic modulus [7-10]. At the same time, exposure to oral fluids promotes the release of possibly harmful chemical compounds and raises questions of biocompatibility. These concern residual monomers [11], filler amount [12], polymerization activators and inhibitors [13], and degradation products such as formaldehyde [14] and methacrylic acid [15], which may leach from resin-based materials and exert a toxic effect on surrounding fibroblasts [16] and odontoblasts [17]. Allergenic, mutagenic, and genotoxic effects [20] have also been reported in the literature. Released residual monomers have been reported to stimulate bacterial growth around dental restorations [21]. Thus, water sorption and solubility are properties worthy of great interest when assessing the ability of a material to comply with the specifications for which it was designed.

The aim of this study was to evaluate water sorption capacity and solubility, and analyse the effect of filler amount on these properties in three flowable composite resins in order to determine whether filler amount should be amongst the criteria used by dentists when selecting dental restorative materials.

2. Materials and Methods

Table 1 lists the three experimental flowable resin composites used in the study. Ten disk-shaped specimen of each material were made according to ISO specification 4049: 12-1998. Samples were carried out in a jig consisting of a Teflon mold (15mm in diameter by 1mm in thickness)

compressed between two glass slabs with 50 μ m thick polyester separating sheets, the filling materials were packed into the molds, care being taken to minimize air inclusion. Materials were light-cured from both sides with a LED unit (Elipar Freelight 2, 3M Dental Products, St. Paul, MN), the light intensity of which being tested at regular intervals. The light tip was first directed over the center of the sample for 40s, and then irradiated eight peripheral overlapping sectors for 20s each. The specimens were immediately stored in an incubator at 37°C for 15 min. Then the excess material was removed with a scalpel blade. The rim was trimmed and polished with 1000 grit silicon carbide grinding paper until the diameter of the final product was maintained within 14.9 ± 0.1 mm average diameter obtained from two measurements at perpendicular planes with an electronic caliper (Digimatic, model 500-181U, Mitutoyo Corporation, Tokyo, Japan). After that, the specimens were immediately placed in a desiccator together with silica gel (Silicagel, Prolabo, Paris, France) and the whole set was stored in an incubator maintained at $37^\circ\text{C} \pm 1^\circ\text{C}$. According to the ISO standard, disks were weighed every day for a 35d period by using an analytical balance (Model M-120, Denver Instrument, Arvada, CO) with a repeatability of 0.1mg, until a constant mass (m_1) was obtained (i.e., until the mass loss or gain of each sample was less than ± 0.2 mg in any 24h period). The volume V of the disk-shaped specimens was then determined by measuring, with the electronic caliper, the specimen diameter from two perpendicular planes and the thickness from five measurements, one at the center and four at equally spaced points on the specimen circumference. This initial cycle allows free water to be removed, as recommended in ISO standard test.

Table 1. Used materials

Code	Monomers	Fillers
EXP1	33wt% Bis-GMA 33wt% UDMA	silanized dental glass, silica (7 μ m) 65wt%
EXP2	33wt% TEGDMA 1wt% photoinitiation system (camphorquinone/amine)	silanized dental glass, silica (7 μ m) 55wt%
EXP3	and butylated hydroxytoluene (BHT)	silanized dental glass, silica (7 μ m) 45wt%

Each sample was then suspended in a flask containing 40ml of distilled water and stored in the incubator at $37^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 7d. After that time period, the samples were removed, washed briefly with water, wiped up with absorbent paper, and shaken in air for 15s. Samples were weighed 1 min after removal from the incubator to record the mass (m_2). This second cycle gives a combination of water sorption and dissolution of the soluble components from the sample.

After weighing, the disks were reconditioned at a constant mass (m_3) in a desiccator and incubator following the stages of initial cycling described before. This third cycle allows measuring the mass loss.

The values for sorption and solubility W_{sp} and W_{sl} , respectively, in $\mu\text{g}\cdot\text{mm}^{-3}$, were calculated for each specimen by using the following equations:

$$W_{\text{sp}} = \frac{m_2 - m_3}{V}; \quad W_{\text{sl}} = \frac{m_1 - m_3}{V},$$

where m_1 is the mass in μg before immersion in water; m_2 is the mass in μg after immersion in water for 7d; m_3 is the reconditioned mass in

μg , and V is the volume of the sample in mm^3 . Statistical analysis of the results was carried out with Kruskal-Wallis tests and Bonferroni correction multiple-comparison procedures.

3. Results

Table 2 gives the mean values for the water sorption and solubility of the three materials. The Kruskal-Wallis non-parametric test indicated significant differences in water sorption and solubility ($p < 0.0001$). Bonferroni correction multiple comparison procedures indicated that EXP1 absorbed significantly less water than did EXP2 ($p < 0.05$), and that EXP2 absorbed significantly less than EXP3 ($p < 0.05$). They also indicated that EXP1 was solubilised significantly less than EXP2 ($p < 0.05$), and that EXP2 was solubilised significantly less than EXP3 ($p < 0.05$).

Table 2. Mean water sorption (W_{sp}) and water solubility (W_{sl}) in $\mu\text{g}\cdot\text{mm}^{-3}$ and Standard Deviation (SD)

Material	W_{sp} (SD)	W_{sl} (SD)
EXP1	21.37(0.46) ^a	0.93(0.04) ^a
EXP2	24.43(0.40) ^b	1.21(0.06) ^b
EXP3	27.84(1.43) ^c	1.81(0.28) ^c
In each column, results with same superscript letter are not statistically different		

4. Discussion

Water sorption and solubility affect the behaviour of resin-based dental restorative materials, both in terms of their bio-functionality and biocompatibility and are, therefore, extremely important properties to measure with regard to the clinical performance of dental restorative materials.

The results we obtained with values ranging from $21.4\mu\text{g}\cdot\text{mm}^{-3}$ to $27.8\mu\text{g}\cdot\text{mm}^{-3}$ for water sorption and from $0.93\mu\text{g}\cdot\text{mm}^{-3}$ to $1.81\mu\text{g}\cdot\text{mm}^{-3}$ for solubility for the three experimental resins are below maximum values ($40\mu\text{g}\cdot\text{mm}^{-3}$ and $7.5\mu\text{g}\cdot\text{mm}^{-3}$) of the ISO 4049 standard.

Water is able to diffuse into the resin matrix because its molecular diameter (about 0.16nm), is smaller than the distance between two polymer chains [22]. In the literature, there are two explanations for water diffusion into a polymer network. According to the *free volume theory*, the concentration of water at equilibrium is related to microvoids or other morphological defects through which water diffuses without chemical reaction related to the material structure. The *interaction theory* explains the diffusion as resulting from the formation of linkages between water molecules and the polar groups of the polymer chains. Both theories are accepted [23] since both mechanisms can occur simultaneously. However, polymers absorb water variably depending on their micro-structures and molecular specificities [24]. Thus, the water sorption capacity of these materials may be affected by the polarity of the polymer's molecular structure, the availability of hydroxyl groups, the length and three-dimensional structure of the matrix chains and the presence of residual hydrophilic compounds [25-27].

In our study, the three experimental flowable composite resins had the same resin matrix composed of Bis-GMA, UDMA, and TEGDMA, which are all well-known and tested monomers, in identical proportions of up to a third of the mass for each one. It is known that the nature and proportion of different monomers affect the water sorption capacity and the solubility of materials [27]. Studies have shown water sorption to be greater for Bis-GMA-based resins compared to urethane resins [28], and lowest for ethoxylated Bis-GMA (Bis-EMA) resins that do not contain the hydroxyl groups of Bis-GMA or the urethane linkages of UDMA [29]. Furthermore, water uptake is known to be greater for Bis-GMA resins containing higher concentrations of TEGDMA due to the hydrophilic

ether linkages contributed by the TEGDMA [30]. Moreover, TEGDMA polymers form very dense but heterogeneous networks, which favour water storage due to the formation of micro-pores between polymer clusters [29].

As for solubility, some studies show no apparent correlation between solubility and water sorption [31], whilst others show that once immersed in water, the material releases the filler and soluble components forming micro-voids, which promote the rapid diffusion of water molecules throughout the structure [32]. Indeed, the rapid appearance of a rigid polymer network during radical polymerization leaves many unconverted monomers potentially water soluble. Conversion rate appears to be one of the main factors affecting solubility. The nature of the monomers is also involved; several studies have indicated that the more TEGDMA the composite contains, the more soluble it is likely to be [33-38]. This could be explained by the smaller size of the TEGDMA monomer, which is more mobile and thus more easily released than a monomer of greater molecular weight [39].

The presence of bubbles in the material could also have an impact: bubbles trap oxygen, which inhibits polymerization and thus reduces the conversion rate promoting water solubility [7]. So, it would appear to be important to take into account the ease with which a dental material is handled and inserted without creating too many air bubbles. The three experimental flowable composite resins used in this study were packed in syringes with metal inter-changeable tips, facilitating injection, and guaranteeing that the material remained in contact with the walls of the cavity to be filled, thus reducing the risk of air inclusion.

The fact that we used three identical experimental matrices enabled us to ignore the criterion: “the nature and proportion of monomers”. Although the composition of the matrix did affect results in absolute values, it was not the cause of the difference in results.

Our data showed the importance of filler amount on water sorption and solubility. The material with the highest filler amount, EXP1, absorbed significantly less than the other two and was significantly less

solubilised. The material with the lowest filler amount, EXP3, absorbed significantly more than the other two and was significantly more solubilised. This may be explained simply: at equivalent volumes, the greater the filler amount, the less resinous matrix there is; and we know that this resinous matrix is mainly responsible for water sorption and solubility [40]. Other factors, however, are involved: the quality of the linkages between filler and matrix are equally important. Any limited adhesion between them may determine capillary penetration pathways which transport and store water [41], thus affecting water sorption capacity. Intrusion of water might generate silane hydrolysis and rupture between filler and matrices, thus aggravating the phenomenon by promoting micro-fissures [42]. Indeed, in order to be incorporated into the polymer network and not behave as defects or stress concentrators, mineral amount is rendered organophilic by using a bi-functional coupling agent with an organophilic pole and a mineralophilic pole: organo-silanes such as methacryloxypropyl-trimethoxy-silane, octyltrimethoxy-silane or acryloxypropyl-trimethoxy-silane are usually used for this. Two recent studies showed that silane, in an aqueous medium, is likely to be hydrolysed, thus potentiating the capacity of the material to store water, due to rupture between organic and mineral elements [43, 44]. The nature of the filler is another important factor; water is likely to cause erosion on the surface of the filler. Although fillers consisting of pure silica or quartz are practically inert in water, the same is not true for Ba-Al-B-F-silicate glass fillers, which are much more soluble [12]. Having said that, if the polymer network surrounding the filler protects the filler effectively, as it should, then the theoretical solubility of these elements does not result in any loss in material mass.

Flowable composite resins were designed for clinical use and need to be highly resistant to wear and tear, but their essential characteristic, for which they were developed, is their ability to spread. Recent reports claim that there is no relationship between filler amount and the rheological behaviour of this family of materials; and that their rheological behaviour is in fact more closely related to the shape and surface processing of fillers [45, 46]. In parallel, the micro-hardness of these materials appears to

be a good indicator of their resistance to wear. In general, the higher the filler amount, the better the material will resist wear. In other words, high filler amounts that promote good mechanical properties are not incompatible with good spreading capacity. The shape of fillers is another important factor. In our study, we used fillers of irregular and angular shape. It would be more appropriate to use spherical particles, since more filler could be incorporated into the matrix [47].

Finally, the term “flowable” composite resins is rather vague and basically it is clinical experience, which guides the dentist towards products which manufacturers describe as “flowable”, whilst remaining somewhat vague as to their products’ actual rheological qualities. The interest of our work was to demonstrate how filler amount alone greatly influences properties as fundamental as water sorption and solubility. In our study, the higher the filler amount, the less the flowable resin was solubilised and the less it absorbed. It would seem that for reasons related to both bio-functionality and to biocompatibility, filler amount is an essential parameter and should be a decisive criterion for dentists choosing restorative material.

It is important to point out that the ISO 4049 standard recommendations were intended to define the specifications of water sorption and intrinsic solubility of monomers for manufacturers. However, the procedures are not similar to those used in the clinic. For example, the first drying cycle, obviously impossible in a real-life situation before any contact with oral fluids, tends to reduce the material’s solubility, and a higher solubility is expected in real clinical situations [48]. Similarly, immersing samples in artificial saliva or in solutions with different pH values would mimic the oral environment more effectively [49]. However, the ISO 4049 standard is a useful protocol: it is accurate and reproducible and used by many researchers, thus facilitating inter-study comparisons.

5. Conclusion

In this work, we aimed to show that a high filler amount, without affecting the spreading capacity of a flowable resin composite, could reduce water sorption and solubility. It is known that water sorption and solubility are responsible for reducing mechanical properties, for variations in size deleterious for interface tightness, for colorimetric instability, and for potential effects detrimental to bio-compatibility.

6. Clinical Significances

Given our results, a high filler amount could be an essential parameter of flowable composite resins and could be a major criterion for dentists, when they are choosing restorative material.

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