The role of the ionomer glass component in polyacid-modified composite resin dental restorative materials

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In order to model the processes that occur within polyacid-modified composite resin (“compomer”) dental restoratives, a series of experiments has been carried out with silanated and silane-free ionomer glass G338, and silanated and silane-free unreactive glass (Raysorb T-4000). In an acid-base reaction with dental grade aqueous maleic acid–acrylic acid copolymer solution, the setting time of the silanated G338 was found to be 9 min, compared with 5 min for the silane-free glass. Inclusion of each glass in an experimental composite resin system showed that the formulations which contained G338 absorbed more water than the formulations which contained Raysorb T-4000, regardless of whether or not the glass was silanated. Biaxial flexure strength was superior for experimental composites containing Raysorb T-4000, with highest results being obtained with the silanated glass. Overall these results demonstrate that silanation of the filler is essential for optimal physical properties but that, for the ionomer glass, it inhibits the acid-base reaction. The presence of ionomer glass led to an increase in water uptake compared with the unreactive glass, regardless of the presence of silane.
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Introduction
Polyacid-modified composite resins, known trivially as “compomers”, are dental restorative materials designed to incorporate features of both traditional composite resins and glass-ionomer cements [1]. These are aesthetic materials that set entirely by polymerisation, usually photochemically initiated, but they also incorporate acid-functional macromonomers and some reactive (ionomer-type) glass as filler [2]. When placed in the mouth, they take up a small amount of moisture, which triggers a neutralisation reaction [3, 4]. The fully set material therefore displays certain properties of glass-ionomer cements, notably fluoride release [4, 5] and the capability of buffering the acids responsible for dental caries [6].

Polyacid-modified composite resins have been shown to perform well under clinical conditions. This was apparent with the earliest formulations, which, for example, performed well in a three-year clinical trial [7]. More recent reports have confirmed this generally positive impression for later commercial materials of this type [8] and it has been suggested that they are among the possible alternatives to amalgam restorations in paediatric dentistry [9].

Despite this clinical success, there are problems with these materials. Wear characteristics, particularly of the early formulations were poor and significantly inferior to the wear behaviour of traditional composite resins [10]. However, later versions are much improved in this respect and in a recently reported clinical trial, the compomer Dyract AP was found to show only limited wear, as well as only slight marginal discoloration or marginal damage after two years placement in permanent molars [11]. The authors concluded that this material was suitable for use in stress-bearing areas of the mouth. Nonetheless, there is a fundamental physico-chemical problems with trying to create a hybrid material that involves both the hydrophobic chemistry of traditional composite resins and the hydrophilic chemistry of the

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glass-ionomer. It is apparent that the latter aspect still creates problems in the successful formulation and deployment of these materials.

In order to formulate a successful composite material of any type, a good bond is required between the matrix and filler phases. In the technology of dental composite resins, this is achieved by silanation of the inorganic filler phase, typically using γ-methacryloxy propyl trimethoxy silane [12]. In fabricating a compomer, the reactive glass must also be silanated. However, this process would be expected to inhibit the secondary acid-base reaction, a reaction that is necessary in order for a material to develop the glass-ionomer side of its character. The extent to which silanation inhibits setting, and the effect on mechanical properties have been investigated in the present study, and we now report the results.

A further unknown aspect of the behaviour of compomers is the effect of including ionomer glasses in a matrix of resin monomers. These are typically macromonomers, such as bisGMA, usually with di- or tri-ethylene glycol dimethacrylates as diluents. These monomers have a modest amount of polar character, as a result of the presence of hydroxyl groups. This is sufficient for fully formulated composite resins to show some water uptake, typically in the range of 0.8–2.3% [13]. The effect of including ionomer glass fillers has not hitherto been studied. We have also considered this question and report results of experiments to measure water uptake of model systems that contain ionomer glass filler but no acid functional monomer.

Materials and methods
The materials used are listed in Table I. The glass, G338, was silanated as follows: To prepare 100 g of silanated glass, finely divided glass powder (99.0 g) was added to 1.0 g of γ-methacryloxy propyl trimethoxy silane dissolved in 30 cm³ of 70:30 acetone:distilled water, the mixture stirred and allowed to settle for 15 h. It was then heated on a water-bath at 60°C for 2 h, then on a water-bath at 90°C for a further 2 h, after which it was transferred to a drying oven for the acetone:water mixture to be evaporated. The glass powder obtained was washed with water, centrifuged and the concentrated glass slurry isolated by decantation and dried at 70°C in an oven containing silica gel desiccating agent.

Glass-ionomer cements were prepared using either silanated or unsilanated G338 together with the aqueous polymer solution from Ketac Molar, this being a 47.5% aqueous solution of 2:1 acrylic acid: maleic acid copolymer. The powder: liquid ratio was 2.25:1 by mass in all cases. Setting characteristics were determined using the oscillating rheometer, a device whose detailed working has been described in several previous publications [14, 15]. Setting was also followed using Fourier Transform Infrared spectroscopy on a Nicolet FT800 spectrometer using a diamond ATR cell.

Specimens for biaxial flexure strength determination of dimensions 13.2 mm diameter × 1.2 mm depth were prepared by mixing glass powder and liquid, then transferring the freshly mixed pastes to the moulds, and storing them at 37°C for 1 h, after which they were removed from the moulds and stored for a further 24 h prior to testing.

Experimental composites were prepared by blending together the appropriate components as shown in Table II. Four series of cements were prepared, two based on the ionomer glass G338, one of which used silanated G338, the other of which used unsilanated G338. As controls, two series were prepared using the conventional filler Rasorb T-4000, again in either silanated or unsilanated form. Disc-shaped specimens (13 mm diameter × 1 mm thickness) were prepared by light curing with a Prismetic Lite II blue halogen lamp (nominal output 600 mW cm⁻²), each side being irradiated for 40 s through a glass microscope slide. They were weighed prior to storage in water, and again on removal from water after 24 h storage, which allowed the extent of net water uptake to be determined. The same specimens were then used to determine biaxial flexure strength, using a universal testing machine (Instron 1195), with specimens supported on a metal ring of diameter 10 mm as previously described [16]. Biaxial flexure strength was calculated from load at failure using the following equation [17]:

$$\sigma = \frac{AP}{t^2}$$

where \( P \) is the load at failure, \( t \) the thickness of the specimen and the factor \( A \) is determined by:

$$A = \frac{3}{4\pi} \left[ 2(1 + \nu) \ln(a/r_0) + (1 - \nu)(2a^2 - r_0^2)\right]/2b^2$$

+ \( 1 + \nu) \]

where \( a \) is the radius of the support circle, \( b \) is the radius of the specimen, \( \nu \) is Poisson’s ratio and \( r_0 \) is the radius of the ball used on the loading surface (0.1 cm in the current experimental arrangement). A value of 0.3 was assumed for Poisson’s ratio, this being typical value for materials of this type [18].

Differences between experimental values obtained were tested for statistical significance using one-way ANOVA and Student’s \( t \)-test as appropriate.

<table>
<thead>
<tr>
<th>Component</th>
<th>Supplier</th>
</tr>
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<tbody>
<tr>
<td>BisGMA</td>
<td>Esotech, USA</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>Esotech, USA</td>
</tr>
<tr>
<td>Camphorquinone</td>
<td>Aldrich, UK</td>
</tr>
<tr>
<td>DMAEM</td>
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<tr>
<td>Rasorb T-4000 glass filler</td>
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<tr>
<td>Silane A174</td>
<td>Witco, UK</td>
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<td>G338 reactive glass filler</td>
<td>First Scientific, Germany</td>
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<tr>
<td>Ketac Molar liquid, aqueous</td>
<td>3M-ESPE, Germany</td>
</tr>
<tr>
<td>solution of copolymer</td>
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