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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 silanted 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 silanted. 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.

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 trimethoxysilane [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 trimethoxysilane dissolved in 30 cm^3 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.

TABLE I Materials used

Component	Supplier
BisGMA	Esstech, USA
TEGDMA	Esstech, USA
Camphorquinone	Aldrich, UK
DMAEM	Aldrich, UK
Raysorb T-4000 glass filler	Esstech, USA
Silane A174	Witco, UK
G338 reactive glass filler	First Scientific, Germany
Ketac Molar liquid, aqueous solution of copolymer	3M-ESPE, Germany

TABLE II Composite formulations

Component	Composition (%)
BisGMA	14.6
TEGDMA	4.9
Camphorquinone (initiator)	0.3
DMAEM (amine accelerator)	0.2
Filler (G338 or Raysorb T-4000)	80.0

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 Raysorb T-4000, again in either silanted 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]:

$$\sigma = AP/t^2$$

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

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

where a is the radius of the support circle, b is the radius of the specimen, ν 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 III Properties of experimental glass-ionomer cements

	Unsilanated G338	Silanated G338
Setting time (min)	5	9
Biaxial flexure strength (MPa)	32.1 (SD 2.2)	4.9 (SD 1.0)
Net water uptake (%)	2.6 (SD 0.5)	4.1 (SD 1.8)

Results

The setting time, biaxial flexure strength and percentage hydration for the experimental glass-ionomer cements are shown in Table III. The glass-ionomer cement containing the silanated G338 glass took longer to set than the cement prepared from silane-free G338 and gave a material that was significantly weaker in biaxial flexure ($p < 0.001$). However, observed differences in net water uptake were not significant.

Results for the experimental composite resins are shown in Tables IV and V. For both fillers (G338 and Raysorb T-4000), the silanated glasses gave materials with higher biaxial strengths than the equivalent silane-free glasses. In both cases, these differences were statistically significant ($p < 0.001$). They also gave lower water uptakes ($p < 0.01$ for G338, $p < 0.001$ for Raysorb T-4000). Data in these tables also allow comparison of the effect of including either G338 or Raysorb T-4000 glass as filler, and show that in both silane-free and silanated states, Raysorb T-4000 gave higher biaxial strengths and lower net water uptakes, in each case to extents that were statistically significant ($p < 0.001$).

Discussion

The results in Table III illustrate the effect of silanation of G338 on the properties of the resulting cement. They show that silanation increases the working time and decreases the strength. The increase in working time presumably arises because the silane coats the surface of the glass, and this needs to be penetrated by the aqueous acid solution before the setting process can begin. It is not clear why this inhibition of the setting reaction should lead to a significant reduction in the biaxial flexure strength, but the correlation between slow setting and low strength has been known for many years for these materials [19, 20]. It may be speculated that not all of the glass particles take part in the setting reaction, which leads to a less cohesive matrix, and thus decreases the biaxial flexure strength. The findings are important for compomers, and also resin-modified glass-ionomers, in that they demonstrate that the acid-base reaction will be inhibited in these materials relative to a silane-free glass, and that the contribution to the overall strength of the salt part of the matrix will be correspondingly small.

TABLE IV Properties of experimental composite resins filled with G338 reactive glass

	Silane-free G338 glass	Silanated G338 glass
Biaxial flexure strength (MPa)	38.4 (SD 4.7)	68.0 (SD 6.0)
Net water uptake (%)	1.0 (SD 0.1)	0.7 (SD 0.1)

TABLE V Properties of experimental composite resins filled with Raysorb T-4000 unreactive glass

	Silane-free Raysorb glass	Silanated Raysorb glass
Biaxial flexure strength (MPa)	104.8 (SD 11.0)	152.0 (SD 6.1)
Net water uptake (%)	0.4 (SD 0.0)	0.1 (SD 0.0)

The effect of including G338 in the composite resin formulation is shown from the data in Tables IV and V. Better properties were achieved with silanated G338, and this formulation had the greater biaxial flexure strength and the lower water uptake. The water uptake figure was towards the low end of the spectrum of results previously reported [13], but nonetheless significantly greater than for Raysorb T-4000. As expected (Table V), the latter filler gave the best properties in its silanated form, and showed a much higher biaxial flexure strength and a lower water uptake than G338 whether silanated or silane-free. This demonstrates that the simple inclusion of the ionomer glass in compomers, even with silane pre-treatment, leads to a material with poorer properties than a conventional composite. The ionomer glass is itself sufficiently hydrophilic to enhance the water uptake of the compomer formulation, without any additional contribution from the relatively polar active monomer. The reduction in strength caused by the presence of G338 glass is not easily explained from the data that we have obtained. It may be that the particle size or distribution of the G338 varied significantly from that of the Raysorb T-4000. It may also be that this glass, even with its silane pre-treatment, is more difficult to wet with the organic monomers, leading to inferior dispersion and compromised adhesion between filler and matrix. Whatever the explanation, the data are unambiguous: inclusion of G338 in place of Raysorb T-4000 produces an inferior material.

These results demonstrate that, in formulating a compomer, significant compromises in properties have to be made by comparison with a closely related conventional composite resin. The presence of the ionomer glass enhances the hydrophilic character of the finished material, and leads to a reduction in mechanical strength. Although the potential acid-base reaction is inhibited by the silane treatment, highest strengths are obtained when the glass is silanated, so this step is necessary to optimise physical properties.

Conclusions

Silanation of the reactive (ionomer-type) glass reduces the rate at which that glass can undergo an acid-base reaction. This is important, as the acid-base reaction is an essential secondary cure process within compomer materials. The finding is also significant for resin-modified glass-ionomers, which also employ silanated glasses, and whose acid-base reaction will be similarly slowed. This retardation in the acid-base process leads to statistically significant reductions in the biaxial flexure strengths of the resulting cements and also, the inclusion of the ionomer glass leads to a net increase in water uptake by the composite.

Overall, these results demonstrate that, in preparing compomers as materials that are hybrids of glass-ionomer cement and composite resin, significant compromises in properties have to be made. The resulting material shows lower biaxial flexure strength than a conventional composite resin and the silanation of the reactive glass retards the rate of the potential acid-base reaction.

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