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Water sorption/desorption in polyacid-modified composite resins for dentistry

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Abstract The water sorption and desorption behaviour of three commercial polyacid-modified composite resins used in clinical dentistry have been studied in detail. Cured specimens of each material were subjected to two successive water uptake cycles in an atmosphere of 93% relative humidity, with one intervening desorption cycle in a desiccating atmosphere over concentrated sulfuric acid. Specimens were found to absorb and desorb water according Fick's law until M_t/M_∞ values of approximately 0.5. Diffusion rates for uptake varied between cycles, ranging from 2.37–4.53 × 10^{-9} cm^2 s^{-1} for 1st cycle to 0.85–2.72 × 10^{-8} cm^2 s^{-1} for 2nd cycle. Desorption rates were similar to those for 2nd cycle sorption, and ranged from 0.86 to 5.47 × 10^{-8} cm^2 s^{-1}. Equilibration times for 1st cycle water uptake were greater than for 2nd cycle sorption and for desorption and overall the behaviour of polyacid-modified composites in a high humidity atmosphere was similar to that of conventional composites in water. It is concluded that the hydrophilic components of the former do not bring about an enhanced rate of water transport.

Introduction

Polyacid-modified composite resins ("compomers") are aesthetic dental repair materials [1]. They are very similar to traditional dental composite resins in their chemistry in that they are fabricated mainly from special macro monomers, and cured by an addition mechanism that is usually light-initiated [2, 3]. They are filled predominantly with non-reactive quartz filler that is bonded to the polymeric matrix by silane coupling agents.

These materials have additional components that distinguish them from conventional composite resins, namely small amounts of acid-functional monomer and low volume fractions of reactive glass powder of the type used in glass-ionomer cements [1]. These additional components are triggered into reacting in a post-cure process that is initiated as the compomer absorbs moisture in the mouth. Studies of these materials using FTIR show that changes take place that are consistent with the occurrence of a neutralization reaction between the acid functional groups and the basic glass filler [4, 5]. Despite its importance in regulating the maturation of these materials, there have been few studies of the water-uptake process. Those that have been carried out confirm that these materials gain mass when stored in water, and that a proportion of this water becomes irreversibly bound [6]. The latter finding is also consistent with the occurrence of a neutralization reaction.

The current study has been undertaken in order to gain information about the diffusion of water in these materials under three circumstances, namely (a) initial uptake, (b) desorption and (c) second uptake. In (a), free acid groups were present on the reactive monomer; in (c), because the specimens had equilibrated, it can be assumed that the acid groups had undergone neutralization, and were present in the form of reacted carboxylate groups rather than free acid. Desorption following prior equilibration inevitably involves specimens that have been able to undergo neutralization, and also contain predominately carboxylate rather than carboxylic acid groups.

Water sorption has been studied in several glassy polymers used in dentistry. Composite resins [7, 8], soft lining [9] and poly(methyl methacrylate) denture bases

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[10] have all been shown to absorb water and, at the early stages, this sorption follows Fick's law of diffusion. For disc-shaped specimens, edge effects can be neglected, and sorption follows the form of the so-called Stefan approximation, ie:

$$M_t/M_\infty = 2(Dt/\ \pi l^2)^{1/2}$$

where M_t is the mass uptake at time t (s), M_∞ is the equilibrium uptake, 2 l is the thickness of the specimen and D is the diffusion coefficient [11]. The later stages up to equilibrium are given by:

$$M_t/M_\infty = 1 - (8/\pi^2)\sum 1(2n+1) \times \exp[-\pi^2 D/4l^2(2n+1)t]$$

The diffusion coefficient, D, can be determined by measuring water uptake at convenient time intervals, then plotting M_t/M_∞ against $t^{½}$. If Fick's law is obeyed, this gives a straight line of slope *s*, where:

$$s = 2(D/\ \pi l^2)^{1/2}$$

from which

$$D = s^2\ \pi\ l^2/4$$

Typically, studies have been carried out with specimens immersed in pure water. An initial cycle is used to wash out any water-soluble components, such as monomers, unreacted initiator fragments, and so on, whose loss would otherwise impede the determination of mass gain. Diffusion characteristics have then been determined in these conditioned specimens. For compomers, this approach is not possible because, as has been mentioned, the first cycle would trigger the acid-base reaction. Hence, in the present study, a humid atmosphere was used in which to store the specimens. They were stored in a humidity chamber over saturated $Na_2SO_4{\cdot}10H_2O$, a solution known to give an atmosphere of 93% relative humidity at equilibrium a temperature of 20 °C [12]. The subsequent desorption stage was carried out using a similar chamber, but with specimens stored over concentrated sulfuric acid as dessicant. Following this desorption, a second sorption cycle was performed, and in this way the diffusion behaviour of water in both fresh and neutralized compomers was determined.

Materials and methods

The following materials were used:

F2000 (ex. 3M-ESPE, Germany), shade A3, lot ICJ 2004-01.

Compoglass F (ex. Ivoclar, Leichtenstein), shade 105, lot D51361.

Dyract AP (ex. DeTrey Dentsply, Germany), shade A2, lot 0212000899.

Disc-shaped specimens of dimensions 20 mm diameter × 2 mm depth were prepared by extruding unset compomers from their capsules into silicone rubber moulds of the appropriate dimensions, then compressing them between glass microscope slides. Both faces were irradiated in turn through the microscope slides for 40 s using a dental curing lamp (Kent Light, ex Kent Dental, UK), which emitted light with a maximum wavelength at 470 nm. A single specimen was used for the detailed kinetic experiments, but an additional five specimens were prepared to allow means and standard deviations to be determined for (a) equilibrium water uptake (1st cycle), (b) irreversible mass gain following subsequent desorption and (c) equilibrium water uptake (2nd cycle).

Specimens were stored initially in a sealed chamber over saturated $Na_2SO_4{\cdot}10H_2O$, a medium that gives an atmosphere of 93% relative humidity at 20 °C [12]. They were weighed at hourly intervals for the first seven hours, daily for five days, then weekly thereafter until equilibrium was achieved, a situation that was considered to be indicated by three successive weekly weights being the same. Following equilibration, specimens were transferred to a desiccator containing concentrated sulfuric acid as desiccant (Spectrosol®, ex BDH, Poole, approximately 98% H_2SO_4). Again, they were weighed every hour for the first day, every day for the first five days and weekly thereafter until equilibration had occurred. Finally, they were returned to the humidity chamber, and allowed to take up water until they had equilibrated, with masses being determined at the same time intervals as for the initial water sorption cycle.

Data were plotted as M_t/M_∞ against $t^{½}$, as required for Fick's law. Slopes of the straight line portions of the graphs were determined by least squares regression, and the results used to calculate diffusion coefficients. Mean equilibrium mass changes were determined, and the statistical significance of differences between results estimated using one-way ANOVA.

Results

The effect of storage in a high humidity environment of compomer specimens is shown in Tables 1–4. Diffusion coefficients are given in Table 1, for the period of linearity in the M_t/M_∞ against $t^{½}$ plot. For the 1st cycle, this lasted for approximately the first four days of water sorption; for desorption and 2nd cycle sorption, the period of linearity was of the order of the first 6–7 h. A typical plot of M_t/M_∞ against $t^{½}$ for Dyract AP is shown in Fig. 1.

Table 1 Diffusion coefficients for water sorption/desorption ($cm^2\ s^{-1}$)

Material	F2000	Compoglass F	Dyract AP
1st cycle	3.30×10^{-9}	2.37×10^{-9}	4.53×10^{-9}
Desorption	2.07×10^{-8}	5.47×10^{-8}	8.65×10^{-9}
2nd cycle	1.96×10^{-8}	2.72×10^{-8}	8.49×10^{-9}

Table 2 Ratios of diffusion coefficients

Material	F2000	Compoglass F	Dyract AP
2nd:1st cycle	5.9	11.5	1.9
Desorption:1st	6.3	23.3	1.9
Desorption:2nd	1.06	2.01	1.02

Ratios of diffusion coefficients are given in Table 2. These show that the initial diffusion is slower than the second cycle, especially for F2000 and Compoglass F, whereas the rates of desorption and 2nd cycle sorption are similar.

Table 3 shows that for F2000, the 1st cycle gain in mass was significantly greater than the 2nd cycle gain ($p < 0.01$), whereas for Compoglass F and Dyract AP, differences in 1st and 2nd cycle water uptakes were not significant. F2000 showed a net loss after desorption. By contrast, both Compoglass F and Dyract AP showed small residual gains in mass following 1st cycle equilibration at high humidity.

For all three materials, the equilibration time for 1st cycle water uptake was of the order of 4 months (17 weeks), but subsequent desorption was much quicker (6–7 weeks depending on material), as shown in Table 4. Equilibration times for 2nd cycle water uptake varied widely, with that for Dyract AP being much longer than for Compoglass F, which in turn was longer than that for F2000.

Table 3 Equilibrium water uptake (%, Standard deviations in parentheses)

Material	F2000	Compoglass F	Dyract AP
1st cycle gain	3.32 (1.65)	1.50 (0.14)	1.71 (0.21)
Residual gain	–0.48 (0.39)	0.37 (0.24)	0.64 (0.62)
2nd cycle gain	0.66 (0.39)	1.56 (0.40)	1.45 (0.62)

Table 4 Equilibration times/weeks

Material	F2000	Compoglass F	Dyract AP
1st cycle	17	17	17
Desorption	6	7	6
2nd cycle	5	11	18

Discussion

The current study has shown that polyacid-modified composite resins are sufficiently hydrophilic to take up water from a high humidity atmosphere. This water uptake is Fickian up to approximately $M_t/M_\infty = 0.5$, after which the rate declines compared with that predicted by Fick's law.

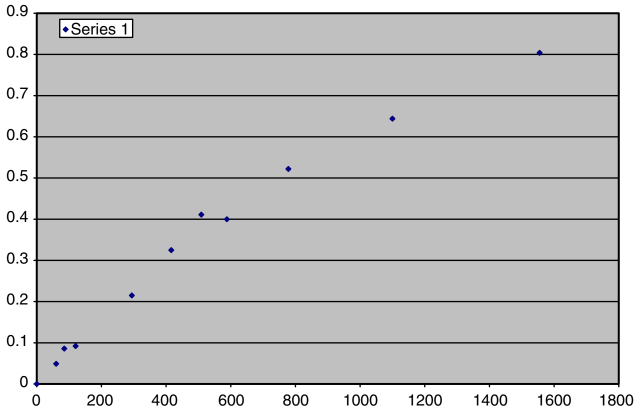

Fig. 1 1st cycle water absorption for Dyract AP. *Y*-axis caption: M_t/M_∞; *X*-axis caption: $t^{1/2}/s^{1/2}$

The diffusion coefficients that have been determined are comparable to those reported for composite resins soaked in water, despite the difference in the form of the water and hence in the driving force for sorption [7, 8, 13]. Also, as for conventional composite resins in water [13], diffusion coefficients from a high humidity atmosphere were lower for the 1st cycle than for the 2nd. For conventional composite resins in water, these differences have been attributed to the plasticizing effect of water within the polymer structure [14]. However, this interpretation does not explain the observation in the current study that the 2nd cycle sorption occurs at more or less the same rate as desorption. Rather, this observation suggests that the 1st cycle causes irreversible changes to the polymer, probably a slow change in conformation to one through which water molecules can pass more easily. The resulting increased ease of water transport would be expected to affect both desorption and 2nd cycle sorption, as observed experimentally for compomers.

Equilibrium water uptake was generally higher than has been found for conventional composite resins soaked in water, except for the 2nd cycle sorption by F2000. This material was also the only one for which the 1st and 2nd cycle values differed by a statistically significant amount. Since these materials are proprietary no information is available on their detailed composition, so the reason for this behaviour is not clear. One possibility is that, for this material only, micro-voids within the structure are effectively sealed as a result of plasticization of the polymer component by water and the subsequent chemical reaction between the acid functional groups and the ionomer glass fraction of the filler.

Previous studies have shown that fully formulated composites take up about 1.5 times as much water as the pure polymer matrix [13]. This has led to the suggestion that the additional water collects at the interface between the organic matrix and the inorganic filler [15]. If this is where the water collects in polyacid-modified composites, either on soaking or in the high humidity atmosphere, as in the current experiments, it is beneficial because this is the zone in which the secondary acid-base between the functional groups on the acidic monomer and the basic ionomer-type glass must occur. Not all of the water taken up at equilibrium is used to promote the secondary cure reaction as indicated by the fact that these materials are able to give up water in a desiccating environment.

Previous studies have demonstrated that the presence of the ionomer glass in polyacid-modified composites increases the equilibrium water uptake on soaking from 0.1% to 4.1% in an otherwise identical composite [16]. Similarly, the active monomer component containing carboxylic acid functional groups would also enhance the hydrophilic character of the final material. It is known that varying the hydrophilic/hydrophobic balance in monomers leads to changes in the extent of water uptake in dental composites [13]. In the three polyacid-modified composites studied, their enhanced hydrophilic character was found to result in an equilibrium water uptake in the high humidity atmosphere that exceeded that of conventional composite resins soaked in water.

In the present study, the rate of water transport in compomers at high humidity was found to be similar to that in conventional composite resins soaked in pure water. Although the conditions employed for compomers differed significantly from those previously used for the study of composite resins, diffusion coefficients were all of the same order, and in both types of study, the rate of the 1st cycle was lower than that of the 2nd cycle. This suggests that similar processes are involved in both types of materials in these widely varying conditions, and that, overall, the water uptake behaviour of the polyacid-modified composites is dominated by their hydrophobic components.

Conclusions

This study has shown that compomers take up water at different rates in a high humidity environment depending on whether it is the first cycle or second cycle of water sorption. The initial uptake, when the material still contains unreacted acid groups, is slower than both the desorption in desiccating conditions and the second cycle uptake, both of which occur at roughly similar rates, and both of which involve water transport in a material containing neutralized carboxylate functional groups.

Water uptake behaviour in one of the three compomers studied (F2000) differed from that of conventional composite resins soaked in water in that the equilibrium value for 1st cycle water uptake was significantly greater than for the 2nd cycle ($p < 0.01$). However, the other two compomers showed more conventional behaviour, in that there were no significant differences between 1st and 2nd cycle uptakes. Equilibration times for initial water uptake were slightly greater than those reported for composite resins soaked in water, being of the order of 4 months compared with 4–6 weeks, though the amount of water absorbed at equilibrium was comparable or lower.

In relation to sorption data, polyacid-modified composite resins were found to show Fickian diffusion until M_t/M_∞ values of approximately 0.5, a finding which is similar to those reported previously. The values of diffusion coefficients were also of the same order of magnitude as for composite resins soaked in water. Overall the hydrophilic components that are the distinguishing feature of these modified composites make little or no difference to either the rate of water transport or the equilibrium uptake of water.

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