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The physics of water sorption by resin-modified glass-ionomer dental cements

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The water-sorption characteristics of two commercial resin-modified glass-ionomer dental cements (Baseline VLC, ex. Detrey Dentsply, and Vitremer lining cement, ex. 3M Dental Products) have been studied in more detail than previously. Water sorption in both cements proved to be rapid, reaching equilibrium at approximately 48 h for Baseline VLC and at approximately 10 d for Vitremer. Over the first 8 h or so, absorption was shown to follow Fick's law, with a diffusion coefficient of 1.56×10^{-7} cm^2 s^{-1} for Baseline VLC (cured for 20 s) and 5.09×10^{-7} cm^2 s^{-1} for Vitremer (also cured for 20 s). As expected, sorption of water was found to be faster in specimens cured for shorter cure times and slower for those cured for longer times. In the presence of sodium chloride, both at 0.9% and at 1 M, diffusion coefficients were significantly greater than in pure water, but did not vary significantly with sodium chloride concentration, being approximately 3.3×10^{-7} cm^2 s^{-1} for Baseline VLC and 8.0×10^{-7} cm^2 s^{-1} for Vitremer. This is attributed to conformational changes in hydrophilic segments of the polymer on absorption of aqueous sodium chloride in which the molecules form more compact coils than in the presence of pure water. They thus create a microstructure that is more permeable to water. Sorption in salt solutions became non-Fickian much sooner than in pure water, i.e. at 3–4 h for both cements. This is probably due to concentration changes of salt within the cement, suggesting that these materials possess a degree of permselectivity. Finally, equilibrium water uptakes varied with salt concentration, being least in 1 M NaCl, which reflects the different chemical potentials of water in the various storage media.

1. Introduction

Resin-modified glass-ionomers are a group of dental restorative materials that consist substantially of glass-ionomer components, i.e. water-soluble polymeric acid, ion-leachable glass and water, together with organic, photopolymerizable monomers and their associated initiation system [1]. The first of these materials was described in a patent application, since abandoned, and comprised simply a mixture of ingredients, including 2-hydroxyethylmethacrylate (HEMA) to act as cosolvent for the organic and aqueous components [2]. Shortly afterwards, the development of a cement-forming system based on graft copolymers of poly(acrylic acid) was announced. In these materials, a minor proportion of the carboxylic acid functional groups were replaced with cross-linkable branches that were terminated in vinyl groups [3]. For these materials, too, HEMA was required in order to retain all of the components in a single phase.

The resin-modified glass-ionomers, whatever the detail of their composition, have been shown to adhere to enamel and dentine [4], and also to release clinically useful amounts of fluoride [5, 6]. Conversely, they have been found to swell in aqueous media [7]. This swelling seems to be driven by the chemical potential of the solvent system, hence is greater in pure water than in, for example, 0.9% sodium chloride solution [8]. To date, however, studies have not considered the mechanism of water uptake in any detail, and in particular have not established whether the sorption behaviour in these materials is Fickian or not.

The water absorption of a number of dental polymers with a glassy morphology has been studied previously. For example, composite restorative materials [9, 10], soft linings [11] and poly(methylmethacrylate) denture bases [12] have all been shown to absorb water in a way that, in the early stages at least, follows Fick's law of diffusion. For disc specimens, where edge effects can be neglected, this means that sorption follows the equation

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

where M_t is the mass uptake at time t (s), M_∞ is the equilibrium uptake, $2l$ is the thickness of the specimen, and D the diffusion coefficient [13]. The later stages up to equilibrium are given by

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

The diffusion coefficient, D, can be determined by measuring water uptake at convenient intervals, then plotting M_t/M_∞ against $t^{1/2}$. Assuming Fick's law is obeyed, this will give a straight line of slope s such that

$$s = 2(D/\pi l^2)^{1/2} \tag{3}$$

from which

$$D = s^2 \pi l^2/4 \tag{4}$$

The current study was carried out in order to determine which features of the resin-modified glass-ionomers influence the way in which water is taken up, and in particular, under what circumstances, if any, sorption follows Fick's law. The features considered were (i) effect of cure time, (ii) effect of sodium chloride in the storage medium, both at physiological concentration of 0.9% and at 1 M, and (iii) effect of temperature. Results from the latter part of the study enabled activation energies for diffusion to be determined.

2. Materials and methods

The following materials were used, each in accordance with manufacturers' instructions.

(a) Baseline VLC (ex. Dentsply, Konstanz, Germany). This was mixed at the liner/base powder : liquid ratio of 1.3 : 1 by mass. The material is based on mixtures of acid-base and polymerizable components.

(b) Vitremer (ex. 3M Dental, St Paul, MN 55144, USA). Shade C2, used at a powder : liquid ratio of 2.5 : 1 by mass. This cement contains a graft copolymer of acrylic acid with vinyl-terminated branches, together with some HEMA.

Disc-shaped specimens of dimensions 6.0 mm diameter and 2.8 mm depth were prepared by placing freshly mixed cements in silicone rubber moulds of the appropriate dimensions between glass microscope slides. Both faces were irradiated in turn through the microscope slide for the required length of time using a dental curing lamp which emitted light at 470 nm. Three specimens were presented for each combination of storage medium/time/temperature.

Specimens were placed in their respective storage medium and weighed at regular intervals until they had equilibrated, after which they were dried in the incubator at 37 °C. They were then re-exposed to the relevant storage medium in stoppered glass vials, and weighed at hourly intervals for up to 8 h, after which they were weighed on a daily basis until they reached equilibrium. Weighings were performed with the specimens blotted dry using absorbent tissues, determinations being made to the nearest 0.0001 g. After weighing, the specimens were returned to the storage medium and stored at 37 (± 0.5) °C or at 2 (± 0.5) °C, as appropriate, between weighings. Following the second absorption cycle, specimens were dried again, and weighed at daily intervals until they had reached equilibrium. The difference between this second dried weight and the initial weight was taken as the water solubles content.

Data were plotted as M_t/M_∞ against $t^{1/2}$, as required for Fick's law. Slopes of the straight line portions of the graphs were determined by least squares regression. Where appropriate, the statistical significance of the differences between results were determined using one-way ANOVA.

3. Results

The effect of storage in water at 37 °C of specimens cured for different lengths of time is shown in Table I. From this table, it can be seen that the proportion of soluble matter goes down with increasing cure time, though the equilibrium water uptake did not vary in a systematic way with time of cure. Sorption of water was found to obey Fick's law for at least the first 8 h for both Baseline VLC and Vitremer (see Figs 1 and 2), with diffusion coefficients declining with increasing cure time (Table I).

Table II shows the effect of storage in aqueous sodium chloride solutions of 0.9% and 1 M concentration at 37 °C. The sorption of water in these two media is plotted in Figs 1 and 2, from which it can be seen that for both materials, departure from Fick's law occurred much earlier than in water, typically within 4 h. This is consistent diffusion into the cements varying with concentration, and the cements themselves exhibiting permselectivity.

Figs 3 and 4 show the effect of sorption in water, 0.9% NaCl and 1 M NaCl for Baseline VLC and Vitremer, respectively, at 2 °C. Table III records diffusion coefficients derived from these plots, and Table IV the activation energies determined by applying the Arrhenius equation in the following form

$$\log D_{37}/D_2 = E_{\text{act}}/R(1/310 - 1/275) \tag{5}$$

TABLE I The effect of storage in water at 37 °C for specimens cured for different lengths of time (standard deviations in parentheses)

Material	Cure time (s)	Solubles (%)	Equilibrium water uptake (%)	Diffusion coefficient (10^{-7} cm^2 s^{-1})
Baseline-VLC	10	2.12 (0.60)	9.72 (0.39)	1.77
	20	1.67 (0.05)	8.83 (0.57)	1.56
	30	1.26 (0.23)	9.33 (0.25)	1.31
Vitremer	10	3.82 (0.14)	8.48 (0.19)	7.91
	20	3.36 (0.15)	8.75 (0.36)	5.09
	30	3.26 (0.19)	7.42 (0.30)	3.36

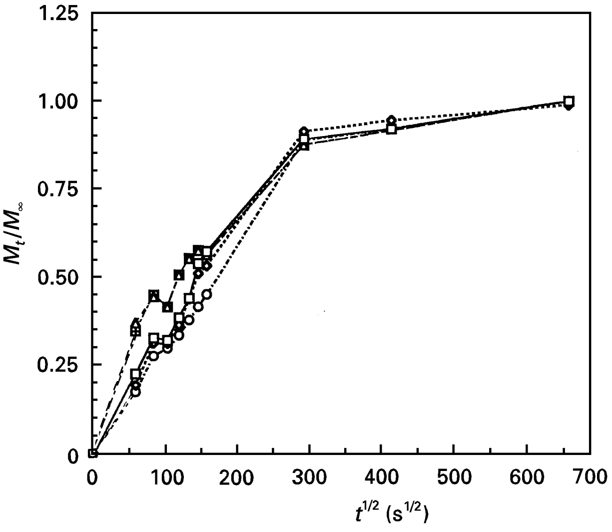

Figure 1 Sorption of water at 37 °C by Baseline VLC cured for (□) 10 s, (◇, △, ⊞) 20 s and (○) 30 s, and stored under different conditions: (□, ◇, ○) VLC, (△) 0.9% NaCl, (⊞) 1 M NaCl.

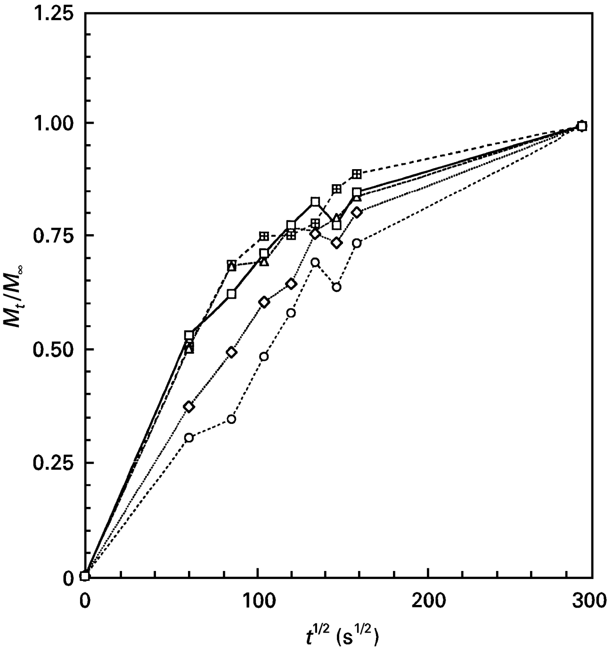

Figure 2 Sorption of water at 37 °C by Vitremer cured for varying times and stored under different conditions: for key, see Fig. 1.

where D_{37} and D_2 are the diffusion coefficients at 37 and 2 °C, respectively; other symbols have their conventional meanings, and 310 and 275 are the respective storage temperatures (K).

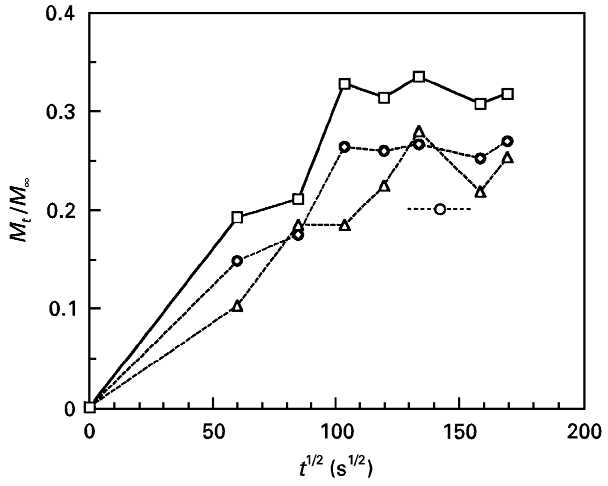

Figure 3 Sorption of water by Baseline VLC (cured for 20 s) in various media at 2 °C: (◇) 0.9% NaCl, (□) H_2O, (△) 1 M NaCl.

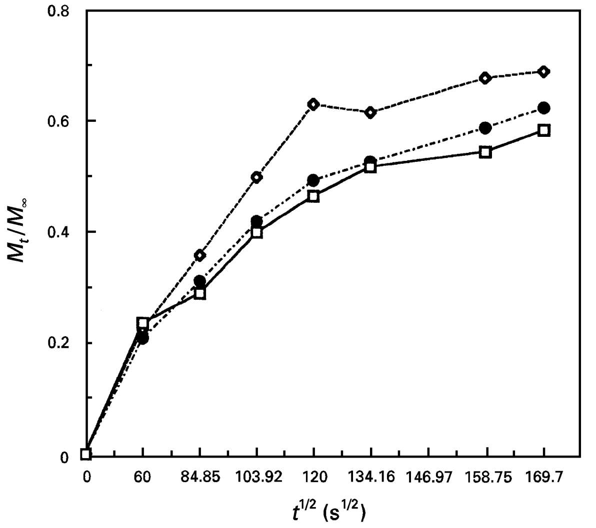

Figure 4 Sorption of water by Vitremer (cured for 20 s) in various media at 2 °C: for key see Fig. 3.

TABLE III Diffusion coefficients for specimens cured for 20 s and stored at 2 °C in various media

Material	Storage medium	Diffusion coefficient (10^{-7} cm^2 s^{-1})
Baseline-VLC	Water	1.27
	0.9% NaCl	0.82
	1 M NaCl	0.87
Vitremer	Water	2.21
	0.9% NaCl	3.33
	1 M NaCl	2.37

TABLE II The effect of storage in salt solutions at 37 °C for specimens cured for 20 s (standard deviations in parentheses)

Material	Storage medium	Solubles (%)	Equilibrium water uptake (%)	Diffusion coefficient (10^{-7} cm^2 s^{-1})
Baseline-VLC	0.9% NaCl	2.30 (0.13)	9.19 (0.28)	3.31
	1 M NaCl	2.42 (0.04)	8.64 (0.45)	3.39
Vitremer	0.9% NaCl	4.21 (0.48)	7.71 (0.39)	7.96
	1 M NaCl	3.35 (0.33)	6.63 (0.21)	8.25

TABLE IV Activation energies for water sorption

Material	Storage medium	Activation energy ($kJ\,mol^{-1}$)
Baseline-VLC	Water	1.81
	0.9% NaCl	12.27
	1 M NaCl	11.93
Vitremer	Water	7.33
	0.9% NaCl	7.67
	1 M NaCl	10.99

4. Discussion

At all three cure times, Vitremer showed significantly greater water-soluble content and diffusion coefficient than Baseline VLC ($p > 0.001$). However, at both 10 and 30 s cure, the equilibrium water uptake by Vitremer was significantly lower than for Baseline VLC ($p > 0.001$). At 20 s cure, the difference was not significant. Although equilibrium water content did not vary in a systematic way with cure time, for each material, there were clear trends in water-soluble content and diffusion coefficient with time, both declining with increased cure time.

These findings are readily accounted for, because at longer irradiation times, there is greater time for free radical reactions to be initiated. This leads to more complete incorporation of potentially soluble material. At the same time, the increased extent of polymerization reduces the ease with which individual water molecules are able to diffuse through the structure.

The specimens stored in salt solutions showed very different behaviour from those stored in pure water: the amount of soluble material extracted from each cement was larger, as were the diffusion coefficients. In both cements, the individual results for mass uptake at any given time were not significantly different for the 0.9% or the 1 M NaCl concentrations. Hence, although the diffusion coefficients were found to be slightly greater in 1 M NaCl than in 0.9% NaCl, the differences were not significant. The equilibrium water contents were slightly higher for Baseline VLC than when it was stored in water, though again the large scatter in the result in water makes this insignificant at any sensible confidence level. By contrast for Vitremer, the water uptakes in sodium chloride solution were both significantly less than in pure water ($p > 0.05$), a finding which agrees with previous results for this type of material [8].

For these materials, the equilibrium water uptake can be related to the chemical potential of water in the surrounding medium. Chemical potential is higher in pure water than in sodium chloride solutions, hence the thermodynamic driving force for water sorption is greater in pure water than in the solutions.

The reason for the greater diffusion coefficients in salt solutions seems likely to be due to the fact that water-soluble polymers adopt more tightly coiled conformations in the presence of low molar mass electrolytes than they do in pure water [14]. Adoption of much smaller conformations by the hydrophilic segments, such as polyHEMA and even, possibly, the neutralized poly(acrylic acid) segments, would lead to a network with larger molecular sized voids in it, and water would be more readily able to permeate through this structure. Diffusion would thus be less hindered and consequently more rapid under these circumstances.

The region of the sorption plot for which diffusion is Fickian is much more limited in sodium chloride solutions for both Baseline VLC and Vitremer. Typically, sorption departed from Fick's law by about 3–4 h, whereas it remained Fickian for at least 8 h for the specimens stored in pure water. Such departures from Fick's law are usually attributed to concentration effects [15]. In other words, these findings are consistent with the occurrence of changes in concentration of the sodium chloride solution as it passes through the cement, which implies that these cements exhibit a degree of permselectivity. This kind of behaviour has been noted before for acrylic acid polymers, either as copolymers with monomers such as *n*-butyl methacrylate [16] or as ionically cross-linked films [17], with Zn^{2+} or Al^{3+} as the cross-linking ions. Membranes of these polymers have been prepared having properties useful, *inter alia*, in haemodialysis [16, 17].

Table III shows the effect of storage at low temperatures, and results listed here enabled activation energies for sorption to be determined, as listed in Table IV. For both cements, activation energy was greater in the sodium chloride solutions than in pure water, though this difference was less marked for Vitremer than for Baseline VLC. This contrasts strikingly with the results for diffusion coefficient. At the descriptive level, this paradox can be explained by the need for the water-soluble segments within the cement to contract on initial absorption of sodium chloride solution, a process that requires energy.

Quantitatively, it can be understood by considering the diffusion coefficient at temperature T K to be given by

$$D = D_0 \exp(-E_{\text{act}}/RT) \qquad (6)$$

The term D_0 may be considered to be made up of a number of terms [14], such that

$$D_0 = (RT/n)\lambda \exp(\Delta S/R) \qquad (7)$$

where λ is the "jump distance", i.e. the distance between neighbouring sites that the water molecule can occupy, ΔS represents the change in entropy, and the other symbols have their conventional meaning. This approach shows that an increase in diffusion coefficient may be brought about by an increase in the jump distance, the entropy change, or both. In salt solutions, the more coiled structure adopted by the hydrophilic segments would increase the jump distance, thereby increasing the value of D_0. On the other hand, the entropy of mixing term as water enters the structure would be expected to be affected only slightly by the change from pure water to salt solution, regardless of any contraction of the coil dimensions. Hence the ΔS term would be expected to change only marginally and, correspondingly, to cause only a small difference to the value of D_0. The change in diffusion coefficient is thus consistent with the conformational changes postulated for the molecules of the cement in sodium chloride solution.

These findings are not only important for the light they cast on the physics of water sorption, but also for a practical point. Because their intended use is as dental restorative materials, their behaviour in aqueous electrolyte solutions is much more important than their behaviour in pure water. This in turn means that any evaluation of these materials should take place in such solutions, rather than in pure water.

5. Conclusion

The sorption of water by resin-modified glass-ionomers has been shown to obey Fick's law in the early stages of the process. Such sorption depends on the time for which the specimens are exposed to light, with diffusion being more rapid in specimens cured for only 10 s than for those cured for 20 s, and these in turn showing faster diffusion than specimens cured for 30 s. In the presence of sodium chloride, either at 0.9% or at 1 M, Fick's law was followed for a much shorter period of time than in pure water, with diffusion being more rapid. The diffusion coefficients varied only slightly with the differing concentrations of salt. These differences are attributed to changes in the conformation of the hydrophilic segments in the polymer molecules of the cement, as they coil more tightly in the presence of the salt, resulting in easier movement of water through the structure in the latter situation. The relatively short period of Fickian diffusion suggests that these materials set up a concentration gradient within themselves, and that these cements are thus permselective.

Activation energies for sorption were found to be greater in salt solutions than in water, considerably so for Baseline VLC, but less so for Vitremer. They ranged from 1.81 kJ mol^{-1} for Baseline VLC in water to 11.93 kJ mol^{-1} for Baseline VLC in 1 M NaCl, while values for Vitremer all fell within the range 7–11 kJ mol^{-1}.

Overall, it is concluded that the water sorption behaviour of resin-modified glass-ionomers in salt solution differs considerably from that in pure water. Because, in use, these materials are exposed to saliva, the most clinically relevant results in this study are those obtained in sodium chloride solutions at 0.9%, i.e. physiological concentration.

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