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Water Transport in Resin-modified Glass-ionomer Dental Cement

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ABSTRACT: Water uptake and water loss have been studied in a commercial resin-modified glass-ionomer cement, Fuji II LC, under a variety of conditions. Uptake was generally non-Fickian, but affected by temperature. At room temperature, the equilibrium water uptake values varied from 2.47 to 2.78% whereas at low temperature (12°C), it varied from 0.85 to 1.18%. Cure time affected uptake values significantly. Water uptake was much lower than in conventional glass-ionomer restorative cements exposed to water vapor. Loss of water under desiccating conditions was found to be Fickian for the first 5 h loss at both 22 and 12°C. Diffusion coefficients were between 0.45 and $0.76 \times 10^{-7} \text{ cm}^2/\text{s}$, with low temperature diffusion coefficients slightly greater than those at room temperature. Plotting water loss as percentage versus $s^{-1/2}$ allowed activation energies to be determined from the Arrhenius equation and these were found to be 65.6, 79.8, and 7.7 kJ/mol respectively for 30, 20, and 10 s cure times. The overall conclusion is that the main advantage of incorporating HEMA into resin-modified-glass-ionomers is to alter water loss behavior. Rate of water loss and total amount lost are both reduced. Hence, resin-modified glass-ionomers are less sensitive to water loss than conventional glass-ionomers.

KEY WORDS: resin-modified glass-ionomer, water sorption, water loss, kinetics.

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INTRODUCTION

Resin-modified glass-ionomers are widely dental restorative materials with particular application in pediatric dentistry [1]. Like conventional glass-ionomers, they contain basic glass powder, poly(acrylic acid), and water, but they also contain 2-hydroxyethyl methacrylate (HEMA) as the so-called resin component [2]. They also contain initiators to bring about addition polymerization of the HEMA. These are usually photosensitive compounds which yield free radicals on irradiation with blue light (470 nm) from a conventional dental curing lamp [2]. Certain brands have HEMA side chains grafted onto the polyacid backbone [3], and these become crosslinked on irradiation with blue light.

Resin-modified glass-ionomers are chemically complex [4], but have many of the desirable properties of conventional glass-ionomer cements. These include fluoride release [5], ability to buffer cariogenic acids *in situ* [6], and the ability to release clinically beneficial ions, such as calcium and phosphate [6].

These materials have been shown to some hydrogel character, a consequence of the presence within them of polyHEMA. They thus take up water [7–9], which occurs to varying extents, depending on the presence of ions in the surrounding medium. Water uptake is greatest from pure water, but much reduced from, say, 0.9% sodium chloride solution [10]. There is some evidence that the set material may consist of domains of differing composition, as a consequence of the tendency for them to undergo a degree of phase separation. This arises from the relatively nonpolar character of HEMA in the aqueous solution of poly(acrylic acid), and is enhanced by the insolubility of polyHEMA in water [6].

Water uptake has been shown in a variety of studies to follow Fick's law [8–10] and diffusion coefficients have been found to be of the order of $5 \times 10^{-7} \text{ cm}^2/\text{s}$ ($5 \times 10^{-11} \text{ m}^2/\text{s}$). These studies have used Fick's second law of diffusion [11] and employed disc-shaped specimens. For these specimens, edge effects can be neglected, and water uptake follows the form of the so-called Stefan approximation, i.e.:

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

where M_t is the mass uptake/loss at time t (s), M_∞ is the equilibrium uptake/loss, $2l$ is the thickness of the specimen and D is

the diffusion coefficient [11]. The later stages up to equilibrium are given by:

$$\frac{M_t}{M_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=1}^{\infty} (2n+1) \times \exp[-\pi^2 D/4l^2 (2n+1)t]$$

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

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

from which

$$D = s^2 \frac{\pi l^2}{4}.$$

This describes precisely the kinetics of water gain in resin-modified glass-ionomers under the conditions studied so far [8–10]. It also describes water loss from conventional glass-ionomer cements [12].

To date, diffusion studies of this kind have employed conditioned specimens, i.e., specimens which have been previously soaked in water to remove residual soluble substances. They have also concentrated on liner/base grades of material, and emphasized water uptake. In the present study, we have investigated the water transport properties of a resin-modified glass-ionomer restorative material for both water uptake and water loss using high humidity and low humidity atmospheres. We have measured either mass gain or mass loss respectively for specimens cured for varying lengths of time, and determined whether or not mass change follows Fickian kinetics. We have also measured equilibrium water contents, and repeated the studies at low temperatures, with a view to determining activation energies for the processes.

MATERIALS AND METHODS

A commercial resin-modified glass-ionomer dental cement (Fuji II LC, ex GC, Japan) was used in this study. It is provided in capsules, and these were mixed on a vibratory dental mixer (Kent Dental, UK) for 10 s, then extruded from the capsule into silicone rubber molds held between microscope slides. The molds gave circular specimens of diameter 6 mm

and depth of 2 mm. They were hardened by irradiating them for set time intervals (10, 20, or 30 s, respectively) from each side, using a dental curing lamp (Euromax, De Trey Dentsply, Germany) which emitted light at around 470 nm wavelength. Irradiation took place through the microscope slides, with the tip of the curing light placed right up against the surface of the microscope slide. Four specimens were prepared per experiment.

Immediately they were cured, the specimens were removed from the molds, weighed and transferred to a controlled-humidity environment in a glass desiccator, either low humidity over concentrated sulfuric acid as desiccant (Spectrosol[®], ex BDH, Poole, approximately 98% H₂SO₄) or high humidity over saturated sodium sulfate solution, a mixture which provides a 93% relative humidity at 20°C [13]. Specimens were weighed at hourly intervals for the first 5 h, then at 24 h, then at daily intervals until equilibrium was achieved and results for mass change were averaged.

Plots were then made of M_t/M_∞ against $t^{1/2}$ and using the slope of this graph, diffusion coefficients were determined. The initial experiments were carried out at room temperature (22°C) and a second set was carried out at 12°C in the refrigerator. Graphs were plotted as best-fit lines using least squares regression, and differences in values were examined for statistical significance using the Student's *t*-test as appropriate.

RESULTS

In the high humidity environment at both room temperature and at 12°C, specimens took up water. However, as shown in the typical example illustrated in Figure 1, uptake was somewhat irregular, and certainly not Fickian. This was the case for water uptake in all specimens under all conditions, except for the specimens cured for 20 s and stored at 93% RH. These showed approximately 1 h induction period, after which uptake did follow Fickian kinetics for the next 4 h.

Equilibrium was reached in 7–8 days, and the equilibrium water uptake values are shown in Table 1. For room temperature cure, they ranged from 2.78 (10 s cure) to 2.47% (30 s cure), but these differences were not statistically significant. For low temperature cure, they ranged from 0.85 to 1.18% respectively, which again were not significantly different from each other. However, they were significantly different ($p < 0.001$) from specimens equilibrated at room temperature.

Water loss, by contrast, was found to be Fickian, though with a slight induction period in many cases. An example of a diffusion plot for water

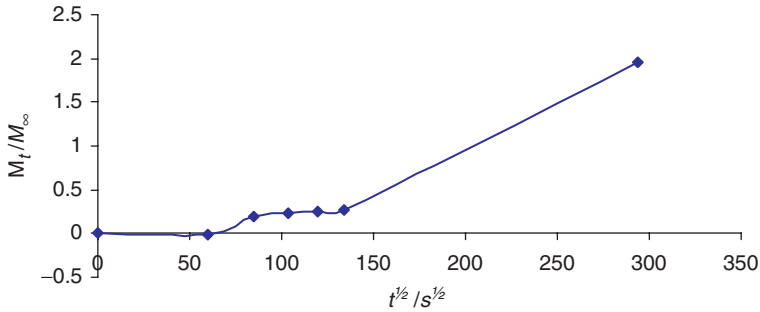


Figure 1. Water uptake by specimens cured for 10 s, stored at high humidity and room temperature.

Table 1. Equilibrium water uptake values.

Temperature (°C)	Cure time (s)	Water content (%)	Standard deviation
22	30	2.47	0.08
22	20	2.70	0.28
22	10	2.78	0.47
12	30	1.18	0.09
12	20	0.98	0.08
12	10	0.85	0.03

loss is shown in Figure 2. Water loss values are shown in Table 2, and as for water uptake, did not differ significantly with variation in cure time, but were significantly lower ($p < 0.01$) for specimens equilibrated at low temperature compared with the specimens equilibrated at room temperature. Specimens took 7–10 days to equilibrate. Diffusion coefficients, calculated according to the Stephan approximation of Fick’s second law, are shown in Table 3.

These diffusion coefficients were determined from plots of M_t/M_∞ against $t^{1/2}$. However, the low temperature diffusion coefficients turn out to be higher than the room temperature ones, a finding which implies that the activation energy for water loss is negative. This is not physically possible, and is an artifact of the way in which the diffusion coefficients are determined. This uses the equilibrium water gain or loss. It is known, though, that for glass-ionomer cements, there is a maturation process that takes place slowly early in the life of a set cement, and which causes a proportion of the water gradually to become tightly

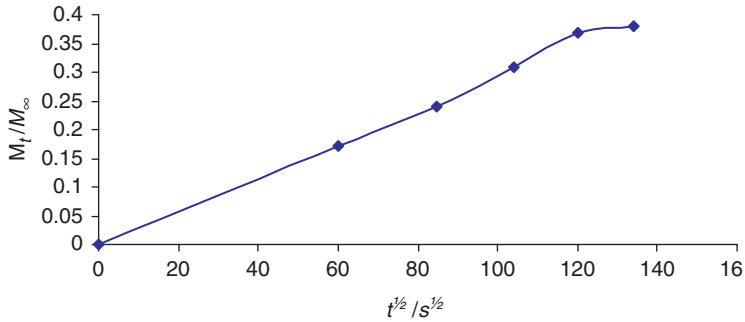


Figure 2. Water loss by specimens cured for 30s, stored at low humidity and room temperature.

Table 2. Equilibrium water loss values.

Temperature (°C)	Cure time (s)	Water content (%)	Standard deviation
22	30	3.10	0.21
22	20	3.44	0.06
22	10	3.13	0.15
12	30	2.43	0.06
12	20	2.48	0.08
12	10	2.37	0.04

Table 3. Diffusion coefficients.

Temperature (°C)	Cure time (s)	Diffusion coefficient ($10^{-7}\text{cm}^2/\text{s}$)
22	30	0.71
22	20	0.64
22	10	0.45
12	30	0.57
12	20	0.76
12	10	0.66

bound [14]. Consequently, the available amount of water declines as the cement ages.

Diffusion was studied over the first 5 h life of the cements, yet they took at least a week (168 h) to equilibrate, often slightly longer. The period of diffusion thus represents only the first 3–4% of the time

Table 4. Rate constants for mass loss.

Temperature ($^{\circ}\text{C}$)	Cure time (s)	Rate constant ($\% \text{ s}^{-1/2}$)
22	30	9.2×10^{-3}
22	20	9.7×10^{-3}
22	10	7.7×10^{-3}
12	30	3.6×10^{-3}
12	20	3.1×10^{-3}
12	10	6.9×10^{-3}

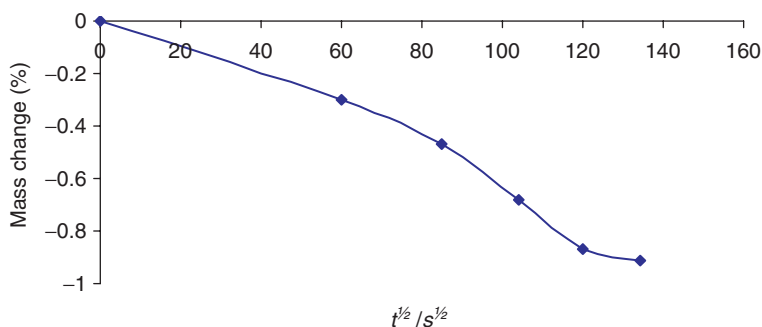


Figure 3. Water loss (%) by specimens cured for 30s, stored at low humidity and low temperature.

to achieve equilibrium. As a reasonable approximation, it can be assumed that only a minor amount of the available water has become tightly bound in this period of time, and therefore the same amount of water is available for diffusion between the specimens stored at room temperature and those stored at 12°C . Hence, it was decided to re-plot the water loss data as a simple percentage loss versus $t^{1/2}$ graph, and to compare the rate constants obtained from their slopes. These are listed in Table 4 and an example is shown in Figure 3. From these, it was then possible to determine meaningful values of activation energy using the Arrhenius equation, and these are listed in Table 5.

DISCUSSION

Water uptake and water loss at equilibrium were both found to be influenced by storage temperature. At room temperature, water loss

Table 5. Activation energies for water loss.

Cure time (s)	Activation energy (kJ/mol)
30	65.6
20	79.8
10	7.7

varied between 3.10 and 3.44%, which is significantly less than that found for modern restorative grades of conventional glass-ionomer [6]. Conventional glass-ionomer materials were found to lose between 6.03 and 8.30% depending on the brand [6]. Similarly, diffusion coefficients for loss of water were found in the current study to be of the order of $0.5\text{--}1.0 \times 10^{-7} \text{ cm}^2/\text{s}$ compared with values of between 5 and $15 \times 10^{-7} \text{ cm}^2/\text{s}$ for restorative grade conventional glass-ionomers [6]. Thus, the effect of incorporating HEMA into these materials is to reduce overall water loss to <50% of the value in conventional materials, and to reduce rate of water loss by approximately one order of magnitude. Diffusion coefficients in the current study were substantially less than those previously reported for liner/base grades of resin-modified glass-ionomer [10]. These results thus confirm those of Kanchanivasita et al. that restorative grades of RMGIC lose water less readily than liner/base grades [9].

Water uptake has been studied in pure polyHEMA and in HEMA copolymers, using both exposure to water vapor [15] and immersion in liquid water [16–18]. The process was Fickian in all cases, and the diffusion coefficient has been determined twice as $1.7 \times 10^{-7} \text{ cm}^2/\text{s}$ [16,17] and once as $1.96 \times 10^{-7} \text{ cm}^2/\text{s}$ [18]. All reported determinations were carried out in the temperature range 35–37°C. Our results did not support the finding of Fickian diffusion for water uptake, though previous studies on resin-modified glass-ionomers have done so. These earlier studies employed conditioned specimens, and a regime involving immersion in water [8–10]. Under these conditions, it was the second cycle for which Fickian diffusion was established [8–10].

The conditioning process for these specimens involved soaking them to equilibrium, then drying them fully. This process always resulted in a net loss in mass, which was assumed to arise from the washing out of water-soluble impurities, for example initiator residues. In the current work, any such soluble residues were still present in the cements, and presumably these are what alter the uptake kinetics. In one previous study, water uptake in HEMA copolymers was found to be non-Fickian [16]. In this case, the other monomer was 1-vinyl-2-pyrrolidone, which

has a degree of polarity, and would not be expected to alter the water uptake significantly. Indeed, the 1 : 1 copolymer did have similar water-uptake behavior, albeit with different kinetics [16]. Our findings appear similar, in that the presence of modest amounts of water soluble species (initiator residues, etc.) in the cements alters the uptake kinetics, and makes them non-Fickian.

The diffusion coefficients for polyHEMA are greater than the diffusion coefficients we have determined for our specimens at lower temperatures, but lower than the values determined previously for restorative grades of glass-ionomer [12]. It thus appears that the HEMA component effectively controls the rate of water loss from the RMGICs, and that it has a much lower value of diffusion coefficient at both 22 and 12°C than it does around 35°C.

Conventional glass-ionomer cements are susceptible to water loss immediately they have been placed. This manifests itself in a change to the appearance of the surface, resulting from slight crazing and the development of a chalky texture [19]. This is overcome clinically by the use of varnishes, or of petroleum jelly [20]. Previous studies have shown that application of varnish leads to a significant reduction in the equilibrium water loss from glass-ionomers, together with improvements in the esthetics of the finished surface. It is apparent from our results that the incorporation of HEMA to make resin-modified glass-ionomers produces a material that loses much less water in the early stages after setting than conventional glass-ionomers. These materials also have a much higher equilibrium water content than conventional restorative glass-ionomer cements. Hence, our results demonstrate that RMGICs have a major clinical advantage over conventional cements, namely that, though they undergo some water loss, it does not occur to a sufficient extent to cause damage to the surface.

CONCLUSIONS

A commercial resin-modified glass-ionomer cement, Fuji II LC, has been shown to take up water under high humidity storage conditions, and to lose water under low humidity conditions. Water uptake was generally non-Fickian and, at room temperature, the equilibrium water uptake values varied from 2.47 to 2.78%. This was significantly greater than the uptake at low temperature (12°C) where uptake, which was also non-Fickian, at equilibrium varied from 0.85 to 1.18%. Variations in the length of cure time were not found to affect these uptake values significantly. The equilibrium water uptake values are much lower than

uptake values for conventional glass-ionomer restorative cements exposed to water vapor under identical conditions.

Loss of water under desiccating conditions, by contrast, was Fickian. This applied to the first 5 h loss at both room temperature and at low temperature (12°C). Diffusion coefficients were found to lie between 0.45 and $0.76 \times 10^{-7} \text{ cm}^2/\text{s}$, with low temperature diffusion coefficients slightly greater than their room temperature equivalents. This is attributed to the occurrence of slow maturation reactions within the cements, which effectively compete for the free water, and thus affect the amount of water that can be removed by the time equilibrium is achieved. Re-plotting water loss in terms of percent versus $\text{s}^{-1/2}$ enabled the Arrhenius equation to be applied, and showed the activation energies for water loss from these cements to be 65.6, 79.8, and 7.7 kJ/mol, respectively for 30, 20, and 10 s cure times. These diffusion coefficients are lower than those observed for conventional glass-ionomers and also for liner/base grades of resin-modified glass-ionomers.

The results lead to the conclusion that the main advantage of incorporating HEMA into resin-modified-glass-ionomers is to alter water loss behavior. The rate of water loss is reduced, and the amount lost at equilibrium is also reduced. Activation energy for water loss from fully cured resin modified glass-ionomers is relatively high, and it is this energy barrier that causes the reduction in water loss. Resin-modified glass-ionomers are thus much less sensitive to desiccation than conventional glass-ionomers.

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