J Mater Sci: Mater Med (2007) 18:127–131
DOI 10.1007/s10856-006-0670-0

Ion leaching of a glass-ionomer glass: an empirical model and effects on setting characteristics and strength

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Received: 17 August 2005 / Accepted: 4 November 2005

Abstract The release of ions from a glass-ionomer glass, which in the polyacid matrix effects the cross-linking and setting of a cement, can be modelled and initiated by acid-treatment in a dilute acid. This study examined the effect of time of acetic acid leaching on the working time, setting time, and strength of a model GIC. A reactive fluoride glass was immersed in hot acetic acid for 0 (control), 5, 15, 35, 65, 95 and 125 min, filtered and dried. The glass was mixed with an experimental GI liquid in a capsule system and the mixed pastes assessed for working and initial setting time. Compressive strength testing was undertaken according to ISO9917:2003. Immersion time had a significant effect on both working and setting time of the resultant pastes only up to 65 min of immersion, and corresponded with a thin-film ion diffusion model. Compressive strength did not vary significantly with immersion time. The glass-ionomer setting reaction can be conveniently retarded by immersion of the powder in acetic acid, without affecting strength. A reactivity model was developed, whereby the effects of various changes to the leaching process may be usefully examined.

Introduction

Glass-ionomer cements cure by means of an acid-base reaction between a polymeric aqueous acid and an ion-leachable glass [1]. The composition of the glass is critical to the setting characteristics and strength of the final cement [2–5].

Acetic acid is a low molecular weight monocarboxylic acid, which gives it significant chemical similarities with polycarboxylic acid. These similarities enable acetic acid to be used as a model for the acid-degradation of the glass-ionomer glass. Even low concentrations of acetic acid in the liquid component can significantly affect the properties of set GICs [6], and the ion-leaching effect of acetic acid makes it useful as a laboratory demineralising agent [7, 8]. Acetic acid can also react with glass-ionomer glasses to form insoluble cements [9], albeit of inferior properties to polyalkenoate cements.

The effects of acetic acid for acid washing have been investigated in ceramics [10–12], where they increased the surface roughness of the materials, and in glass-ionomer glasses. De Maeyer *et al.* [13, 14], building on the work of Barry *et al.* [15], examined the leaching stoichiometry of glass-ionomer glasses in acetic acid, and reported that the distribution and concentration of ions leached were directly related to the composition of the glass, in particular the presence of fluorite-rich (CaF_2) phases. The follow-up study of De Maeyer *et al.* [16] correlated the acid-leaching with X-ray diffraction studies, and found Si-Si bond distances also varied with composition, and may have contributed to the leaching profile. Rafferty *et al.* [17–19] conducted several investigations on leaching of glass-ionomer glasses, and found that calcium and phosphorous were preferentially leached, the surface area of the glass increased, and a silica-rich surface layer remained. Their general findings confirmed those of De Maeyer *et al.* [13, 14].

De Moor and Verbeeck [20] examined the effect of acetic acid immersion on set cements, and concluded that fluoride release profiles were associated with erosion—that is, physical degradation of the glass—as well as with normal diffusion leaching, where the overall structure of the glass remains, but ion diffusion occurs. Testing in lactic acid solutions by Shweiger *et al.* [21] reported that a fluoride-rich surface layer was formed on the glass in the first few minutes of exposure

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to acid, but that further exposure resulted in the preferential leaching of calcium and fluorine from the surface, resulting in a calcium-depleted silicon-rich layer of up to 500 nm after 30 min. Long-term leaching resulted in a silicon-rich surface layer [21]. Maeda's study [22] on setting processes in glass-ionomer cements demonstrated that aluminium was distributed through the set cement, and that the surface of the glass was primarily siliceous, a finding confirmed by others [18, 23]. Williams *et al.* [24] examined the fluoride release characteristics of cements formed from acetic-acid washed glass-ionomer glass, and reported that acid washing reduced the amount of soluble fluoride by around 75%, possibly by pre-removing fluoride (and possibly other ions) from the glass surface.

No study has yet examined systematically the role of acetic acid leaching of glass-ionomer glass on the setting or mechanical properties of the final cement. In particular, a thin-film diffusion model of ion leaching is expected to apply, but no study has taken this approach. This investigation examined the effect of time in an acetic acid leaching solution on the setting and mechanical properties of a glass-ionomer cement, with the null hypothesis that leaching of this type effected neither setting characteristics nor compressive strength. Further, the possibility of a thin-film diffusion model fitting the data was investigated.

Materials and methods

Preparation of glass-ionomer powder and liquid

An ion-leachable glass-ionomer glass (SP2489, Specialty Glass, Oldsmar, FL), with the size and composition defined in Table 1, was used for all experiments. An experimental glass-ionomer liquid, "M50," was provided by SDI Ltd (Bayswater, Victoria, Australia) for this study. This liquid contained polyacrylic acid, tartaric acid, and other proprietary ingredients.

The glass leaching process was conducted by sampling from an experimental scaled-up process. To a steam-jacketed agitated vessel were added 47.5 litres of water and 2.5 kg glacial acetic acid (Deltrex Chemicals, Laverton North, Victoria, Australia), the solution heated to 95°C, and 10.0 kg glass added with impeller agitation. Samples of 200 mL slurry were taken at $t = 5$, 15, 35, 65, 95 and 125 min, and immediately filtered under vacuum. The glass samples were dried at 110°C for 24 h and sieved through a 150-μm mesh to remove agglomerates. Untreated powder was used for data at time $t = 0$.

Sample preparation

For each powder, a commercial capsule system (Riva SC, SDI Ltd) was dosed with powder and liquid at a ratio of 2:1, following a pilot study which determined the maximum ratio that allowed working and setting time determination with unetched powder. Five capsules were prepared for each powder; two were used for working and initial setting time determination, and three for compressive strength sample preparation.

Capsules were activated and mixed for 10 s on a high-speed mixer (Ultramat™ 2, SDI Ltd) prior to extrusion for further testing.

Working time and initial setting time

Working time was determined as the time when the material could no longer cohesively string to a height of 10 mm when lifted with a spatula. Initial setting time was determined in a manner analogous to ISO9917 [25] as the point at which a 1-mm diameter amalgam plugger under a 300-g force no longer caused a permanent indentation in the material.

Compressive strength

Cylindrical specimens of height (6.0 ± 0.1) mm and diameter (4.0 ± 0.1) mm were made and tested for compressive strength according to ISO9917 [25]. The specimens were stored at >80% humidity at 37°C for 1 h, removed from the moulds and immersed in water at 37°C for a further 23 h, removed and examined for defects. Defective specimens were rejected, and the ends of the remaining specimens sanded flat with 600-grit SiC paper and loaded axially to fracture in a universal testing machine (Instron 5566, Instron Ltd, Milton Keynes, UK) at a crosshead speed of 0.5 mm/min.

Table 1 Glass particle size distribution and composition

Particle Size Distribution[1] (μm)			Composition[2] (%w/w, oxide basis)						
$d_{0.1}$	$d_{0.5}$	$d_{0.9}$	F	P_2O_5	SrO	Al_2O_3	Na_2O	SiO_2	ZnO
2.40	7.17	17.16	10.2	3.7	20.4	26.7	1.1	29.7	9.8

[1] Determined by laser diffraction (MasterSizer2000, Malvern Instruments, Malvern, UK).

[2] Determined by Inductively-Coupled Plasma Atomic Emission Spectroscopy and Ion-Selective Electrode (Spectrometer Services, Coburg, Australia).

Table 2 Working time and initial setting time of ion-leached glass. Values in parentheses are standard deviations. Values with identical superscripts within columns are not significantly different ($p < 0.05$) ($n = 2$)

Leaching time (min)	Working time (s)	Initial Setting time (s)
0	19 (2)^{a}	63 (4)^{a}
5	88 (6)^{b}	190 (9)^{b}
15	79 (2)^{b}	173 (3)^{b}
35	168 (3)^{c}	262 (4)^{c}
65	225 (4)^{d}	353 (12)^{d}
95	224 (12)^{d}	335 (4)^{d}
125	238 (4)^{d}	353 (9)^{d}

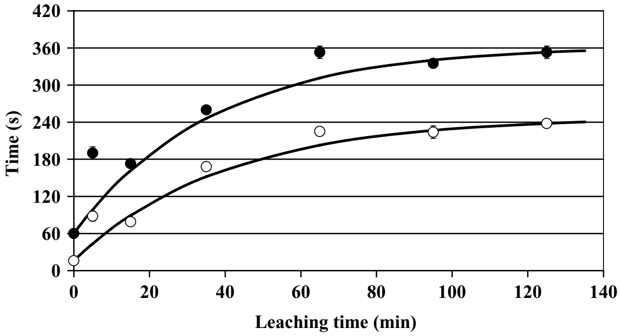

Fig. 1 Working times (○) and initial setting times (●) of cements formed from ion-leached glass. The fitted curves are a result of modelling (see Discussion).

Data were analysed using one-way analysis of variance and pairwise t-tests with a significance level of $\alpha = 0.05$.

Results

Working time and initial setting time

Both the working time and initial setting time increased after immersion of the ion-leachable glass in the hot acetic acid solution (Table 2), up to 65 min ($p < 0.05$), however, there was no significant effect thereafter.

The data are graphed in Fig. 1, where the curve fitted to the data is the result of modelling (see Discussion). The increase in working and setting time appeared to follow an exponential curve, with an asymptote after approximately 65 min acid immersion.

Compressive strength

Although there were significant differences (Table 3, $p < 0.05$) between cements formed from glass powders immersed for different times, there was no overall significant dependence of compressive strength on acid immersion time (Fig. 2).

Table 3 Compressive strength of cements formed from ion-leached glass. Values in parentheses are standard deviations. Values with identical superscripts are not significantly different ($p < 0.05$)

Leaching time (min)	Compressive strength (MPa)	n
0	72.0 (6.6)^{c}	9
5	61.1 (3.9)^{b}	7
15	54.9 (4.6)^{a}	7
35	67.4 (5.9)^{c}	9
65	68.0 (5.7)^{c}	6
95	57.0 (7.2)^{a,b}	5
125	72.6 (8.0)^{c}	7

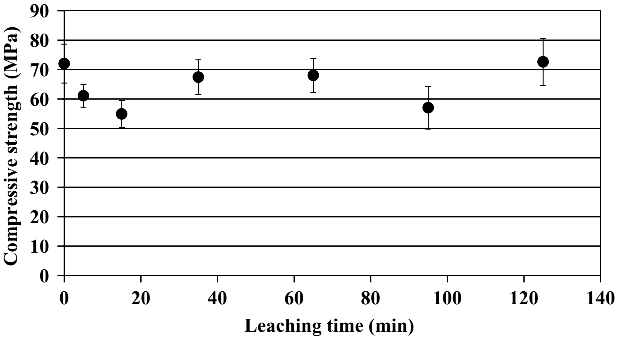

Fig. 2 Compressive strengths of glass-ionomer cements formed from ion-leached glass.

Discussion

Working time and initial setting time

The effect of acetic acid leaching of the glass-ionomer glass on the final cement was significant following even 5 min immersion in the acid, and was most likely due to an ion-leaching process similar to that which occurs during a conventional glass-ionomer curing reaction. Several features of the increase in working time and initial setting time may be observed.

The working and initial setting times, while initially increasing with immersion time in acetic acid, did not increase significantly after about 65 min in the leaching vessel ($p < 0.05$). The leaching of ions into solution is dependent on two primary transport phenomena: diffusion of ions from the bulk of the glass particle to the surface, and diffusion through the boundary layer (a static fluid layer surrounding the particle). After 1 h of immersion in the acid, the leaching reaction apparently reached equilibrium, no further diffusion occurred, and no further lengthening of working or initial setting time was noted. This may have been because of the cessation of leaching due to neutralisation of the acid or equilibrium with the solute, an increase in leaching inhibition by formation of a silica-rich surface layer, or statistical insufficiency to measure the effect. Given the discussion below, a combination of the first and last of these was most likely.

The concentration of leached ions in solution, in ideal systems, follows the standard equation derived for thin-film mass transfer in solid-liquid systems. The concentration c of the leachate in the solute as a function of time t is given [26] as:

$$c = c_s\left(1 - e^{-\left(\frac{k'A}{bV}\right)t}\right) \tag{1}$$

where A is the area of the solid-liquid interface, b the effective thickness of liquid surrounding the particles, c_s the concentration of the saturated solution in contact with the particles, V the volume of the reactor, and k' the diffusion coefficient. Equation (1) is derived from the rate of mass transfer (dM/dt) in the thin-film diffusion equation:

$$\frac{dM}{dt} = \frac{k'A(c_s - c)}{b} \tag{2}$$

In the system under consideration, both working and initial setting times were expected to be proportional to the ion concentration in the solute, because the rate of glass-ionomer reaction will be proportional to the availability of cross-linking ions. Hence both the working and initial setting times were expected to follow equations of this form:

$$x = (x_f - x_i)(1 - e^{-K_x t}) + x_i \tag{3}$$

where x is the working time of the mixed cement, x_f is the maximum working time (where the glass was leached to equilibrium), x_i is the working time with no leaching (non-zero for this system), K_x is the rate of leaching, and t is time. For initial setting time, the variable was called y. In order to fit the equation, it is evident that the derivative of equation (3) yields:

$$\frac{dx}{dt} = K_x(x_f - x_i)(e^{-K_x t}) \tag{4}$$

and

$$\ln\left(\frac{dx}{dt}\right) = \ln[K_x(x_f - x_i)] - K_x t \tag{5}$$

Hence a plot of $\ln(\Delta x/\Delta t)$ against t was expected to yield a straight line with gradient $-K_x$ and x-intercept $\ln[K_x(x_f - x_i)]$.

Table 4 Parameters of equation (3) derived for both working time and initial setting time

Working time		Initial setting time		
Parameter	Value	Parameter	Value	Unit
x_i	16.0	y_i	60.0	s
$x_f - x_i$	231.9	$y_f - y_i$	363.1	s
$\ln[K_x(x_f - x_i)]$	1.7656	$\ln[K_y(y_f - y_i)]$	2.2902	—
K_x	0.0252	K_y	0.0272	min^{-1}
R_x^2	0.94	R_y^2	0.93	—

Negative values of $(\Delta x/\Delta t)$ were removed by taking the mean over two points. Values for x_i and $x_f - x_i$ were set in order to pass through the points at $t = 0$ and $t = 125$. The results are presented in Table 4, along with the respective Pearson correlation coefficients R_x^2 and R_y^2. The data fit the model exceedingly well, and the model may be useful as the basis for further modifications to the leaching method.

An assumption in these equations is that the surface area of the particles remains unchanged. Rafferty *et al.* [18] demonstrated the dependence of surface area on acid surface treatment, but for the relatively weak acid concentrations involved in this study, the silica-rich, ion-depleted surface layer is likely to remain [21], ensuring a constant ion-diffusion area for the purposes of the model. The lack of further changes in working and initial setting times in this model after 65 min leaching is most likely due to approaching equilibrium with the acetic acid solution rather than complete depletion of ions in the glass, demonstrated by the continued ability of the glass to react with the glass-ionomer liquid. Also, the lack of statistically significant change in working or initial setting time with cements formed from glasses leached for over 65 min was most likely due to the standard deviations rather than lack of effect. Possible further investigations include re-leaching the glass to determine the limit of ion extraction, the use of alternative acids, accurate determination of the concentrations and species of leached ions in the filtrate, and an examination of particle size distribution and surface area as factors in surface treatment.

Compressive strength

The independence of the compressive strength on the leaching time indicated that the ion-depletion of the surface did not affect final cross-linking of the polyalkenoate matrix. It is likely that strontium ions, due to their greater availability, were preferentially leached from the surface, while the more significant network-forming aluminium remained. The series of articles by De Maeyer *et al.* [13, 14, 16] indicated that aluminium is the primary component contributing to strength of GICs; the continued strength of the cements in this study indicated that sufficient ions–including aluminium–remained to effect full cross-linking. The relatively low strengths in this study were the result of powder-liquid limitations, as demonstrated by Fleming *et al.* [27].

Conclusion

Ion leaching in acetic acid led to reduced reactivity of the glass-ionomer glass, and hence increased working and setting time of the cement. The effect is consistent with a thin-film diffusion model. The compressive strength of the cements was not significantly affected by leaching time, indicating that surface treatment of this type may be a useful reaction modifier.

Acknowledgments The authors wish to acknowledge the support of SDI Ltd (Melbourne, Australia) in the supply of materials and use of experimental equipment.

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