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The effect of storage in aqueous solutions on glass-ionomer and zinc polycarboxylate dental cements

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Cylindrical specimens (dimensions 6 mm diameter × 12 mm height) of glass-ionomer and of zinc polycarboxylate dental cement have been stored in aqueous solutions for periods of 24 h, 1 week and 1 month. The solutions were of varying composition and affinity for water, and storage in them resulted in fluctuations in mass of the cements, an effect which was attributed to differences in the partitioning of water between the solutions and the cement specimens. Unlike the zinc polycarboxylate, the glass-ionomer gained mass in most of the solutions examined (except Na_2SO_4), showing it to have a much greater affinity for water than the zinc polycarboxylate. Despite the fluctuations in water uptake by the glass-ionomer, and loss of water by the zinc polycarboxylate, no statistically significant differences in compressive strength were recorded in any solution at any storage time. This contrasts with results reported previously for zinc polycarboxylates using smaller specimens, showing that specimen size has an influence on the interaction of cements with storage solutions.

1. Introduction

Glass polyalkenoate and zinc polycarboxylate dental cements are superficially similar materials. Both belong to the class of materials known as acid-base reaction cements [1] and are prepared by reaction of a finely divided base with aqueous poly(acrylic acid) or related polymeric acid. In the case of the glass polyalkenoate (also known by the trivial name glass-ionomer [2]), the base is a calcium or strontium aluminosilicate glass [3], whereas in the case of the zinc polycarboxylate, the base is a deactivated zinc oxide powder [4]. Deactivation is achieved by mixing high purity zinc oxide with about 10% by mass of magnesium oxide, followed by heating. The effect of heating is to drive off a small amount of the oxygen, resulting in the non-stiochiometric oxide $ZnO_{(1-x)}$ where $x < 70$ ppm [5].

These cements each include water in their formulation. The poly(acrylic acid) is typically used as a solution at a concentration of about 45% by mass [1], though it may alternatively be employed as a dry powder, with the necessary amount of water being added to the cement at the mixing stage [6]. This water becomes fully incorporated into the cement as it sets, there being no phase separation. In the solid state, this water can occupy various locations, for example co-ordination sites around the Ca^{2+}, Zn^{2+} or Al^{3+} ions [7] or hydration regions around the polyanion chain [8]. Setting of the glass-ionomer yields a more complex matrix than the zinc polycarboxylate. The latter seems to consist entirely of zinc polyacrylate, where the former consists partly of calcium (or strontium) and aluminum polyacrylates, but also includes an inorganic silicate/phosphate network formed from ion-depleted species from the glass [9, 10].

These differences result in the two cements being very different in their behavior towards water. Zinc polycarboxylate can lose large amounts without adverse effect [11], showing that water is very labile and does not fulfil a structural role. In glass-ionomers, by contrast, water has a much more critical effect: loss of water can lead to cracking and crazing of the surface [12]. Under extremely desiccating conditions, the mechanical strength can drop severely [13]. As these cements age, so the proportion of loosely bound water decreases relative to the proportion of tightly bound water [14]. These states are defined arbitrarily by the case with which water can be removed from the cement, either at 105 °C or over a strong desiccant such as concentrated sulfuric acid, in each case under vacuum. Thus, as glass-ionomers age, so the state of combination of the water within them changes. Initially, too, they relate differently to water than zinc polycarboxylates, taking up water readily as part of the setting and early maturation processes [15] (i.e. those occurring over the first 24 h).

A recent study [16] has shown that glass-ionomer and zinc polycarboxylate cements develop their strength differently when stored in certain aqueous solutions designed to mimic aspects of saliva, namely 0.9% NaCl or 20 mmol lactic acid, compared with pure water. In particular, the zinc polycarboxylate showed very low strengths at 24 h in these solutions compared with water. By 1 week, the strengths in the solutions had changed, increasing to become not significantly different from the strength in pure water, which essentially remained unchanged over this period [16]. The origin of these effects was not clear, though there are likely to be differences in the way water is able to partition between a pure water storage medium and a cement compared with a solution and a cement.

The current study was undertaken in order to examine in more detail how variations in solution composition, and hence water partitioning, alter the mechanical properties of a glass-ionomer and a zinc polycarboxylate cement. Various storage solutions were used, including two selected on the basis of the known humidity they generate in a confined space. These were saturated equimolar mixtures of sodium chloride and potassium nitrate, which generates an atmosphere of 32% relative humidity at room temperature, and saturated sodium sulfate, which gives an atmosphere of 93% relative humidity [17]. These differences were assumed to indicate that the respective solutions have varying affinities for water, and by using such solutions as storage media, the cements would be exposed to aqueous media with differing relative hydrating tendencies.

2. Materials and Methods

A commercial glass-ionomer luting cement (AquaCem) and a zinc polycarboxylate (Poly F Plus, both Dentsply) were used. Both materials are water-activated, and were mixed at the manufacturer's recommended powder : water ratios, i.e. for AquaCem at 3.3 : 1.0; for Poly F Plus at 5.0 : 1.0. Mixing was carried out using a metal spatula on a ceramic tile, with each specimen being prepared individually.

Cylindrical specimens of size 12 mm height × 6 mm diameter were prepared by placing freshly mixed cement pastes in split metal molds of the appropriate size, and storing them at 37 °C for an hour. After this time, they were removed from the molds, weighed and placed in the appropriate aqueous solution in a screw-top bottle, and stored at 37 °C for varying lengths of time (24 h, 1 week or 1 month). Six sets of specimens were made for each solution/time combination. Details of the storage solutions employed are shown in Table I, with further details of the particular artificial saliva used in Table II.

After the required storage period, the cement specimens were re-weighed, then tested to failure using a Universal Testing Machine (Type EU 165, Howden, Leamington Spa, UK) operating at a crosshead speed of 1.0 mm/min. Changes in mass on storage as a percentage of orginal mass were calculated and strength values (in MPa) were calculated from the loads at failure.

Compresive strength and mass change data were analyzed by the Newman-Keuls comparison test in each case.

3. Results and Discussion

The results for change in mass with storage time and solution composition for the glass-ionomer cement are shown in Table III. In all solutions except saturated Na_2SO_4, there were similar effects of gradually increasing mass with storage, the change between 24 h

TABLE I Storage solutions employed

Solution	Solute	Grade and supplier	Concentration
Deionized water	None	—	—
Saline	NaCl	AnalaR (BDH)	0.9%
Artificial saliva	Various	See Table II	See Table II
Sodium sulfate	Na_2SO_4	AnalaR (BDH)	Saturated
Potassium nitrate /sodium chloride	$KNO_3/NaCl$	Specified Laboratory Reagent (Fisons)/AnalaR (BDH)	Saturated

TABLE II Composition of artificial saliva

Component	Grade and supplier	Concentration (g/l)
NaCl	AnalaR (BDH)	0.50
$NaHCO_3$	ACS Reagent (Aldrich)	4.20
$NaNO_2$	Specified Laboratory Reagent (Fisons)	0.03
KCl	AnalaR (BDH)	0.20

TABLE III Mean increases in mass for the glass-ionomer cement under different storage conditions and times (standard deviations in parentheses)

Time	24 h	1 week	1 month
Solution			
Water	1.77 (0.34)	3.48 (0.60)	3.03 (0.44)
Saline	1.04 (0.12)	1.78 (0.17)	2.99 (0.66)
Artificial saliva	2.04 (0.40)	2.02 (0.14)	3.08 (0.60)
Sat. Na_2SO_4	– 0.57 (0.40)	2.14 (0.33)	– 2.19 (0.60)
Sat. $KNO_3/NaCl$	2.67 (0.20)	3.66 (0.35)	4.11 (0.38)

and 1 month generally being significant to at least $p < 0.01$. In pure water and saturated $KNO_3/NaCl$, the change was greatest between 24 h and 1 week, and not significant between 1 week and 1 month. In saline, there was a gradual increase from 24 h to 1 month, with changes being significant between all groups ($p < 0.01$); in artificial saliva, the change between 1 week and 1 month was significant ($p < 0.01$). Finally, results in saturated Na_2SO_4 were anomalous, in that there appeared to be a net gain in mass at 1 week, but a net loss at 24 h and 1 month. The fact that the loss was greater at 1 month than 1 week ($p < 0.01$) suggests that there is a developing trend, and it may be that the samples at 1 week were dried insufficiently prior to being weighed.

The difficulties with the saturated Na_2SO_4 storage medium show that these results should be treated with caution. Nonetheless, there were trends apparent in the results. Regardless of the solution, most specimens had taken up more mass after 1 month than after 24 h, an effect which might be due either to take up of ions or of water, or both, from the storage solutions. The fact that there was a gain in saturated $KNO_3/NaCl$ was especially remarkable since this solution is known to be a relatively dehydrating solution from the fact that it can be used to generate a relative humidity of 32% in a confined space [17]. Only saturated Na_2SO_4 was capable of causing glass-ionomers to lose mass, presumably due to removal of water only, a finding that indicates that this solution is more hydrophilic than the setting cement. These results suggest that glass-ionomers have a high affinity for water, a feature that presumably arises from the existence within them of the ion-depleted siliceous phase [18, 19] which behaves like silica gel in taking up water from the surroundings.

Results for compressive strengths of glass-ionomers in these different storage media are shown in Table IV. There are no statistically significant differences between any of the storage times or solution compositions, showing that, despite the changes in composition, strength is unaffected.

Results for mass changes of the zinc polycarboxylate are shown in Table V. In pure water, specimens showed an insignificant gain in mass at all storage times, but in all other media, there were only losses. By contrast with the glass-ionomer, the zinc polycarboxylate appeared to lose water to the dehydrating storage solutions, there being some evidence of greater losses at longer storage times. The losses in the two saturated solutions were in the order expected, i.e. greater in the apparently more dehydrating saturated $KNO_3/NaCl$ than in saturated Na_2SO_4. There was some discoloration observed in the specimens stored in saturated $KNO_3/NaCl$, specimens turning orange from their original pale yellow. After compression testing, these specimens could be seen to be pale yellow inside, with the orange color as a surface layer whose thickness varied with age, i.e. was a thin shell in the specimens stored for 24 h, but was almost 1 mm deep in the specimens stored for 1 month. This confirms the earlier suggestion that changes caused by the storage solutions occur predominantly in the surface.

Table VI shows results for compressive strength of the zinc polycarboxylate. As for the glass-ionomer, there are no differences in strength with any combination of solution composition and storage time. The results for saline contrast with those recently reported by us, where we showed that zinc polycarboxylate cement stored in 0.9% NaCl was significantly weaker than when stored in water for 24 h[16]. However, the specimens in our previous study were smaller than those in the current one, i.e. were 6 mm high × 4 mm diameter cylinders, compared with the 12 mm × 6 mm of the present study. These results show that the effect of the different storage media are size-dependent, and taken together with the results for discoloration, suggest that the interiors of the cements are essentially unaffected by the surroundings, at least over the timescale of the current experiments. In the smaller

TABLE IV Compressive strength values (MPa) for glass-ionomer cement under different storage conditions and times (standard deviations in parentheses)

Time	24 h	1 week	1 month
Solution			
Water	99.2 (8.8)	117.4 (20.4)	103.2 (18.0)
Saline	91.6 (10.9)	115.0 (11.4)	125.0 (11.7)
Artificial saliva	107.9 (6.5)	98.7 (17.4)	103.3 (10.1)
Sat. Na_2SO_4	97.6 (18.9)	106.2 (27.0)	134.3 (29.0)
Sat. $KNO_3/NaCl$	109.1 (15.3)	95.6 (14.7)	95.7 (12.0)

TABLE V Mean increases in mass for the zinc polycarboxylate cement under different storage conditions and times (standard deviations in parentheses)

Time	24 h	1 week	1 month
Solution			
Water	0.08 (0.11)	0.23 (0.14)	0.06 (0.22)
Saline	− 0.83 (0.15)	− 0.59 (0.29)	− 0.77 (0.19)
Artificial saliva	− 0.05 (0.06)	− 0.85 (0.11)	− 0.35 (0.09)
Sat. Na_2SO_4	− 6.31 (0.61)	− 8.33 (0.20)	− 9.10 (0.49)
Sat. $KNO_3/NaCl$	− 8.28 (0.59)	− 9.92 (0.54)	− 9.50 (0.13)

TABLE VI Compressive strength values (MPa) for the zinc polycarboxylate cement under different storage conditions and times, (standard deviations in parentheses)

Time	24 h	1 week	1 month
Solution			
Water	86.3 (11.8)	68.8 (14.0)	84.3 (10.5)
Saline	84.5 (10.3)	96.1 (4.6)	83.0 (4.1)
Artificial saliva	81.2 (6.2)	80.7 (8.8)	82.2 (11.0)
Sat. Na_2SO_4	82.9 (11.9)	79.6 (14.5)	95.6 (14.6)
Sat. $KNO_3/NaCl$	77.4 (31.6)	86.1 (11.9)	106.5 (14.5)

specimens, by contrast, there was sufficient time for the variations in external water activity to be felt right through to the center.

4. Conclusions

Exposing specimens of glass-ionomer and zinc polycarboxylate cement to storage solutions of varying dehydrating capabilities has led to wide variations in specimen mass, but to no significant variations in compressive strength. The glass-ionomers were better able to resist dehydration by the storage solutions, particularly the saturated solutions of $KNO_3/NaCl$ or Na_2SO_4 than the zinc polycarboxylates, showing them to have greater affinity for water. The results were different from those reported previously, where at 24 h in 0.9%, the zinc polycarboxylate cements were much weaker than when stored in pure water and did not reach the compressive strength specified in the current ISO standard (70 MPa) [20]. Previous studies were carried out on smaller specimens, which suggests that time is necessary for the effects of varying the composition of storage solutions to be apparent throughout the specimens. This suggestion is supported by the observation that the discoloration of zinc polycarboxylates in saturated $KNO_3/NaCl$ is of restricted depth only, and leaves an unaffected core of cement, even after 1 month.

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