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The interaction of dental cements with aqueous solutions of varying pH

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A study is reported in which a series of dental cements of varying types (zinc phosphate, zinc polycarboxylate, glass-ionomer and resin-modified glass-ionomer) was exposed to aqueous solutions of differing pH for time intervals of a week, after which the pH of the storage solutions was determined. The results showed that all of the acid-base cements altered the pH of their storage solution, regardless of whether that initial solution was weakly acidic, weakly alkaline or close to neutral. All cements were found to act as buffers, because they not only increased the pH of the weakly acidic lactic acid solution, but they also decreased the pH of the weakly alkaline artificial saliva. In deionized water, the zinc polycarboxylate generally increased pH, while all other cements reduced it. In all cases, these results were shown to be repeatable on exposure to fresh-aqueous solutions of the appropriate pH for a further week, such experiments being carried out for up to six weeks. In terms of mass change, in most solutions, there was a modest increase during the first week, after which the mass remained steady. In lactic acid, zinc phosphate and zinc polycarboxylate cements showed a gradual reduction in mass throughout the six weeks, whereas the glass-ionomers showed an initial increase, followed by a much slower decrease in mass. These results confirm that glass-ionomers are the most resistant of the cements towards acid erosion.

1. Introduction

The cements used in dentistry fall into the class of acid-base cements [1]. They are formed by reaction of aqueous acids (typically phosphoric or polyacrylic) with powdered solid bases, either deactivated zinc oxide or special degradable glasses. Reaction occurs fairly rapidly after mixing, though not as rapidly as conventional neutralization reactions that take place entirely in the aqueous phase. These cements harden, without separation of water, to give solid masses of good hardness and high compressive strength [1]. There are a number of types, depending on the starting materials, as illustrated in Table I; one of them, the resin-modified glass-ionomers, have monomers included within their formulation [2], which allows the neutralization mode of setting to be supplemented by a polymerization reaction. However, regardless of type, all share similar structures. They consist of a continuous matrix formed predominantly by neutralization, together with unreacted filler, the latter acting as reinforcement for the overall structure [1].

These cements have a wide variety of uses in clinical dentistry, including as liners and bases, luting both ceramic and metal crowns, and the bonding of orthodontic appliances [3]. In general, their fitness for purpose is assessed by their mechanical properties once set, and also through the speed of their setting reaction. However, glass-ionomers, including their resin-modified counterparts, also have the important physico-chemical property once set of releasing fluoride [4, 5], a phenomenon that probably acts to prevent the occurrence of secondary caries [6, 7].

Recently, a detailed study has been reported of an additional chemical effect that may be of clinical significance, namely that these cements influence the pH of the solutions in which they are stored [8]. The study employed lactic acid at a concentration of 20 mmol dm^{-3}, the same as that used in the current standard erosion test [9], and cements were shown to increase the pH of this medium over a week from 2.60 to between 4.50 and 5.90, depending on the type of cement. All cements displayed this effect, and did so without being dissolved or otherwise seriously degraded in the process. Unlike the zinc phosphate or zinc polycarboxylate cements, the glass-ionomers all increased in mass, though to only modest extents and the full significance of this observation was not clear [8].

The possible clinical benefit of this effect arises from the fact that the pH of active caries is of the order of

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TABLE I Examples of cement used in dentistry

Base	Acid	Type
Zinc oxide (deactivated)	Phosphoric	Zinc phosphate
Zinc oxide (deactivated)	Poly(acrylic)	Zinc polycarboxylate
Glass	Poly(acrylic)	Glass-ionomer
Glass	Poly(acrylic) + monomer (e.g. HEMA)	Resin-modified glass-ionomer

TABLE II Cements employed in the study

Brand name	Manufacturer	Type
Poly F Plus	Dentsply, Germany	Zinc polycarboxylate
Aqua Cem	Dentsply, Germany	Glass-ionomer
Chelonfil	ESPE, Germany	Glass-ionomer
Vitremer luting	3M Dental, USA	Resin-modified glass-ionomer
Kent Dental Zinc Phosphate	Kent Dental, UK	Zinc phosphate

4.9 and is arrested by being increased to just 5.6 [10, 11]. It might follow, therefore, that dental cements can confer some local protection against secondary caries when placed in a tooth. This property might be especially beneficial in glass-ionomer cements, which are known to have generally good resistance to erosion, because it would complement their property of fluoride release.

There is much to explore concerning the ability of dental cements of all types to alter the pH of solutions with which they are in contact. The current paper reports a study of one aspect of this phenomenon, namely the influence of cements on solutions of varying pH, both acid and alkaline. The question of the repeatability of the change in pH has also been addressed, by replenishing solutions at weekly intervals, and measuring the change in pH over the following week. This was done for specimens for up to six weeks.

2. Experimental procedure

The following types of cement were used in this study: zinc phosphate, zinc polycarboxylate, glass-ionomer (two brands) and resin-modified glass-ionomer. Full details appear in Table II.

Cements were mixed on a ceramic tile using a metal spatula at the powder–liquid ratios recommended by the manufacturers. They were then packed into cylindrical metal moulds of internal dimensions 6 mm diameter by 12 mm height, and allowed to set for 1 h at 37 °C. They were then removed from the mould, weighed and placed in 8.0 ml of the appropriate solution in an individually labelled standard glass vial. The solutions employed were: lactic acid at 20 mmol dm^{-3}, deionized water, 0.9% NaCl solution (i.e. 0.9 g of NaCl, Anala R grade, ex. BDH, Poole, made up to 100 cm^3 with deionized water), and an artificial saliva [12], the composition of which is shown in Table III.

After one week of storage at room temperature they were removed from the solution, dried with a laboratory tissue, and reweighed. The pH of the solution was then recorded using a digital pH meter (type PHA, Whatman), after which the solution was discarded, and replaced by a fresh 8.0 ml volume, into which the specimen was placed for further storage. This was repeated at intervals of one week for six weeks, when the experiment was terminated. The uncertainty in the measurement of pH was estimated to be 0.02 units.

For each solution, duplicate specimens were tested and, in addition, control solutions were maintained, which comprised identical solutions to those used to store the individual specimens, 8.0 ml of which was placed in glass vials of the same type as used for storage of the cements. For the control, the mean pH based on the individual values measured at weekly intervals was determined. For the specimens, the means of the pH values for the pair at each weekly interval were determined.

TABLE III Composition of artificial saliva

Component	Concentration (g l^{-1})
NaCl	0.50
$NaHCO_3$	4.20
$NaNO_2$	0.03
KCl	0.20

Experimental data were analysed for statistical significance using two-way ANOVA and the Student's t-test as appropriate.

3. Results

The solutions employed ranged from acidic (lactic acid, 20 mmol dm^{-3}; pH 2.70) to alkaline (artificial saliva, pH 8.43), with two being close to neutrality (deionized water, pH 6.31; 0.9% NaCl, pH 6.64). The pH values of the different solutions following storage of cements for one week for cements aged up to six weeks are shown in Tables IV–VII, and the specimen masses at the same time intervals are shown in Tables VIII–XI.

In all cases, the mean pHs of the solutions in which the cements had been stored were different by amounts that were significant to at least $p < 0.05$. For storage in lactic acid solution (Table IV), all cements showed the ability to neutralize the storage solution repeatedly to some extent; for zinc phosphate and zinc polycarboxylate, there were no statistically significant differences in the extent to which pH was changed. By contrast, for the glass-ionomers, the change in Week 1 was larger than for all subsequent weeks (significant to at least $p < 0.01$), though the differences in subsequent weeks were not significant. All cements showed a steady decline in mass from Week 1 onwards (Table VIII), though this was not statistically significant for either Chelonfil or Vitremer luting. At one week, both zinc phosphate and zinc polycarboxylate showed a decline in mass compared with the initial value, whereas the glass-ionomers all showed an increase in mass.

TABLE IV Values of pH after one week in 20 mmol dm^{-3} lactic acid solution at pH = 2.70, standard deviation 0.10 (duplicate readings; standard deviations in parentheses)

Material	Age (weeks)					
	1	2	3	4	5	6
Poly F Plus	5.25	4.95	5.04	4.94	5.35	4.98
	(0.00)	(0.03)	(0.01)	(0.22)	(0.03)	(0.12)
AquaCem	4.09	3.45	3.35	3.27	3.20	3.02
	(0.05)	(0.04)	(0.03)	(0.02)	(0.02)	(0.01)
Chelonfil	3.76	3.43	3.41	3.31	3.28	3.14
	(0.11)	(0.04)	(0.04)	(0.01)	(0.04)	(0.05)
Vitremer	3.70	3.26	3.18	3.15	3.13	3.10
	(0.05)	(0.04)	(0.06)	(0.04)	(0.03)	(0.03)
Zinc Phosphate	4.74	4.61	4.73	4.54	4.76	4.58
	(0.27)	(0.12)	(0.11)	(0.09)	(0.10)	(0.11)

TABLE V Values of pH after one week in deionized water at pH = 6.31, standard deviation (duplicate readings; standard deviations in parentheses)

Material	Age (weeks)					
	1	2	3	4	5	6
Poly F Plus	6.66	6.55	6.71	6.57	6.42	6.68
	(0.06)	(0.04)	(0.00)	(0.06)	(0.03)	(0.07)
AquaCem	6.09	6.10	6.17	6.17	5.99	6.25
	(0.01)	(0.02)	(0.04)	(0.01)	(0.01)	(0.02)
Chelonfil	6.00	6.03	6.05	6.10	5.93	6.06
	(0.00)	(0.02)	(0.16)	(0.10)	(0.01)	(0.08)
Vitremer	5.65	5.55	5.57	5.59	5.52	5.65
	(0.01)	(0.03)	(0.01)	(0.03)	(0.05)	(0.04)
Zinc Phosphate	6.41	6.13	6.24	6.10	5.98	6.10
	(0.08)	(0.02)	(0.01)	(0.33)	(0.14)	(0.19)

TABLE VI Values of pH after one week in 0.9% NaCl solution at pH = 6.64, standard deviation 0.32 (duplicate readings; standard deviations in parentheses)

Material	Age (weeks)					
	1	2	3	4	5	6
Poly F Plus	7.28	7.24	6.55	6.56	6.82	7.03
	(0.15)	(0.03)	(0.09)	(0.19)	(0.02)	(0.00)
AquaCem	5.80	5.74	5.19	5.45	5.72	5.69
	(0.01)	(0.02)	(0.03)	(0.00)	(0.02)	(0.01)
Chelonfil	5.97	6.00	5.66	5.60	5.85	5.85
	(0.02)	(0.02)	(0.01)	(0.01)	(0.02)	(0.03)
Vitremer	5.93	5.68	5.19	5.40	5.67	5.62
	(0.05)	(0.05)	(0.00)	(0.01)	(0.02)	(0.04)
Zinc Phosphate	6.43	6.55	5.94	5.83	6.12	6.46
	(0.16)	(0.11)	(0.14)	(0.12)	(0.13)	(0.13)

TABLE VII Values of pH after one week in artificial saliva at pH = 8.43, standard deviation 0.18 (duplicate readings; standard deviations in parentheses)

Material	Age (weeks)					
	1	2	3	4	5	6
Poly F Plus	8.15	8.11	7.73	8.00	8.13	8.10
	(0.08)	(0.10)	(0.14)	(0.13)	(0.11)	(0.08)
AquaCem	6.65	6.87	6.72	6.92	6.83	7.23
	(0.02)	(0.08)	(0.08)	(0.04)	(0.04)	(0.05)
Chelonfil	7.74	7.80	7.69	7.72	7.90	7.93
	(0.05)	(0.06)	(0.04)	(0.08)	(0.06)	(0.02)
Vitremer	7.14	7.17	6.99	7.20	7.29	7.34
	(0.01)	(0.00)	(0.03)	(0.01)	(0.14)	(0.09)
Zinc Phosphate	7.75	7.84	7.86	7.89	8.03	8.03
	(0.22)	(0.11)	(0.02)	(0.04)	(0.04)	(0.07)

TABLE VIII Values of mass as percentage of original after one week in 20 mmol dm^{-3} lactic acid solution at pH = 2.70, standard deviation 0.10 (duplicate readings; standard deviations in parentheses)

Material	Age (weeks)					
	1	2	3	4	5	6
Poly F Plus	99.99	99.58	99.05	98.53	98.13	97.73
	(0.01)	(0.01)	(0.01)	(0.01)	(0.03)	(0.00)
AquaCem	101.26	101.05	100.64	100.21	99.93	99.71
	(1.16)	(1.00)	(0.75)	(0.91)	(0.92)	(0.97)
Chelonfil	100.60	100.36	99.99	99.61	99.31	99.06
	(0.10)	(0.12)	(0.21)	(0.10)	(0.06)	(0.01)
Vitremer	102.26	101.96	101.46	101.03	100.75	100.42
	(1.03)	(1.20)	(1.23)	(1.15)	(1.10)	(1.10)
Zinc Phosphate	99.45	98.94	98.24	97.67	97.12	96.59
	(0.02)	(0.16)	(0.08)	(0.22)	(0.13)	(0.28)

TABLE IX Values of mass as a percentage of the original after one week in deionized water at pH = 6.31, standard deviation 0.9 (duplicate readings; standard deviations in parentheses)

Material	Age (weeks)					
	1	2	3	4	5	6
Poly F Plus	100.19	100.13	100.10	100.17	100.11	100.18
	(0.21)	(0.21)	(0.21)	(0.32)	(0.21)	(0.25)
AquaCem	101.46	101.51	101.33	101.60	101.77	101.71
	(0.15)	(0.25)	(0.01)	(0.01)	(0.22)	(0.23)
Chelonfil	101.11	101.20	101.23	101.39	101.38	101.43
	(0.26)	(0.29)	(0.34)	(0.35)	(0.47)	(0.37)
Vitremer	101.98	102.05	102.17	102.31	102.26	102.43
	(0.19)	(0.08)	(0.12)	(0.25)	(0.18)	(0.04)
Zinc Phosphate	100.24	100.22	100.13	100.25	100.11	100.15
	(0.03)	(0.09)	(0.02)	(0.07)	(0.04)	(0.04)

For storage in water (Table V), the zinc polycarboxylate raised the pH to a mean value of 6.60, which was a slight but statistically significant ($p < 0.001$) increase compared with the mean of 6.31 (standard deviation, SD = 0.09) for the control. By contrast all of the glass-ionomer cements reduced pH slightly, again by amounts that were small but statistically significant (at least $p < 0.01$); the zinc phosphate did not alter the pH of deionized water by an amount that was statistically significant. All cements made a modest gain in mass during the first week of storage (Table IX), as has been shown previously for glass-ionomers [13], but thereafter did not change by an amount that was significant. For AquaCem, the change in mass in water was not significantly different from that in lactic acid, which contrasts with previous findings [4] that showed that there was a gain in mass in lactic acid that was significant to $p < 0.05$. This is

TABLE X Values of mass as a percentage of the original after one week in 0.9% NaCl solution at pH = 6.64, standard deviation 0.32 (duplicate readings; standard deviations in parentheses)

Material	Age (weeks)					
	1	2	3	4	5	6
Poly F Plus	100.21	100.11	100.16	100.08	100.16	100.21
	(0.00)	(0.08)	(0.01)	(0.07)	(0.03)	(0.03)
AquaCem	102.28	102.13	102.28	102.58	102.57	102.59
	(0.01)	(0.04)	(0.09)	(0.01)	(0.11)	(0.13)
Chelonfil	100.98	100.82	101.01	101.09	101.04	101.17
	(0.44)	(0.34)	(0.53)	(0.37)	(0.46)	(0.43)
Vitremer	102.42	102.48	102.59	102.79	102.70	102.89
	(0.28)	(0.13)	(0.41)	(0.35)	(0.25)	(0.27)
Zinc Phosphate	100.26	100.23	100.15	100.18	100.28	100.29
	(0.06)	(0.07)	(0.17)	(0.01)	(0.03)	(0.09)

TABLE XI Values of mass as a percentage of the original after one week in artificial saliva at pH = 8.43, standard deviation 0.18 (duplicate readings; standard deviations in parentheses)

Material	Age (weeks)					
	1	2	3	4	5	6
Poly F Plus	100.20	100.17	100.12	100.14	100.28	100.26
	(0.01)	(0.02)	(0.04)	(0.11)	(0.06)	(0.06)
AquaCem	102.85	102.30	102.88	102.72	102.79	102.79
	(0.09)	(0.42)	(0.13)	(0.59)	(0.38)	(0.49)
Chelonfil	101.18	101.19	100.99	101.16	101.18	101.29
	(0.66)	(0.65)	(0.50)	(0.35)	(0.27)	(0.42)
Vitremer	102.97	103.04	103.64	103.48	103.61	103.45
	(0.25)	(0.20)	(0.05)	(0.29)	(0.14)	(0.37)
Zinc Phosphate	100.18	100.16	100.17	100.15	100.18	100.16
	(0.01)	(0.04)	(0.00)	(0.01)	(0.01)	(0.00)

probably a reflection of the smaller number of specimens employed in the current study than in the previous one.

Results for storage in 0.9% NaCl were similar to those for storage in deionized water (Table VI): zinc polycarboxylate increased the pH, whereas the other cements reduced it. The decreases brought about by zinc phosphate, by contrast with the results for deionized water, were significant to $p < 0.001$. These decreases were also less than those for the glass-ionomers. The differences between pH values at different time intervals were not statistically significant, nor were the changes in mass in Weeks 1–6 though, again, all cements increased in mass during the first week (Table X).

Cements stored in artificial saliva, which is mildly alkaline, reduced the pH, with the glass-ionomers being more effective than either the zinc phosphate or the zinc polycarboxylate (Table VII). All cements gained mass during the first week (Table XI), but thereafter none of the changes were significant.

4. Discussion

The most striking finding from this study is that all of the cements employed altered the pH of the solution in which they were stored, and this effect was repeatable on exposure to fresh solution of the original pH, at least up to six weeks. Results for storage in lactic acid are different from those in other solutions, in that the medium had an erosive effect on the cements. This was apparent immediately for zinc phosphate and zinc polycarboxylate, but was not apparent until after the first week for glass-ionomers, because they showed an initial increase in mass over this period. Also, for glass-ionomers, there was a greater change in pH in this first week than in all subsequent weeks. In all other solvent systems, cements showed a modest gain in mass, but by Week 1 had reached a steady state, so that in subsequent weeks the mass did not alter despite the repeated interaction of the cement with fresh aqueous solution.

Zinc polycarboxylate behaved differently from other cements, tending to increase pH in solutions close to neutral, as has been reported previously [14]. In fact, neither the deionized water nor the 0.9% NaCl solution was actually at pH 7, due to the well known equilibrium set up by carbon dioxide from the air with water, which can be written

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$$

The acid dissociation constant, K_a, for this carbonic acid system is 4.5×10^{-7} [15]. Hence only fairly small amounts of carbon dioxide need to dissolve in water to give the kind of pH values recorded in the present work.

The zinc polycarboxylate cement interacted with deionized water to raise the pH by a mean of 0.27 units, but with 0.9% NaCl to reduce pH by a mean of 0.35 units. The remaining cements, by contrast, all reduced the pH slightly in both of these solutions. This result was surprising because all of the cements contained an excess of basic filler, so all might have been expected to behave like zinc polycarboxylate in deionized water, and raise the pH of their storage solutions. This is certainly what occurs in lactic acid but not, as is observed, in dilute carbonic acid. It does not happen, either, for zinc polycarboxylate in 0.9% NaCl solution, though the reason for this difference in behaviour between the solutions is not clear.

Instead, it appears that, at low levels, acids are leached from these cements. This mechanism is certainly plausible for glass-ionomers, which are known to retain a small proportion of unreacted acid within their structure [16], a feature that contrasts with the behaviour of zinc polycarboxylates [17]. Consequently, assuming these cements remain sufficiently permeable to aqueous solutions, they will retain the capability of slightly acidifying those solutions. The reservoir of unreacted acid is obviously limited, so this effect is likely to become exhausted after a certain time.

The ability to reduce the pH of storage solutions was shown by all cements when exposed to the mildly alkaline artificial saliva. In this solution, the alkalinity arises due to the presence of the sodium hydrogen carbonate. While all cements tended to neutralize this solution to some extent, the glass-ionomers were considerably more effective than the zinc polycarboxylate. All of these cements, but especially the glass-ionomers, may therefore be considered buffers, raising the pH of acidic solutions and reducing the pH of alkaline ones. However, this effect is not extendable to highly alkaline solutions, because strong alkalis are known to destroy cements. For example, 3% aqueous potassium hydroxide has been used to dissolve glass-ionomer cements prior to analysis [18].

The effect of these cements in being able to change the pH of their storage medium repeatedly on exposure to fresh solution was not found to make any measurable difference to the mass of the specimens. Presumably the change in pH is brought about by chemical reaction with some component of the cement, following which a change in mass would be expected, either up or down, depending on whether or not the product is insoluble in the storage medium. The absence of such changes presumably indicates that there are compensating changes in water balance within the cement. Whatever the reaction that led to these pH changes, no effect was apparent on the mass of the cements.

The cements behaved differently in lactic acid. Glass-ionomers were found to be less effective at neutralizing this solution that zinc phosphate or zinc polycarboxylate, although they showed an initial gain in mass, rather than a loss, and the gradual loss that did occur was less severe than in the other cements. Lactic acid at a concentration of 20 mmol dm^{-3} is used in the impinging jet acid erosion test for water-based dental cements [9]. In this test, cements are exposed to an erosive stream of acid solution at a constant pressure until at least 0.02 mm of the surface of the specimens has been removed. Glass-ionomers have been found to be significantly more resistant to erosion in this test than either zinc phosphate or zinc polycarboxylates [19], a result confirmed by *in vivo* studies [20] and that parallels the findings in the present study.

In zinc polycarboxylates, erosion has been found to take place predominantly at the site of the filler [21], though it does also occur within the matrix [14]. A similar effect would be expected for glass-ionomers, though its structure is probably less permeable than that of zinc polycarboxylates, due to the secondary setting reactions involving inorganic species formed by breakdown of the glass [22, 23], hence the erosion processes occur less readily.

Resin-modified glass-ionomers have previously been shown to swell in water and other aqueous solutions [24, 25], but to extents that vary depending on the nature of the solutes present [26, 27]. In the present study, the resin-modified glass-ionomer (Vitremer luting) showed a steady gain in mass when stored in water and in 0.9% NaCl solution, but not (to a statistically significant extent) in artificial saliva. In lactic acid, by contrast, it showed a steady reduction in mass after Week 1, whereas in the first week it, too, showed an initial increase in mass.

5. Conclusions

The results reported here show that all types of the acid-base cements considered alter the pH of their storage solution. This change occurs regardless of whether that initial solution is weakly acidic, weakly alkaline or almost neutral. Except in lactic acid, these changes were not associated with detectable changes in mass of the cement specimens, suggesting that there are subtle balances maintained between soluble or insoluble reaction products and the degree of hydration of the cement. What is clear is that these pH changes can be repeated with fresh solutions at least up to six weeks.

The behaviour of the zinc polycarboxylate in deionized water generally differed from that of the other cements because it increased the pH, whereas all other cements reduced pH. Lactic acid caused different types of behaviour compared with other aqueous solutions; both zinc phosphate and zinc polycarboxylate increased the pH in this medium considerably more than the glass-ionomers, but began to lose mass from the start of their exposure to the acid. The glass-ionomer cements, by contrast, showed an initial gain in mass, with a subsequent slower reduction in mass. These results parallel previous findings for the behaviour of these cements in the lactic acid impinging jet erosion test. This resistance of glass-ionomers to erosion suggests that they might survive for much longer in the mouth in exposed locations than zinc phosphate or zinc polycarboxylate cements. They might thus be able to influence the local pH for some considerable time following placement.

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