JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **10** (1999) 449–452

The long-term interaction of dental cements with lactic acid solutions

J. W. NICHOLSON
Dental Biomaterials Department, King's Dental Institute, Caldecot Road, London, SE5 9RW, UK

B. CZARNECKA, H. LIMANOWSKA-SHAW
Department of Experimental Dentistry, Karol Marcinkowski University of Medical Sciences, Poznan, Poland

A study of the interaction of dental cements with lactic acid solutions has been carried out in which individual cement specimens were repeatedly exposed to 20 mmol dm^{-3} lactic acid for periods of a week. After each week of storage, the mass of the specimens was recorded and the pH of the solution determined. The glass-ionomers showed an initial increase in mass, followed by a decline that became steady from 6 weeks. Zinc polycarboxylate and zinc phosphate cements, by contrast, showed no early gain in mass, but eroded steadily more or less from the start of their exposure to lactic acid. For all cements, acid erosion followed linear kinetics, at rates ranging from 0.5%/week for the zinc phosphate to 0.28%/week for one of the glass-ionomers, Chelonfil (ESPE, Germany). At the end of six months, the zinc phosphate had lost 14.2% of its initial mass, the zinc polycarboxylate 9.9% and the glass-ionomers between 6.2 and 7.2%.

Erosion was accompanied on every occasion by neutralization of the acid solution. Both erosion and neutralization continued steadily throughout the experiment. The effectiveness of neutralization was in the following order: zinc polycarboxylate > zinc phosphate > glass-ionomer. The pH change in Week 1 was much greater for the glass-ionomers and the zinc polycarboxylate than in all subsequent weeks.

1. Introduction

Acid–base cements are widely used in clinical dentistry [1]. Although the varying types differ in their chemical composition, they all have essentially similar structures when set. They consist of: (i) a continuous matrix formed predominantly by a neutralization reaction between the base and an aqueous acid solution; and (ii) reinforcing filler, comprising that fraction of the base left unreacted following the setting reaction [1]. The acid–base nature of the various dental cements means that they are able to influence the pH of solutions in which they are stored [2–4]. For example, in a recent study, they have been shown to alter the pH of a lactic acid solution in which they were stored towards neutral [2]. The solution employed was at a concentration of 20 mmol dm^{-3}, i.e. the same as that used in the current standard erosion test [5] and the cements increased the pH over one week from 2.60 to between 4.50 and 5.90, depending on cement type [2]. This change in pH was not accompanied by any serious degradation. In fact, unlike the zinc phosphate or zinc polycarboxylate cements, the glass-ionomers all increased in mass over the week, due to the absorption of water, an effect that has been found to be independent of the inital pH of the solution [6].

It has been suggested that this buffering effect may be beneficial under clinical conditions [2]. The pH of active caries is of the order of 4.9 and is arrested by being increased to just 5.6 [7, 8]. Therefore the ability of cements to increase local pH might confer some protection against secondary caries. This could be especially beneficial in glass-ionomer cements, since it would complement their fluoride release.

In the current paper, we report results of a long-term study of the neutralization effect. By repeatedly exposing specimens to fresh lactic acid for a period of 6 months, we have determined the extent to which cements retain the ability to buffer the pH of their storage solution. We have also recorded the mass of the specimens at weekly intervals and determined rates of erosive loss in each cement.

2. Materials and methods

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

Duplicate specimens of each cement were prepared by

Author for correspondence: Dr J.W. Nicholson. E-mail: john.nicholson@kcl.ac.uk.

TABLE I Brand names and types of dental cement employed

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

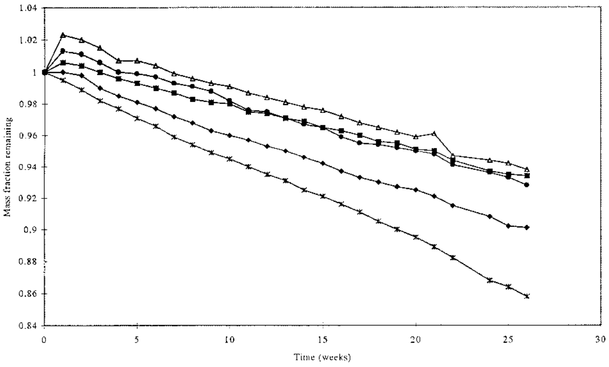

Figure 1 Graph of specimen mass against time for the storage of dental cements in lactic acid solution. Zinc polycarboxylate; glass-ionomer (Chelonfil); glass-ionomer (AquaCem); glass-ionomer (Vitremer luting); zinc phosphate.

TABLE II Mass change data for cements

Cement	Initial mass gain (%)	Net mass loss at 6 months (%)	Steady state erosion rate (%/week)
Zinc polycarboxylate	–	9.9	0.39
Glass-ionomer (AquaCem)	1.3	7.2	0.35
Glass-ionomer (Chelonfil)	0.6	6.6	0.28
Resin-modified glass-ionomer	2.3	6.2	0.33
Zinc phosphate	–	14.2	0.52

TABLE III Solution pH following storage of cements

Cement	pH at week 1	Mean pH (weeks 2–26 inclusive); [SD]
Zinc polycarboxylate	5.28	4.76 [0.27]
Glass-ionomer (AquaCem)	4.11	3.18 [0.17]
Glass-ionomer (Chelonfil)	3.78	3.22 [0.15]
Resin-modified glass-ionomer	3.73	3.16 [0.16]
Zinc phosphate	4.77	4.59 [0.19]

Mean pH of control solution: 2.65, SD 0.16.

mixing the components on a ceramic tile using a metal spatula at the powder/liquid ratios recommended by the manufacturers. The resulting pastes were packed into cylindrical metal molds of internal dimensions 6 mm diameter by 12 mm height, and allowed to set for 1 h at 37 °C. After this, they were removed from the mold, weighed, and placed in 8.0 ml of the appropriate solution in an individual glass vial. The solution employed was lactic acid at 20 mmol dm^{-3}, a solution which has a pH of approximately 2.7.

After 1 week of storage at room temperature the specimens 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 1 week for 26 weeks, when the experiment was terminated. The uncertainty in the measurement of pH was estimated to be 0.02 units.

In addition to the storage of specimens in lactic acid solution, a control solution was maintained, which comprised an 8.0 ml aliquot of the identical lactic acid solution stored in a glass vial. The pH of this control solution was measured after 1 week, and a fresh aliquot of aqueous lactic acid was taken, to act as the control solution for the next week.

Experimental data were analyzed for statistical significance using 2-way ANOVA and Student's *t*-test as appropriate.

3. Results

Changes in mass with time for all of the cements are shown in Fig. 1, with additional data given in Table II. All three glass-ionomer cements showed an initial increase in mass, followed by a gradual decrease. From approximately week 6 until the experiment was terminated at the end of week 26, their mass declined linearly at rates ranging from 0.28 to 0.35%/week depending on type.

The zinc phosphate and zinc polycarboxylate cements showed no increase in mass. The zinc polycarboxylate took two weeks before any reduction in mass was observed, and steady, linear mass loss did not begin until week 3. By contrast, the zinc phosphate showed a steady decline in mass from week 1. The steady state rates of erosion for zinc polycarboxylate and zinc phosphate were 0.39 and 0.52%/week respectively, the figure for the zinc phosphate being the highest recorded in the present work.

For all cements except the zinc phosphate, the change in pH during the first week was much higher than in all succeeding weeks, as shown in Table III. For this reason, the mean pH change determined is for weeks 2 to 26, rather than for the entire storage period. There were slight variations in the values of pH recorded, possibly due to small changes in temperature within the laboratory. For the control solutions, the mean pH was 2.65 (standard deviation: 0.16), which compares satisfactorily with the pH value for 20 mmol dm^{-3} lactic acid quoted in the current ISO standard, i.e. 2.7 ± 0.1 [5].

The values of pH change for the glass-ionomers did not differ from each other to any statistically significant extent. By contrast, the values for both the zinc polycarboxylate and the zinc phosphate were significantly greater ($P < 0.001$) than the glass-ionomers. Although the difference between zinc polycarboxylate and zinc phosphate was only 0.19 pH units, this was also significant, to at least $P < 0.02$.

4. Discussion

The data presented here confirm that when acid–base cements are exposed to lactic acid solution, they increase the pH of the solution and lose mass. For the glass-ionomers, there was an initial gain, due to their well-established property of taking up water from their surroundings. This is probably caused by the formation of a small amount of hygroscopic silica phase within the cement [9–11], the fully hydrated structure that results contributing to the final strength of the cement [12]. Once the silica phase is formed, glass-ionomers begin to lose mass as they are eroded by the lactic acid solution.

Our results show that the rate at which glass-ionomers erode is lower than for zinc polycarboxylate or zinc phosphate cements under the same conditions. This is in agreement with previous results using the impinging jet erosion test [13], where erosion is determined by measuring the surface loss of specimens mounted in cylindrical metal holders [14]. The fact that glass-ionomers show greater resistance, when the zinc cements are based on much stronger metal chelates, has attracted surprisingly little comment. It is, in fact, likely to be an effect of the formation of the secondary matrix within glass-ionomers based on silicate/phosphate species generated by reaction of the ion-depleted glass [9].

All cements except the zinc phosphate showed a much greater change in pH in week 1 than in all subsequent weeks. This suggests that there is an extra neutralizing effect in this first week compared with the other weeks. One possible explanation is that erosion occurs mainly by attack at the matrix, as has been demonstrated previously in the case of the zinc polycarboxylate cement [3]. However, in freshly prepared cements, some filler may be close enough to the surface to be available for attack by the acid. Hence, in the first week, there would be enhanced neutralization; at the same time, this available fraction of filler would be reacted away. Following this, with most of the filler protected by the matrix from further acid attack, erosion would become more focused on the matrix. Clearly, as matrix erodes away, so some additional filler becomes available for reaction, but the balance remains shifted towards erosion of the matrix once the initial exposure to acid is over.

The relationship between erosion and change in pH of the acid solution varies according to the type of cement, and the effects are not simply correlated. Nonetheless, our results show that they are linked and that steady loss by erosion is parallelled by steady and repeatable changes in solution pH. Thus, neutralization of the acid can be seen to yield soluble products that dissolve in the storage solution. This suggests that the possible clinical benefits of the neutralization will gradually diminish as the cement is eroded away. To date, erosion of cements has been seen as a wholly undesirable property, but our results suggest that this is not the case. Some local neutralization, leading to relatively slight changes in pH may be clinically beneficial and assist in arresting caries. The current practise of formulating cements to have maximum resistance to erosion may therefore not be the best clinical option. Further work is needed to show what extent of *in situ* neutralization by cements is desirable in order that the phenomenon can be fully exploited to the benefit of patients.

5. Conclusion

Acid erosion of dental cements has been shown to follow linear kinetics over a 6 month exposure time, though in the case of glass-ionomers, there was an initial gain in mass, due to absorption of water. This counteracts erosive loss in the first 2 or 3 weeks, but after six weeks, erosive loss predominated. Zinc polycarboxylate and zinc phosphate showed no early gain in mass, but instead eroded steadily for almost all of their time of exposure to lactic acid solution. Zinc phosphate showed the highest erosion rate (0.52%/week) of all the cements studied, whereas one of the glass-ionomers, Chelonfil, showed the lowest (0.28%/week). At the end of 6 months, the zinc phosphate had lost 14.2% of its initial mass, approximately twice the net loss of the glass-ionomers.

Erosion was accompanied in every case by neutralization of the acid, and both erosion and neutralization were continuing steadily after six months, at which point the experiments were ended. The greatest degree of neutralization was exhibited by the zinc polycarboxylate cement, and the least by the glass-ionomers, between which there were negligible differences. For the glass-ionomers and the zinc polycarboxylate, the pH change in week 1 was much greater than in all subsequent weeks. From this, it is concluded that the balance between the neutralization processes is different in this initial period from that in the subsequent ones.

Finally, because erosive loss is linked with neutralization, we conclude that some erosion is desirable, since it provides a mechanism that may inhibit secondary caries.

Acknowledgments

We thank the British Council for financial support for our collaboration, and Professor J.G. Shaw (Poznan, Poland) for helpful comments on earlier drafts of the current paper.

References

1. A. D. WILSON and J. W. NICHOLSON, ''Acid–base cements'', (The University Press, Cambridge, 1993).
2. J. W. NICHOLSON, B. CZARNECKA and H. LIMANOWSKA-SHAW, *Biomaterials* **20** (1999) 155.
3. S. MATSUYA, M. KODA, Y. MATSUYA, Y. YAMAMOTO and M. YAMANE, *Dent. Mater. J.* **2** (1983) 76.
4. K. YOSHIDA, M. TANAGAWA and M. ATSUTA, *J. Oral Rehab.* **25** (1998) 285.
5. International Organization for Standardization: Specification for dental water-based cement, ISO 9917 (1991).
6. J. W. NICHOLSON and M. A. AMIRI, *J. Mater. Sci.: Mater. in Med.* **9** (1998) 549.
7. S. HOJO, N. TAKAHASHI and T. YAMADA, *J. Dent. Res.* **70** (1991) 182.
8. S. HOJO, M. KOMATSU, R. OKUDA, N. TAKAHASHI and T. YAMADA, *ibid.* **73** (1994) 1853.
9. E. A. WASSON and J. W. NICHOLSON, *Brit. Polym. J.* **23** (1990) 179.
10. S. MATSUYA, T. MAEDA and M. OHTA, *J. Dent. Res.* **75** (1996) 1920.

11. K. A. MILNE, N. J. CALOS, J. H. O'DONNELL, C. H. L. KENNARD, S. VEGA and D. MARKS, *J. Mater. Sci.: Mater. in Med.* **8** (1997), 349.
12. E. A. WASSON and J. W. NICHOLSON, *J. Dent. Res.* **72** (1993) 481.
13. A. D. WILSON, D. M. GROFFMAN, D. R. POWIS and R. P. SCOTT, *Biomaterials* **7** (1986) 217.
14. R. W. BILLINGTON, J. A. WILLIAMS and G. J. PEARSON, *ibid.* **13** (1992) 343.

Received 22 June
and accepted 20 July 1998