JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE **12** (2001) 647–652

Variations in the compressive strength of dental cements stored in ionic or acidic solutions

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The compressive strengths of various dental cements (a zinc polycarboxylate, a zinc phosphate, a glass-ionomer and two resin-modified glass ionomers, RMGICs) have been determined following storage in pure water, 0.9% sodium chloride solution or 20 mmol dm^{-3} lactic acid solution for periods of time ranging from 24 h to 3 months. The glass-ionomer cement showed no differences between different storage solutions or at different storage times, whereas the zinc polycarboxylate, zinc phosphate and the resin-modified glass ionomer cements showed significant differences following storage in the solutions for 24 h compared with pure water. The zinc polycarboxylate cement was significantly weaker at 24 h in 0.9% NaCl and lactic acid than in pure water, whereas most of the other cements were significantly stronger in both 0.9% NaCl and lactic acid. One of the RMGICs (Vitremer luting, ex. 3M), however, was significantly stronger only in the NaCl solution, not in the lactic acid. In general, by 1 week, the strengths all reverted to being essentially the same as for specimens stored in pure water for most subsequent storage times, and did not change significantly on storage for up to 3 months. This effect of storage medium on the early strength has not been reported previously and since the media were chosen to model certain characteristics of natural saliva, the changes observed seem likely to occur *in vivo*. It is concluded that pure water is not the best medium for storing these cements if they are to behave as they do under clinical conditions.

1. Introduction

Dental cements are well-established materials used for a variety of purposes, including retention of crowns, bridges, inlays, onlays, laminates, and posts and pins for large restoration [1, 2]. Zinc polycarboxlates are used in paediatric dentistry for the cementation of orthodontic brackets [3] and glass-ionomers, including resin-modified versions, are used as restorative materials [4], for example in cervical lesions, so-called Class V restorations.

Current cements are assessed for clinical use on the basis of the ISO Standard 9917, which requires cement specimens to be stored in water at 37 °C for 24 h before testing for strength [5]. All cements have some measurable solubility in water, a property that would be influenced by whether the water were pure or had other solutes dissolved in it. In addition, resin-modified glass-ionomers are known to take up water in an osmotic process [6, 7], and this depends on the chemical potential of water, a thermodynamic property that is a maximum for pure water, and which is reduced by increasing quantities of solute.

The present study was carried out aimed at determining whether storage in different aqueous solutions affected the physical properties of the cements. The experimental approach has been simple: to store specimens of these cements for varying lengths of time in one of three aqueous media (deionized water, 0.9% aqueous NaCl, 20 mmol dm^{-3} lactic acid solution) and then to test compressive strength. The lactic acid solution was the same as that used in the impinging-jet acid–erosion test of the current Standard [5]. It is of interest because all of cements have recently been shown to increase the pH this substance while experiencing only minor erosive loss [8, 9], and the present study gave the opportunity of determining whether, as the lactic acid was neutralized and the specimens eroded, there was any other effect on these materials.

2. Materials and methods

The following commercial dental cements were used in this study:

Zinc polycarboxylate (PolyF Plus, ex. Dentsply, Konstanz, Germany);

Zinc phosphate cement (De Trey Zinc, ex. Dentsply, Konstanz, Germany);

Resin-modified glass-ionomers (Fuji Lute, ex. GC,

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Japan; and Vitremer Luting, ex. 3M Dental, St Pauls, Mn, USA);

Conventional glass-ionomer (AquaCem, ex. Dentsply, Konstanz, Germany).

In all cases, they were used at the powder : liquid ratios recommended by the manufactures, i.e. PolyF Plus 5.0 g powder to 1.0 ml of water; DeTrey Zinc 2.8 g powder to 1.0 ml of liquid; Fuji Lute 1.0 g of powder to 0.5 ml of liquid; Vitremer Luting 0.8 g of powder to 0.5 ml of liquid; and AquaCem 1.0 g of powder to 0.3 ml of water.

Compressive strengths were determined using the method described in ISO 9917 (1991), i.e. sets of six cylindrical specimens (6 mm high × 4 mm diameter) were prepared for each determination, each cylinder being prepared individually from a separate mix of powder and liquid. Specimens were stored at 37 °C in the molds for 1 h, then transferred to the relevant solution, or to pure water, in which they were stored until testing. Storage periods employed ranged up to 3 months and included 1 day, 1 week, and 1 month. Storage solutions used were (a) deionized water, (b) lactic acid at a concentration of 20 mmol dm^{-3} and (c) sodium chloride at a concentration of 0.9%, equivalent to 0.154 mol dm^{-3}. Testing was carried out using a universal testing machine (Type EU500, ex. Howden, Leamington Spa, UK) using a cross-head speed of 1.0 mm/min. Loads at failure were converted to strength values, and means and standard deviations determined for each set of specimens. Differences between compressive strength values were examined for statistical significance using one-way ANOVA, followed by the Newman–Keuls Multiple Comparison Test with values of $p < 0.05$ considered significant.

3. Results

Compressive strength values for the zinc polycarboxylate cement are shown in Table I and Fig. 1. After 1 day, the specimens stored in both saline and lactic acid were weaker than those stored in pure water. Thereafter, differences in strength between specimens stored in different media for 1 week, 1 month and 3 months were not significant, with the exception of the specimens stored in pure water for 3 months where the increase was significant.

Compressive strength results for the zinc phosphate cement are shown in Table II and Fig. 2. For this cement, standard deviations were generally found to be higher than for the zinc polycarboxylate. Such scatter is an indication that this material is more brittle than the zinc polycarboxylate. There were no significant differences between any of the storage media or times, except at 24 h, where the specimens stored in either saline or lactic acid were significantly stronger than all other specimens. In both of these solutions, the high strength at 1 day was followed by a significant reduction by 1 week to values comparable with those for specimens stored in pure water.

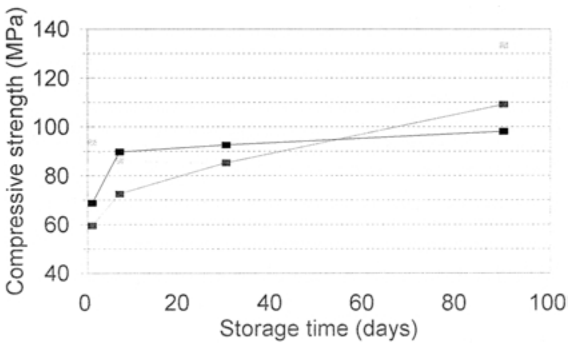

Figure 1 Zinc polycarboxylate.

Compressive strengths for the conventional glass-ionomer, AquaCem, are shown in Table III and Fig. 3. There are no significant differences between any of these values.

The compressive strengths of the two resin-modified glass-ionomers are shown in Tables IV and V, and in Figs 4 and 5. Both cements were significantly stronger when stored in 0.9% NaCl for 24 h than than with other combinations of storage medium and time. For Fuji Lute, specimens stored in lactic acid were also significantly stronger at 24 h, but this was not the case for Vitremer luting. After 1 week, the strength in these solutions had fallen to values that did not differ to a significant extent at any other time period, or by comparison with specimens stored in pure water.

4. Discussion

With the exception of the glass ionomer cement, all of the cements used in this study showed early differences in compressive strength in both 0.9% saline and most of them showed differences in lactic acid solution. For the zinc phosphate and the resin-modified glass-ionomers these values were higher than others recorded, whereas for the zinc polycarboxylate, they were lower. In deionized water at all time periods, and in the solutions at times of 1 week, 1 month and 3 months, the strengths were effectively the same, except for zinc polycarboxylate and one of the resin-modified glass-ionomers, Fuji Lute in water, where at 3 months, the strength had risen slightly. These differences show that, particularly when

TABLE I Compressive strength (MPa) of zinc polycarboxylate cement (PolyF Plus) stored in different media for various time intervals (standard deviations in parentheses)

	Storage medium		
Time	Water	0.9% Nacl	20 mmol lactic acid
1 day	93.6 (9.4)	59.5 (14.4)	68.7 (11.3)
1 week	86.1 (19.3)	72.5 (12.4)	89.7 (21.3)
1 month	84.9 (10.2)	85.3 (24.8)	92.6 (14.2)
3 months	133.4 (9.7)	109.2 (15.3)	98.1 (13.8)

TABLE II Compressive strength (MPa) of zinc phosphate cement (De Trey Zinc) stored in different media for various time intervals (standard deviations in parentheses)

	Storage medium		
Time	Water	0.9% NaCl	20 mmol lactic acid
1 day	102.5 (35.7)	157.2 (17.0)	164.2 (8.7)
1 week	81.3 (25.8)	60.4 (11.7)	99.2 (14.1)
1 month	87.5 (18.7)	94.9 (14.8)	94.7 (27.4)
3 months	93.6 (24.3)	82.8 (20.2)	109.1 (34.4)

TABLE III Compressive strength (MPa) of glass-ionomer cement (AquaCem) stored in different media for various time intervals (standard deviations in parentheses)

	Storage medium		
Time	Water	0.9% NaCl	20 mmol lactic acid
1 day	110.7 (6.1)	97.5 (10.3)	86.4 (7.3)
1 week	97.7 (12.7)	100.0 (10.1)	95.8 (7.9)
1 month	94.4 (16.4)	110.0 (20.7)	113.8 (12.2)
3 months	111.6 (24.5)	114.9 (18.9)	103.6 (12.3)

freshly prepared, these cements are sensitive to the nature of their storage medium.

Any consideration of these results must begin from a recognition that, when a material is placed in water, there are two main processes that may occur, namely (a) water uptake and (b) dissolution. Both are likely to be affected by the presence of solutes in the water, though the effect on water uptake is more complicated, since water uptake could be driven by a variety of factors, including chemical potential of the water and the kinetics and thermodynamics of the hydration reaction for the individual ionic species within the cement. These factors will now be considered in detail for each type of cement.

For zinc phosphate, there have been numerous previous studies of the solubility and setting and, briefly, we know that there is an initial acid–base reaction that gives rise to a soluble acidic zinc phosphate [10].

$$ZnO + 2H_3PO_4 \rightarrow Zn(H_2PO_4)_2 + H_2O$$

Further reaction of this acidic zinc phosphate leads to the rapid formation of the insoluble zinc orthophosphate, $Zn_3(PO_4)_2$ [10]. This latter substance is essentially amorphous, and prevented from crystallising by the presence of aluminum in the cement-forming liquid [11]. However, over long periods of time, some of it does crystallise, forming the hydrated phase $Zn(H_2PO_4)_2 \cdot 4H_2O$ known as hopeite [12]. Growth of hopeite, which occurs at the surface, is favored by elevated temperatures and high humidity, though even after over 40 years in the mouth, this crystalline component represents only a fraction of the cement mass [12]. This hydration is slow and therefore unlikely to influence the strength at 24 hours.

As the zinc phosphate cement sets, there are considerable changes in the amount of soluble material that may be eluted [10]. Relatively little zinc dissolves at any time, the major soluble species being phosphate. The amount of this phosphate depends *inter alia* on the pH of the storage solution, which itself depends on the amount of material leached. Solubility has been shown to drop rapidly as pH rises from 4.5 to 5.0, then rise again more slowly as neutral conditions are approached [13]. The fact that the amount of previously dissolved cement has an influence on total solubility suggests an explanation for the observations in the current work.

The presence of solutes, either sodium chloride or lactic acid, probably reduces the relative solubility of the leachable phosphates. Such an effect early in the life of the cements may lead to the development of relatively non-porous and flaw-free specimens. These would be expected to be stronger than those zinc phosphate cements from which relatively large amounts of soluble species have been leached, i.e. those stored in pure water. As the cements age, however, and species are formed with different relative solubilities, there may be some

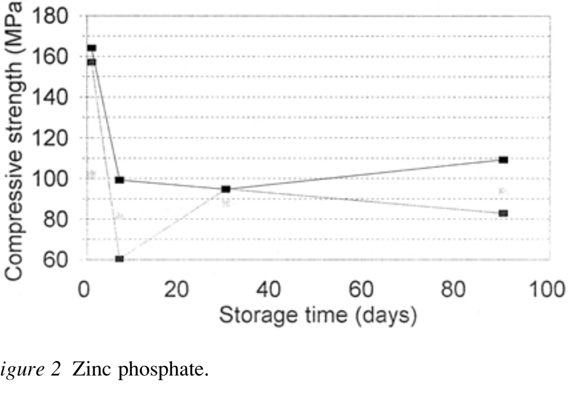

Figure 2 Zinc phosphate.

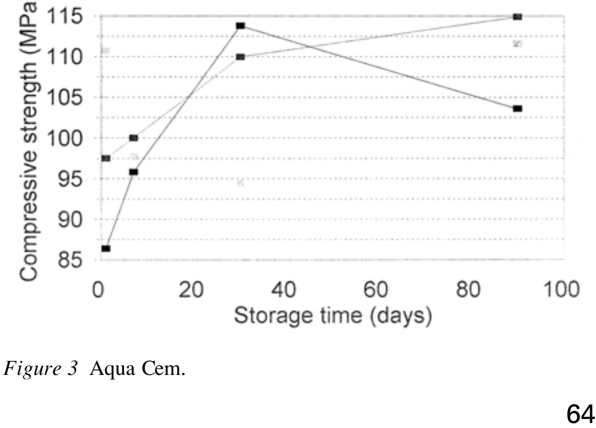

Figure 3 Aqua Cem.

TABLE IV Compressive strength (MPa) of resin-modified glass-ionomer cement (Vitremer luting) stored in different media for various time intervals (standard deviations in parentheses)

	Storage medium		
Time	Water	0.9% NaCl	20 mmol lactic acid
1 day	97.1 (7.4)	147.0 (11.9)	116.6 (10.2)
1 week	104.6 (11.9)	103.4 (8.1)	104.0 (13.1)
1 month	103.4 (9.7)	111.6 (20.8)	100.4 (7.2)
3 months	125.7 (16.6)	113.8 (14.6)	123.5 (13.0)

TABLE V Compressive strength (MPa) of resin-modified glass-ionomer cement (Fuji Lute) stored in different media for various time intervals (standard deviations in parentheses)

	Storage medium		
Time	Water	0.9% NaCl	20 mmol lactic acid
1 day	138.7 (2.5)	180.5 (22.1)	168.1 (17.8)
1 week	136.0 (17.0)	139.4 (9.0)	139.0 (14.6)
1 month	125.8 (12.8)	130.8 (6.5)	130.9 (9.4)
3 months	160.0 (12.9)	125.1 (18.3)	100.2 (6.6)

modest dissolution, leading after all to the development of the stress-concentrating flaws. Consequently, the strength drops to the same value as those cements stored in pure water. The fact that the presence of sodium chloride has a similar effect to that of lactic acid suggests this phenomen is related to solubility, rather than to pH change.

For the zinc polycarboxylates, specimens stored in 0.9% sodium chloride or lactic acid are both weak by comparison with their counterparts stored in water, but after an appropriate length of time, strength rises to the same as for cements stored in pure water. However, after 3 months in water, strength shows another modest rise. The early weakness is potentially important, because the mean strengths were below the minimum required by the current ISO Standard [5].

In this case, the effect seems unlikely to be connected with enhanced dissolution, since dissolution would probably increase on prolonged storage, making the cements weaker; the experimental results show that, in the solutions, strength was initially low but increases on storage. The addition of sodium chloride to zinc polycarboxylate cements has previously been shown to have no effect on compressive strength, though the rate of the setting reaction was altered [14]. Thus, the weakening effect at 24 h that we have demonstrated cannot be due to taking up NaCl from solution. Instead the weakness seems to be associated with changes in the partitioning of water between the cement and the storage media. Water does not seem to be essential for the maturation of zinc polycarboxylates, since they have previously been shown to become very strong when stored in a highly desiccating environment [15]. In other words, a mature and strong zinc polycarboxylate cement does not require a particularly hydrated structure. Given this insensitivity to hydration, it is not clear why zinc polycarboxylate cement stored in 0.9% NaCl or in lactic acid solution is weaker at 24 h than when stored in water. Whatever the reason, after 1 week, full maturation has been able to occur, and at all subsequent times shown in Table III, the cements are sufficiently mature to have compressive strengths in the region of 90 MPa. In pure water, after 3 months there was a slight but statistically significant rise in compressive strength, and again the reason for this is unclear and would benefit from further investigation.

The setting of glass-ionomer cements is known to be complex [16]. It involves initial formation of calcium polyacrylate, followed by later formation of aluminum polyacrylate, both of which are probably co-ordinated by water molecules. In addition, there is evidence of an inorganic reaction involving ion-depleted species from the glass [17], and this seems to bind in water. It is also frequently associated with an increase in strength [18, 19], though the extent to which this occurs varies with the brand of material studied [20]. In the present study, there

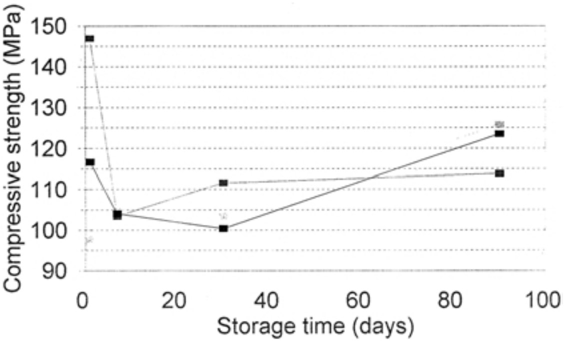

Figure 4 Vitremer luting.

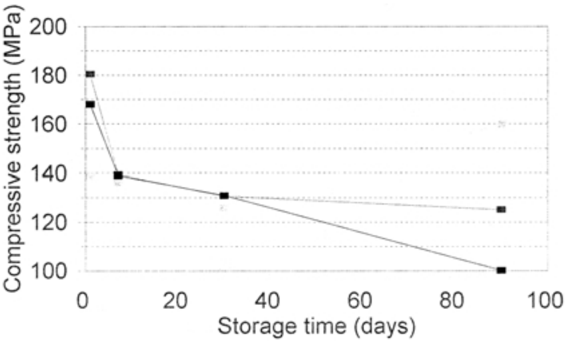

Figure 5 Fuji Lute

was no significant increase in compressive strength with time, which is fairly unusual but not unique [20]. More important from the point of view of this study, there were no significant differences in behavior between the different storage solutions, indicating that this particular conventional, self-hardening glass-ionomer is relatively insensitive to variations in availability of water from the storage solutions.

Resin-modified glass-ionomers have a complex morphology based on blends of conventional cement with hydrogel domains [6, 21]. The latter arise from polymerization of the 2-hydroxyethyl methacrylate component. In *in vitro* studies on materials containing excess monomer, significant swelling has been shown to occur, with a change in failure mode from brittle to tough, and a considerable fall in strength [22]. It may be that the extent to which these hydrogel phases were able to take up water influenced the development of strength of the specimens in the current study. Water uptake characteristics of resin-modified glass-ionomers are known to be complex [23] and to be influenced by the presence of solutes in the surrounding solution.

In the present study, these materials were found to be much stronger at 1 day when stored in 0.9% NaCl rather than pure water, though at this time, uptake of water would still be far from equilibrium. Nonetheless, if the amount of water taken up at 24 h were less for the specimens stored in solutions, as might be expected from previous results, there would be little or no swelling of the hydrogel domains, and thus no weakening effect. After longer periods of time, however, sufficient water might have been absorbed to cause softening of these domains, and a reduction in the overall strength. In pure water, by contrast, uptake may well be sufficiently rapid to develop softened hydrogel domains more rapidly, so that at 24 h, the strength has reached its final value. For Fuji Lute, similar results were obtained for storage in lactic acid, and similar arguments apply. Also for Fuji Lute, the slight increase in strength at 3 months may be due to increasing strength of the polysalt phase produced by the acid-base reaction.

It is worth reflecting for a moment on the solutions employed in this study. They were chosen to reflect certain aspects of saliva, and hence of the conditions that occur in the mouth. Saliva is known to be a complex natural solution with a substantial ionic content [24] and in the presence of caries, the local pH may be quite low, i.e. in the region of 4.7 [25]. The solutions employed, one ionic and one acidic, were designed to reflect these features to an extent. The unexpected and significant changes we have found in the compressive strengths of these cements at 24 h seem likely to occur *in vivo*. We therefore conclude that pure water is not the best storage medium for determining the probable behavior of these materials under clinical conditions, although much additional work is required before an alternative storage medium could be proposed.

5. Conclusions

The compressive strengths of various dental cements have been found to show variations at 24 h when stored in solutions of sodium chloride or lactic acid as opposed to pure water. Such changes have not been reported previously. The zinc polycarboxylate was weaker in the solutions, by comparison with storage in pure water, and achieved strengths of only 59.5 and 68.7 MPa, respectively, i.e. below the minimum (70 MPa) specified in the current ISO standard for luting cements. The zinc phosphate and resin-modified glass-ionomers, by contrast, generally showed very high early compressive strength in these solutions, before weakening to become the same strength as specimens stored in pure water. The saline and lactic acid storage media were chosen to model aspects of natural saliva, hence the early variations in strength that were found in these media seem likely to occur when these materials are used clinically. The fact that these variations were not exhibited by specimens stored in deionised water suggests that water itself is less appropriate as a model for the conditions in the mouth than has hitherto been supposed.

Acknowledgments

We acknowledge financial support from 3M Dental, UK (to MAM) and from the Wellcome Trust (to RG), and we thank Dentsply, 3M and GC (UK) for the gift of materials used in this study.

References

1. B. G. N. SMITH, P. S. WRIGHT and D. BROWN, ''Clinical Handling of Materials'', 2nd edn. (Butterworth-Heinemann, Oxford, 1994).
2. F. J. HARTY, ''Concise Illustrated Dental Dictionary'', 2nd edn (Butterworth-Heinemann, Oxford, 1994).
3. K. J. DONLY, *Cur. Sci.* **1** (1991) 554
4. J. W. NICHOLSON, and T. P. CROLL, *Quintessence Internat.* **28** (1997) 705.
5. International Organisation for Standardization, 1991: Specification for Dental Water-Based Cements, ISO 9917.
6. H. M. ANSTICE and J. W. NICHOLSON, *J. Mater. Sci. Mater. Med.* **3** (1992) 447.
7. J. W. NICHOLSON, *J. Mater. Sci. Mater. Med.* **8** (1997) 691.
8. J. W. NICHOLSON and M. A. AMIRI, *J. Mater. Sci. Mater. Med.* **9** (1998) 549.
9. J. W. NICHOLSON, B. CZARNECKA and H. LIMANOWSKA-SHAW, *Biomaterials* **20** (1999) 155.
10. A. D. WILSON, G. ABEL and B. G. LEWIS, *Br. Dent. J.* **137** (1974) 313.
11. S. CRISP, I. K. O'NEILL, H. J. PROSSER, B. STUART and A. D. WILSON, *J. Dent. Res.* **57** (1978)
12. J. MARGERIT, B. CLUZEL, J. M. LELOUP, J. NURIT, B. PAUVERT and A. TEROL, *J. Mater. Sci. Mater. Med.* **7** (1996) 623.
13. A. D. WILSON, G. ABEL and B. G. LEWIS, *J. Dent.* **4** (1976), 28
14. J. W. NICHOLSON, *J. Mater. Sci. Mater. Med.* **6** (1995) 404.
15. J. W. NICHOLSON, S. J. HAWKINS and E. A. WASSON, *J. Mater. Sci. Mater. Med.* **4** (1993) 32
16. J. W. NICHOLSON, *Biomaterials* **26** (1998) 485.
17. S. MATSUYA, T. MAEDA and M. OHTA, *J. Dent. Res.* **75** (1993) 1920.
18. J. A. WILLIAMS and R. W. BILLINGTON, *J. Oral Rehab.* **16** (1989) 475.
19. C. SHEN and N. GRIMAUDO, *Dent. Mater.* **10** (1994) 190.
20. J. A. WILLIAMS and R. W. BILLINGTON, *J. Oral Rehab.* **18** (1991) 163.

21. W. KANCHANAVASITA, G. J. PEARSON and H. M. ANSTICE, *Biomaterials* **16** (1995) 921.
22. H. M. ANSTICE, *Chem & Ind (London)* (1994) 899.
23. A. YAP and C. M. LEE, *J. Oral Rehab.* **24** (1997) 310.
24. G. N. JENKINS, ''The Physiology of the Mouth'', 3rd edn (Blackwell, Oxford, 1966).
25. S. HOJO, N. TAKAHASHI and T. YAMADA, *J. Dent. Res.* **70** (1991) 182.

Received 23 July 1999
and accepted 26 June 2000