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The interaction of lactic acid–glass cements with aqueous solutions

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Cylindrical specimens of experimental lactic acid–glass cements (6 mm high × 4 mm diameter) were prepared, matured at 37 °C for one week sealed in their molds, then exposed either to water (pH 6.6) or aqueous lactic acid (pH 2.7) for a further week. Solutions were analyzed by ICP-OES and their pH values recorded. In both solutions, cement specimens were found to release aluminum together with smaller amounts of calcium, sodium, silicon and phosphorus. They also formed soft gels that ICP-OES analysis showed were comprised mainly of aluminum and phosphorus species. These dissolution and gelation processes were accompanied by changes in the pH of the storage media (water to pH 4.9; lactic acid to 4.2). It is concluded that further work is necessary in order to fully characterize the species of aluminum released from these cements.

Introduction

Glass–ionomers are widely used as cements in restorative dentistry [1–3], and find particular application in pediatric dentistry [4]. They consist of special ion-leachable glasses, containing calcium (or strontium), aluminum, silicon and usually phosphorus. These glasses may also contain sodium, and typically contain fluoride. Glass–ionomer cements also consist of an acidic polymer, typically poly(acrylic acid), but also possibly acrylic/maleic acid copolymer. This polymer is activated by the presence of water, either because the polymer is in solution, or because the cement is presented as a mixture of dry polymer with glass, the setting of which is activated by adding water [1–3].

The setting of these cements has been shown by several techniques [5–7] to involve the neutralization of the acidic polymer, which also has the effect of rendering it insoluble in water. Many workers have since concluded that this neutralization represents the full extent of the setting chemistry of these cements [8, 9], albeit one that continues slowly with time after initial hardening is complete. Moreover, the importance of the polymer component is demonstrated through the quantitative relationship that exists between molecular weight and fracture toughness [10].

However, some time ago Wasson and Nicholson showed that ion-release from the glass component included silicon and phosphorus, presumably as anionic species, i.e. silicate or phosphate [11]. They further suggested that these anionic species could undergo a setting reaction of their own, not detectable in the infrared region of conventional spectrometers. In support of their hypothesis, they went on to prepare cements from acetic acid, which were insoluble in water despite the fact that all of the candidate metal acetates (sodium, aluminum and calcium) are extremely soluble [12]. Moreover, they demonstrated that development of insolubility did not correlate with neutralization, a process that was shown to be complete several hours before the cements had become fully insoluble. They also showed that the physical properties of this cement changed significantly with time, up to about three months [13], again without altering in any detectable way the organic component of the cement. All of these observations were claimed to be consistent with the occurrence of a secondary setting process, entirely inorganic in nature, involving the metal cations and the anionic fragments of the glass that enter the matrix phase during the initial attack by the aqueous acid solution [13].

More recently, as part of our interest in the interaction of cements with lactic acid, the principal substance responsible for the development of dental caries, we have prepared cements by reaction of this acid with an ionomer glass [14]. As with acetic acid, although lactic acid is monomeric, it was shown to form cements that remained intact if aged for 24 h before exposure to water. This relative stability in water did not correlate with neutralization, since the cement became completely neutralized within a few minutes of mixing, yet did not become water-resistant until several hours had elapsed.

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Specimens of these cements had some strength in compression at 24 h, and though were very weak (9–35 MPa) they did not increase in compressive strength significantly over three months [14]. Such cements have the potential to give further information on the setting chemistry and microstructure of glass–ionomer cements, and can be regarded as useful models of at least some aspects of glass–ionomers. In the current paper, we report a further study of lactic acid–glass cements, one aimed at studying further the nature of their interaction with water and with dilute lactic acid. In particular, changes in the pH of the storage solutions caused by these cements and the associated release of metal ions by these cements have been studied, and results compared to those from glass–ionomer cements stored in the same aqueous media.

Materials and methods

Cements were prepared as described previously [14] using glass G338 (First Scientific Limited, Roseheyworth Business Park, Abertillery, Blaenau Gwent, Wales) and 75% aqueous lactic acid (lactic acid: AnalaR grade, BDH, Poole, Dorset, England), mixing being achieved by spatulating the components together on a glass block. Freshly mixed pastes were packed into cylindrical molds (6 mm high × 4 mm diameter) and stored sealed in these molds at 37 °C for one week. Five specimens were made for each storage solution.

After this time they were weighed, then transferred to 5 cm^3 volumes of liquid (either deionized water at pH 6.6, or 20 mmol dm^{-3} lactic acid solution, pH 2.7) in individual sample vials, and stored for one week. After this time, in all cases, large volumes of soft gel had formed at the bottom of each vial. The pH of the supernatant was determined using a glass electrode (type CW711, Whatman, UK). It was then removed by decantation, and the water and lactic acid solution respectively bulked. In each case, the remaining gel plus specimen was weighed, after which each specimen was removed, wiped clean using tissue, and weighed. In this way, the mass of gel formed, and the change in mass on storage of each specimen was determined.

The bulked supernatants were analyzed by ICP-OES, and results determined as mg dm^{-3} (which is equivalent to ppm). The gels were diluted by a known amount (approximately 1 g in 20 mL of deionized water), and these solutions also analyzed by ICP-OES. Results for the gels were recorded as mg of ion per g of gel.

Changes in mass and pH were subjected to statistical analysis using Student's *t*-test.

Results

Results for changes in solution pH are given in Table I. Changes in each case were statistically significant ($p < 0.01$), with water being shifted from nearly neutral to moderately acidic, and aqueous lactic acid from quite acidic to much less acidic. In each storage solution, specimens lost mass (Table II), though the difference between the two storage media was not significant. In each case, relatively large volumes of soft, watery gels were formed immediately adjacent to the cement specimens. The total mass of these gels was over three times that of the original specimen mass; and the differences in mean amounts formed in water and lactic acid were not significant.

The storage solutions were found to contain large quantities of aluminum, and much lower amounts of calcium, sodium and phosphorus (Table III). In lactic acid, there was slightly less aluminum than in water, but more of all the other ions determined.

The gels were found to contain very small amounts of ions (Table IV), and when these values are recalculated on a mole ratio basis (Table V) it can be seen that the gels are predominantly alumino-phosphates with traces only of calcium, sodium or silicon.

TABLE I pH values of storage solutions after one week (standard deviations in paretheses)

Storage medium	Original pH	pH after one week
Water	6.6 (0.1)	4.9 (0.1)
Lactic acid	2.7 (0.1)	4.2 (0.1)

TABLE II Changes in mass (Standard deviations in parentheses)

Medium	Loss in mass (%)	Mass of gel formed (as per cent of original specimen)
Water	13.5 (9.6)	348.6 (20.4)
Lactic acid	7.8 (7.6)	319.2 (20.4)

TABLE III Composition of storage solutions (mg dm^{-3})

Ion	Water	Lactic acid
Al	1642	1587
Ca	47	77
Na	58	71
P	29	51
Si	47	29

TABLE IV Composition of gels (mg/g)

Ion	Water	Lactic acid
Al	4.20	2.93
Ca	0.21	0.14
Na	0.09	0.07
P	2.30	1.34
Si	0.14	0.09

TABLE V Mole ratios of ions in gels

Ion	Water	Lactic acid
Al	39.00	36.33
Ca	1.33	1.33
Na	1.00	1.00
P	18.50	14.33
Si	1.25	1.00

Discussion

The experimental lactic acid–glass cements showed differences and similarities to glass–ionomer cements. Like glass–ionomers, they released ions into solution, generally in greater amounts in lower pH solutions than in higher pH ones. Unlike glass–ionomers in similar static tests [15, 16], this ion-release was associated with the formation of relatively voluminous amounts of soft gel, that proved to be rich in aluminum and phosphorus. This gel formation was not observed previously [14], possibly because in our previous studies, cements were exposed to water after 24 hours, rather than after one week.

The compositions of the gels formed in water and in lactic acid were similar, though this is not surprising in view of their pH and mass loss values, both of which indicate that substantial proportions of the cements dissolved in the storage media. In the case of water, the final value of pH indicated that there was a substantial amount of free lactic acid arising from the dissolved specimens. This means that the region of solution close to the specimens contained the same chemical species (Na^+ and Ca^{2+} ions, water, lactate ions, silicon, phosphorus and aluminum) as the cements themselves, though presumably at lower concentrations. The various interactions that lead to cement formation could also occur in this region, but to produce gel rather than cement because of the relatively high amount of water.

Previous studies of the interaction of lactic acid with dental cements have found gelatinous deposits on cements made from similar glasses to G338, used here [17]. However, these gels were found to be rich in silicon, and not to contain aluminum. They were therefore assumed to be simply silica gel. In the present study, by contrast, the gels were quite clearly aluminophosphates of some sort, and had only minor amounts of other elements in them. Aluminum is well known for forming gelatinous precipitates, for example, aluminum hydroxide [18], though generally at much higher values of pH than those used in our experiments. The now obsolete dental silicate cement, which was based on structurally similar glasses to the one used in the present study [2] was shown to be based on a mixture of aluminum phosphate polymers and phosphate and hydroxyl bridges between metal ions [19]. Such species are known to be capable of being formed in aqueous solution [20].

Unlike glass–ionomer cements, very large amounts of aluminum were released into aqueous solution by these experimental cements. Recent studies have shown that in both water and lactic acid solution, sodium is the most abundant ion released from glass–ionomers, followed by aluminum [21]. For example, in water, the ratio of sodium to aluminum after one week was approximately 4 : 1 and in lactic acid was approximately 2 : 1. By contrast in the experimental cements used in the current study, it was of the order of 0.0375 : 1. In a previous study of ion release from G338 glass directly into aqueous lactic acid, the ratio varied from 0.65 to 0.76 : 1 [11]. This means that there is relatively much more aluminum released from the glass into acid solutions than is released by fully set glass–ionomer cements into such solutions. However, surprisingly, our experimental lactate cements released even more aluminum than unreacted glass has been found to. This may imply that, in forming these cements, the lactic acid solution preferentially attacks regions of the glass that are rich in aluminum and the observed high aluminum release may thus be a consequence of the known phase separation of G338 [11, 22].

The precise nature of the aluminum species released cannot be determined from the data presented here. Previously a variety of cationic species, including AlF_2^+ and AlF^{2+} [23], and $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ [24] have been shown to occur in aqueous solution. In addition, species such as AlO_2^-, AlO_3^{3-} and AlF_4^- are possible. In the absence of data on fluoride release, proper charge balance calculations cannot be made, so that it is not possible to determine what species of aluminum are present, nor whether they are predominantly anionic or cationic. Further investigations are underway to try and establish the exact form or forms in which aluminum are released by these cements.

Conclusions

Experimental lactic acid–glass cements that have been allowed to age for one week prior to exposure to water have been found to have complex interactions with aqueous storage media (distilled water or lactic acid solution). In both solutions, they released significant amounts of aluminum with much smaller amounts of calcium, sodium, silicon and phosphorus. They also formed soft gels that were high in aluminum and phosphorus, but low in silicon. Hence, unlike superficially similar material produced in previous experiments [17], these gels were clearly not silica gel, but some sort of aluminum phosphate polymer of the type previously identified in aqueous solution [20] and also as the underlying structural species in dental silicate cements [19].

The interactions of the cements led to changes in the pH of the storage media. Water went from almost neutral to pH 4.9, whereas lactic acid was partly neutralized, changing from pH from 2.7 to 4.2.

Overall, these experiments raise important questions of the nature of the aluminum species released by cements of this type, including dental grade glass–ionomer cements. In particular, the question of the ratio of anionic to cationic species needs addressing, and further work is in hand to clarify this point.

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References

1. G. J. MOUNT, ‘‘An Atlas of Glass–Ionomer Cements’’, 3rd edn (Dunitz, London, 2002).
2. A. D. WILSON and J. W. NICHOLSON, in ‘‘Acid-Base Cements’’ (The University Press, Cambridge, 1993).
3. G. J. MOUNT and W. R. HUME, in ‘‘Preservation and Restoration of Tooth Structure’’ (Mosby, London, 1998).
4. T. P. CROLL and J. W. NICHOLSON, *Pediat. Dent.* **24** (2002) 423.

5. S. CRISP, M. A. PRINGEUR, D. WARDLEWORTH and A. D. WILSON, *J. Dent. Res.* **53** (1974) 1420.
6. J. W. NICHOLSON, P. J. BROOKMAN, O. M. LACY and A. D. WILSON, *J. Dent. Res.* **67** (1988) 1451.
7. S. MATSUYA, T. MAEDA and M. OHTA, *J. Dent. Res.* **75** (1996) 1920.
8. Z. OUYANG, S. L. SNECKENBERGER, E. C. KAO, B. M. CULBERTSON and P. W. JAGONZINSKI, *Appl. Spectrosc.* **53** (1999) 297.
9. E. DE BARRA and R. G. HILL, *J. Mater. Sci.* **33** (1998) 5487.
10. R. G. HILL, C. P. WARRENS and A. D. WILSON, *J. Mater. Sci.* **24** (1989) 89.
11. E. A. WASSON and J. W. NICHOLSON, *Br. Polym. J.* **23** (1990) 179.
12. E. A. WASSON and J. W. NICHOLSON, *Clin. Mater.* **7** (1991) 289.
13. E. A. WASSON and J. W. NICHOLSON, *J. Dent. Res.* **72** (1993) 481.
14. J. W. NICHOLSON, H. TAWFIK and B. CZARNECKA, *J. Mater. Sci.: Mater. Med* **13** (2002) 417.
15. J. W. NICHOLSON, B. CZARNECKA and H. LIMANOWSKA-SHAW, *Biomaterials* **20** (1999) 155.
16. J. W. NICHOLSON and M. AMIRI, *J. Mater. Sci.; Mater. Med* **9** (1998) 549.
17. A. D. WILSON, D. M. GROFFMAN, D. R. POWIS and R. P. SCOTT, *Biomaterials* **7** (1986) 217.
18. N. N. GREENWOOD and A. EARNSHAW, in ''The Chemistry of the Elements'' (Pergamon, Oxford, 1984).
19. A. D. WILSON, B. E. KENT, R. J. MESLEY, R. P. MILLER, D. CLINTON and K. E. FLETCHER, *Nature* **225** (1970) 272.
20. J. E. SALMON and J. G. WALL, *J. Chem. Soc.* (1958) 1128.
21. B. CZARNECKA, H. LIMANOWSKA-SHAW and J. W. NICHOLSON, *Biomaterials* **23** (2002) 2783.
22. T. I. BARRY, D. J. CLINTON and A. D. WILSON, *J. Dent. Res.* **58** (1979) 1072.
23. J. W. AKITT, N. N. GREENWOOD and G. D. LESTER, *J. Chem. Soc. A* (1971) 2450.
24. D. N. WATERS and M. S. HENTY, *J. Chem. Soc. Dalton Trans.* (1977) 243.

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