J Mater Sci: Mater Med (2007) 18:649–652
DOI 10.1007/s10856-007-2315-3

Ion release by endodontic grade glass-ionomer cement

Beata Czarnecka · Honorata Limanowska-Shaw · Richard Hatton · John W. Nicholson

Received: 21 July 2004 / Accepted: 24 October 2005

Cylindrical specimens (6 mm high × 4 mm diameter) of the endodontic grade glass-ionomer (Ketac Endo) were exposed to various media for 1 week, after which changes in their mass, pH of storage medium, and ion release were determined. In water, this cement was shown to release reasonable amounts of sodium, aluminium and silicon, together with smaller amounts of calcium and phosphorus, as well as taking up 2.41% by mass of water. A comparison with the restorative grade materials (Ketac Molar, ex 3M ESPE and Fuji IX, ex GC) showed both ion release and water uptake to be greater. All three cements shifted pH from 7 to around 6 with no significant differences between them.

Other storage media were found to alter the pattern of ion release. Lactic acid caused an increase, whereas both saturated calcium hydroxide and 0.6% sodium hypochlorite, caused decreases. This suppression of ion-release may be significant clinically. Aluminium is the most potentially hazardous of the ions involved but amounts released were low compared with levels previously reported to show biological damage.

Introduction

Endodontic treatment of pulpless teeth involves removal of root canal contents, thorough preparation of the root canal space, followed by tight sealing [1]. Conventionally, this sealing is carried out using gutta percha points and a sealant [2]. A number of materials have been used as the cement sealant including, in recent years, glass-ionomer cements. For this purpose, glass-ionomers have excellent adhesion, including to human radicular dentine [3], and also they release fluoride, an element with known antimicrobial properties [4].

Glass-ionomers have been used in other areas of restorative dentistry for approaching 30 years. Invented and originally described by Wilson and Kent [5], they consist of a basic glass powder and a water-soluble acidic polymer, such as poly(acrylic acid). The glass powder is a calcium (or strontium) aluminofluorosilicate [6]. Setting occurs by neutralization, and involves initial formation of calcium or strontium polyacrylate and later formation of aluminium polyacrylate. There is also evidence for a later, slow reaction involving the ion-depleted inorganic species from the acid-attacked glass [7, 8].

The occurrence of a variety of ions in glass-ionomers makes them capable of releasing ions to surrounding storage media [9]. Of these, the most widely studied has been fluoride. This has been shown to be released over periods of several years [10], and to be released by a mechanism involving, in part, diffusion-control [11].

Other ions are also known to be released, with proportions varying with pH of the external medium. Sodium (a minor constituent of the glass), aluminium, silicon and phosphorus have been shown to be released under all conditions [12], though only minor amounts of calcium(or strontium) have been detected under neutral conditions [13]. Acidic conditions enhance release of all ions, and cause relatively large amounts of calcium to be released [12]. This enhanced release in acid is not uniform, but occurs to different extents for each ion [12]. Despite these diferences, this ion release tends to lead to fairly uniform shifts in pH of the extraction medium towards neutral [14, 15].

B. Czarnecka · H. Limanowska-Shaw
Department of Biomaterials and Experimental Dentistry, University of Medical Sciences in Poznan, POLAND

R. Hatton · J. W. Nicholson (✉)
Medway School of Science, University of Greenwich, Chatham, UNITED KINGDOM
e-mail: J.W.Nicholson@gre.ac.uk

Studies of the release of the ions Na, Ca, Al, Si and P (the latter of which occur as silicate and phosphate anions) have concentrated on restorative grades of glass-ionomer, and used conditions that might occur in the mouth, *ie* mildly acidic to neutral; in the present study, we have studied release of these ions from an endodontic grade of glass-ionomer. This material is designed to be slower setting than restorative grades, a feature which is likely to affect the extent to which ions are bound into the cement, especially soon after setting. Endodontic treatment may involve the use of calcium hydroxide cement for disinfection and stimulation of bone repair. It also usually includes the use of dilute sodium hypochlorite solution for sterilisation of the root canal system.

The aim of the study was to determine the extent of ion release from an endodontic grade glass-ionomer sealer, and how this was affected by the presence of either dilute sodium hypochlorite or saturated calcium hydroxde. In addition, for completeness, we have used both neutral and acidic storage conditions to determine the ion-release behaviour of the cement.

Materials and methods

The main material used in this study was the endodontic glass-ionomer cement Ketac Endo (3M-ESPE, Seefeld, Germany). In addition, for comparison purposes, the restorative grade cements Ketac Molar (3M-ESPE) and Fuji IX (GC) were also used. In each case, the material is supplied in capsules, and these were mixed on a vibratory mixing device (Linea TGC, Kent Dental), then extruded into cylindrical moulds of dimensions 6 mm height $\times$ 4 mm diameter. They were stored in the moulds for 24 hr at 37°C, then removed, weighed, and placed in storage solutions. One capsule contained sufficient material to fill one mould.

The following storage solutions were used: deionised water, 10 mmol dm^{-3} lactic acid, saturated calcium hydroxide (using GPR grade $Ca(OH)_2$ supplied by BDH, Poole, UK) and 0.6% sodium hypochlorite solution (Parcan solution, 3%, from Sepodont, Paris, diluted at 1 cm^3 in 20 cm^3 deionised water). Values of pH for each solution were determined prior to storage using a PHP-100-020M pH electrode (Whatman). Six specimens of Ketac Endo cement were stored in each type of solution, with each specimen exposed to an individual 5cm^3 volume of liquid. In addition, six specimens of Ketac Molar were stored in water, again with each specimen stored in 5cm^3.

After 1 week of storage, the specimens were removed, and reweighed. The pH of each individual solution was determined, then the solutions bulked and analysed for ion content (Na, Ca, Al, Si and P) using an appropriately calibrated Optima 4300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (Perkin Elmer).

Table 1 Details of interactions of Ketac Endo with storage solutions (Standard deviations in parentheses)

Storage solution	Initial pH	Final pH	Mass gain (%)
Water	7.0	5.9 (0.2)	+2.41 (0.79)
10 mmol lactic acid	3.1	4.5 (0.1)	+0.67 (0.37)
Sat. $Ca(OH)_2$	12.5	12.0 (0.5)	+3.33 (1.11)
0.6% NaOCl	10.9	7.0 (0.4)	+2.65 (1.41)

Table 2 Concentrations of ions from Ketac Endo in storage solutions (ppm)

	Water	10 mmol lactic acid	Sat $Ca(OH)_2$	0.6% NaOCl
Na	7.54	20.64	3.51	Excess
Ca	0.34	27.21	Excess	0.15
Al	3.70	24.46	0.00	0.30
Si	5.90	15.70	0.08	0.00
P	0.19	0.55	0.00	0.00

Table 3 Interaction of Ketac Molar and Fuji IX with water and corresponding ion release

	Ketac Molar	Fuji IX
Final pH	6.0(0.1)	6.5 (0.6)
Mass gain %	1.05(0.14)	1.20(0.10)
Ion release/ppm: Na	2.7	3.35
Ca	0.29	0.27
Al	1.73	1.71
Si	0.00	0.00
P	0.13	0.16

Changes in mass and pH were subjected to statistical analysis by one-way ANOVA as appropriate followed by the Neumann-Keuls test ($p < 0.05$).

Results

Changes in mass and pH of Ketac Endo specimens are shown in Table 1. There were no statistically significant differences between the values of mass gain for water, saturated calcium hydroxide or NaOCl. However, the net mass gain in lactic acid was significantly lower ($p < 0.05$) than for the other storage media.

Levels of ions released are shown in Table 2. For comparison, Table 3 shows equivalent data for the restorative grade cement Ketac Molar and Fuji IX in water.

Comparison of the data in the Tables shows that Ketac Endo took up significantly more water than Ketac Molar and Fuji LC, though made no significant difference to the final pH of the storage medium. Release of all ions was found to be higher from Ketac Endo than from the restorative grade cements.

Discussion

All storage media were buffered by the presence of Ketac Endo. The two alkaline media had their pH shifted towards neutral, though the change in saturated calcium hydoxide was only slight. The lactic acid solution had its pH shifted from a low value to a higher one, and similar pH shifts have been observed for several glass-ionomer cements stored in acidic solutions [12, 14]. Although there was a mass gain in lactic acid, it was significantly less than in the other media, which suggests that this is partly offset by erosive loss of cement of the type previous observed [12, 14].

In comparison with the restorative grade cements Ketac Molar and Fuji IX, Ketac Endo showed a greater gain in mass on storage in water but a similar shift in pH. It also showed a greater ion release.

Release of Na, Ca, Al, Si and P was found to occur in water though, as previously observed, the amount of calcium and phosphorus released was very low [9]. In lactic acid, release of all ions increased, though in the case of phosphorus, the increase was small. This is significant because inflamed tissue is acidic, hence to prevent the accumulation of damaging metal ions, chronic inflammation of periapical tissue should be dealt with prior to the use of a glass-ionomer sealant. Thus glass-ionomers cannot be recommended for single-session treatments. Instead, any inflammation should be treated separately (using calcium hydroxide paste) and, once it has healed, the root canal sterilised with sodium hypochlorite solution. Only then should a glass-ionomer be used to seal the root canal.

By contrast, ion-release was found to be reduced in both saturated calcium hydroxide and in 0.6% sodium hypochlorite. These solutions were chosen because of their clinical relevance since either or both substances may be introduced to the root canal during treatment. Conventional endodontic procedures involve rinsing and drying before sealing, but residues of these substances may remain in the root canal. In this case, release of ions by the cement would be suppressed.

Of the ions detected, aluminium is a slight cause for concern. In endodontics, it can be transferred only to the periodontal ligament, and thence to the surrounding bone. Aluminium is known to accumulate in the bone mineral where, because if its small size, it is able to occupy suitable vacancies within the hydroxyapatite crystal structure [16]. Cell culture studies have shown that osteoblasts are capable of attaching to glass-ionomer cements and, having done so, to function satisfactorily and produce extracellular matrix [17]. However, they take up aluminum from the substrate [18], and this leads to the deposition of bone with a deficient mineral structure [19]. It has been demonstrated that aluminum remains in bone surrounding glass-ionomer cement for at least 12 months following implantation [20], where it partly inhibits the osteogenic response [19] and leads to the demonstrated development of deficient bone [21]. However, the concentration of aluminium that has been shown to cause these adverse effects is very much higher than we have found to be released by the restorative grade glass-ionomer cements, *ie* of the order of 1000 ppm [19], compared to a maximum of approximately 25 ppm that we have found. This suggests that any damage to the surrounding bone caused by expression of aluminium from the apex of an endodontically restored tooth is likely to be small.

Conclusions

The endodontic grade glass-ionomer Ketac Endo has been shown to release reasonable amounts of sodium, aluminium and silicon, and also traces of calcium and phosphorus under neutral conditions. It was also shown to take up water. By comparison with restorative grade materials, ion release was greater, as was water uptake. The shift in pH, however, was not significantly different.

In other media, ion release was altered. In lactic acid, it increased, whereas in either saturated calcium hydroxide or 0.6% sodium hypochlorite, it decreased. The latter ion-rich media thus suppress ion-release from the cement, a factor that may be significant clinically. Aluminium is of some concern, because of its well documented adverse biological properties. However, amounts released were low compared with levels required to show biological damage. Overall, we conclude that the use of this material as an endodontic sealer, when used in association with either calcium hydroxide or sodium hypochlorite, is likely to be safe and is therefore clinically acceptable.

Acknowledgement We thank the UK Engineering and Physical Sciences Research Council for the provision of a Visiting Fellowship (to BC) to allow her to work at the University of Greenwich.

References

1. T.R. PITT FORD, The restoration of teeth. (Oxford: Blackwell Scientific, 1985).
2. K. J. ANUSAVICE, Phillips' Science of Dental Materials, (Philadelphia: W.B. Saunders, 1996).
3. R. WEIGER, T. HEUCHERT, R. HAHN AND C. LOST, *Endodont. & Dent. Traumatol.* **11** (1995) 214.
4. A. K. MICKEL, P. SHARMA AND S. CHOGLE, *J. Endodont.* **29**(2003) 259.
5. A. D. WILSON AND B. E. KENT, *J. Appl. Chem. Biotechnol.* **21** (1971) 313.
6. R. G. HILL AND A. D. WILSONHILL RG, *Glass Technol.* **29** (1988) 150.
7. S. MATSUYA, T. MAEDA AND M. OHTA, *J. Dent. Res.* **75** (1996) 1920.
8. E. A. WASSON AND J. W. NICHOLSON, *Br. Polym. J.* **23** (1990) 179.

9. A. D. WILSON, D. M. GROFFMAN AND A. T. KUHN, *Biomaterials* **6** (1985) 431.
10. L. FORSTEN, *Scand. J. Dent. Res.* **98** (1991) 179.
11. R. M. H. VERBEECK, E. A. P. DE MAEYER, L. A. M. MARKS, R. J. G. DE MOOR, A. M. J. C. DE WITTE, AND L. M. TRMPENEERS, *Biomaterials* **19** (1998) 509.
12. B. CZARNECKA, H. LMAINOWSKA-SHAW AND J. W. NICHOLSON, *Biomaterials* **23** (2002) 2783.
13. S. CRISP, B. LEWIS AND A.D. WILSON, *J. Dent.* **8** (1980) 68.
14. J. W. NICHOLSON. B. CZARNECKA AND H. LIMANOWSKA-SHAW. *Biomaterials* **20** (1999) 155.
15. J. W. NICHOLSON AND M. A. AMIRI, *J. Mater. Sci. Mater. Med.* **9** (1998) 549.
16. P. J. ATKINSON AND S. WITT, Characteristics of bone, In: D. C. SMITH and D. F. WILLAIMS (Eds), Biocompatibility of dental materials, (Boca Raton, Fl: CRC Press, 1985).
17. U. MEYER, D. H. SZULCZEWSKI, K. MOLLER, H. EIDE AND D. B. JONES, *Cells & Materials* **3** (1993) 129.
18. U. MEYER, D. H. SZULCZEWSKI, R. H. BARCKHAUS, M. ATKINSON AND D. B. JONES. *Biomaterials* **14**(1993) 917.
19. D. H. CARTER, P. SLOAN, I. M. BROOK AND P. V. HATTON. *Biomaterials* **18** (1997) 459.
20. P. V. HATTON AND I. M. BROOK, *Micron Microsc. Acta* **23** (1992) 363.
21. K. H. W. LAU, A. YOO AND S. P. WANS, *Molec Cell. Biochem.* **105** (1993) 93.