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LETTER

The influence of ultrasonic setting on fluoride release from glass polyalkenoate cements

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Glass polyalkenoate cements (GPCs) are formed by the reaction of an ion leachable alumino-silicate glass with an aqueous solution of poly(alkenoic) acid (PAA). Water is used as the reaction medium. This acid–base reaction, whereby the acid attacks and degrades the glass structure, results in the formation of a hydrogel polysalt matrix [1].

GPCs can be formulated to release fluoride [2, 3] and this can remineralise enamel and softened dentine [4]. Fluoride release and its cariostatic effect will become more important with the increasing use of tooth saving preparation methods, such as tunnel techniques where there is a greater risk of leaving carious dentine behind than with conventional box cavities.

There is extensive literature on fluoride ion (F^-) release from GPCs [5–7]. However, there is little consensus on the possible mechanism of release, or the relationship between glass composition and release rates. Kuhn and Wilson [8] hypothesized that F^- release occurs principally by a counter ion mechanism where one F^- is released along with a positively charged counter ion. Hill et al. [9] have shown that the major mechanism of release is by an ion exchange process, with F^- being exchanged for a hydroxyl ion (OH^-).

GPCs are now being developed for use as in situ cements for medical applications [10] where biocompatibility of the cement is important. F^- release can stimulate apatite deposition in bone [11] as well as osteoblast mitosis. However excessive release has been associated with a cytotoxic response [12–15]. The ability to both control and understand F release is critical for optimising the biocompatibility of GPCs. Stanislawski et al. [16] analysed the possible cytotoxicity of some ions, including fluoride, from six GPCs and found that while the F^- release varied between each of the cements the concentration was too low to be toxic to pulp cells. This was in agreement with Muller et al. [17] where F^- release from GPCs was of a level that would be beneficial in vivo.

The authors have previously shown that GPCs can be command set by ultrasound imparted from a dental scaler [18–20]. However, such command setting, whilst known to improve the mechanical properties of the resultant cements, may have a deleterious effect on ion release as the pathways for release may be compromised.

This letter compares F^- release from a series of GPCs that have been set both chemically and ultrasonically. The following GPCs were assessed:

- Ketac Cem (KC) GPC (ESPE, Germany); Batch #165450.
- Fuji I (FI) GPC (GC, Japan); Batch #0306041.
- Experimental GPCs. These cements were based on two different aluminosilicate glasses. Both glasses contained silica, alumina, phosphate and strontia, but the first glass, A, contains half strontium, half calcium, whilst the second, B, is fully strontium substituted.

$$4.5SiO_2.3Al_2O_3.1.5P_2O_5.3SrO.2CaF_2 \quad (A)$$

$$4.5SiO_2.3Al_2O_3.1.5P_2O_5.3SrO.2SrF_2 \quad (B)$$

These glasses were mixed with two different PAAs; E7 and E8 (Advanced Healthcare Limited, Kent, UK). The molecular weights of the PAAs are included in Table 1. Tartaric acid (TA) was incorporated at 10 wt%. The

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powder:acid:liquid (P:A:L) mixing ratio (glass:acid:water/TA solution) used was 9:2:4; designed to mimic the handling properties of the commercial GPCs.All the GPCs were hand mixed, with a spatula, on a glass slab. Mixing of the commercial GPCs took place in accordance with the directions supplied by the manufacturers. The ultrasonic equipment employed was a Piezon® Master 400 dental scaler (EMS, Nyon, Switzerland), with a frequency of 25–30 kHz. The insert used (DS-003) was developed for scaling applications.

Ten samples from each GPC were prepared for each maturation time. All cements were mixed and placed in 5 mm steel split ring moulds, pressed between PMMA plates and set in an oven at 37 °C (1 h). Five samples for each maturation time was exposed to 30s of ultrasound prior to being placed in the oven. Ultrasound is imparted from the scaler directly onto the surface of the GPC. After setting, each sample was placed in 25 cm^3 of distilled water and stored at 37 °C. The water was tested at 1, 7, 30 and 90 day intervals for F release.

The water was decanted from each sample into a clean beaker. 5 cm^3 of TISAB III was added and the solution was then diluted to 50 cm^3 with distilled water. The potential of each sample solution was then measured and the concentration of F^- present was assessed from a standard curve. The average mass of the samples was 0.0417 g. The amount of fluoride (ppm) per gram of cement was calculated.

Figure 1 shows the extent of F^- release from each of the GPCs. Figure 1a represents the release from the chemically set samples and Fig. 1b represents the release from the ultrasonically set samples. Depending upon the cement in question, there is up to a 40% increase in F^- release from the ultrasonically set samples. Regardless of setting regime, the commercial samples exhibited a greater F^- release than the experimental GPCs.

It is outside the remit of this study to compare the ion release from the different GPCs with each other with respect to composition. Rather, this study attempts to show the effect on ion release caused by the setting regime. A series of GPCs were examined to show that increased release occurs, to some extent, regardless of GPC composition.

The authors have previously shown that ultrasonic setting of luting GPCs results in increased compressive strength and a snap set [21]. The results contained herein show that there is a greater release of fluoride from the ultrasonically set samples than those set chemically, regardless of the GPC composition. This is surprising as the increased speed of set and more integral network,

Table 1 Molar mass details of the PAAs

CODE	Mw	Mn	PD
E7	25,700	8,140	3.2
E8	51,900	21,900	2.4

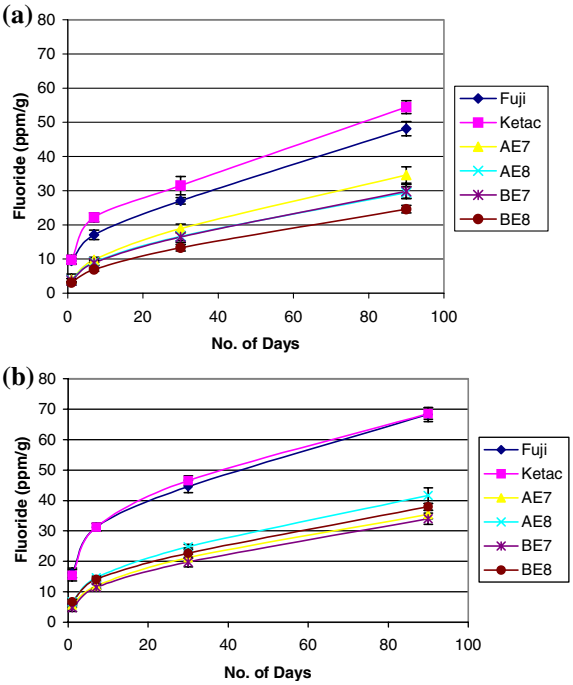

Fig. 1 (**a**) Cumulative fluoride release from chemically set GPCs. (**b**) Cumulative fluoride release from ultrasonically set GPCs

implied by the increased mechanical properties [21], would be expected to retard ion release. The snap set caused by the ultrasound is likely to be due to a combination of cavitation, improved mixing of the constituents and better compaction. Cavitation has previously been observed in GPCs where mean particle size was reduced after ultrasonic application [18] indicating that collisions between particles are occurring. The reduction in mean particle size may also be a result of breaking up agglomerates of particles. This offers a greater glass surface area for reaction with the acid thereby explaining the increased speed of set with ultrasonically treated GPCs. The authors postulate that the increase in ion release from ultrasonic setting may be due to the increased surface area of glass, which would allow higher levels of ion release into the surrounding environment whilst also accelerating the speed of set.

From this and previous studies by the authors [18–21], it is evident that ultrasonic setting results in improved cements for dental applications as setting time, mechanical properties and therapeutic ion release are optimised. Such materials could have great commercial benefit in the orthodontics field where ultrasound can be applied, through a dental bracket, to command set the cement and hold the orthodontic appliance firmly in place. The cement would release high levels of therapeutic ions, thereby retarding the onset of secondary caries around bridges and brackets.

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