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The effect of ultrasound on the uptake of fluoride by glass ionomer cements

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Abstract Ultrasound has been shown to improve the set of glass ionomer cements (GICs) and also other cement properties. In particular, the release of fluoride is enhanced. These cements also can take up fluoride ion from liquids. The aim of this study is to investigate the effect of ultrasound on this cement property. Two commercial dental restorative GICs were used together with a modified commercial material and an experimental material based on a F-free glass. All three commercial materials came in capsules which were mixed as makers directed, the experimental material was mixed as in previous papers. Mixed cement was placed polyethylene moulds to create 3 × 2 mm thick discs. These were either allowed to standard set for 6 min or set with ultrasound for 55 s. 18 samples were made for each material/set. Three samples were placed in 4 ml of 0.2% NaF solution for 24 h at 37°C. The cylinders were removed and the F concentration of the solutions measured by ISE using TISAB decomplexant. F uptake was determined by difference from the original NaF concentration. The two conventional GICs showed reductions of 17.4 and 8.5% for ultrasound compared to standard set whereas the modified material increased by 32.3% and the experimental one by 20.6%. It is suggested that the effect of ultrasound may increase the surface area of the residual glass particles in the GIC which would increase F uptake. In GICs where considerable F ion is released into the cement matrix by the enhanced reaction caused by ultrasound this may be sufficient to reverse the former effect producing the reduced uptake observed.

1 Introduction

Glass ionomer cement (GIC) is formed by the acid–base reaction of a glass (generally alumino-silicate) with a polymeric acid (generally carboxylic). They are most often used in restorative dentistry both as filling materials and to cement crowns and bridges. They were derived from an earlier glass based cement (dental silicate cement DSC) in which the acid component was mainly phosphoric acid. In common with DSC glasses GIC glasses are normally formed using metal fluorides as fluxes. In the earliest GICs calcium fluoride and sodium aluminium fluorides were used [1]. Subsequent materials used strontium fluoride [2]. Both GICs and DSCs release fluoride into aqueous liquids. In the oral environment this gives rise to beneficial effects on adjacent tooth tissue [3, 4].

The kinetics of release of fluoride from GICs were investigated and found to have a linear relationship with $t^{1/2}$ (where t is time) after the first few days [5]. Although this was shown to continue for up to 5 years [6, 7] the release versus t naturally diminished considerably.

In 1986 Walls suggested that GICs could possibly take fluoride from toothpaste, mouth wash, gels, etc. [8]. This was indicated by enhanced release after such exposure in vitro [9, 10] and in vivo [11]. This, however, did not provide direct proof of uptake (such exposure might have increased the release of inherent fluoride) but subsequent studies did show very high uptake to occur [12–14].

GICs had several properties that were advantageous in their dental use. In addition to fluoride release they had direct adhesion to tooth tissue, low setting shrinkage, coefficient of thermal expansion close to tooth, low creep, and good colour stability. However they had setting characteristics that were less satisfactory and left the cement vulnerable to early exposure to moisture [15, 16].

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Resin-based materials were better in this respect and use of external radiation (u.v. or visible light) to initiate their polymerisation improved this and gave the clinician greater control over the setting process ("command set").However the addition of resins produced adverse effects on abrasion resistance, dimensional stability, colour stability and possibly biocompatibility. Recently, both ultrasound and radiant heat have been reported to provide similar set improvement in GICs [16, 17]. Both are reported to enhance physical properties [17, 18] but whereas ultrasound increases fluoride release radiant heat decreases it [19].

This study aims to determine the effect of ultrasound on the uptake of F ions by three commercial GICs on which the effect of ultrasound on F ion release has been reported [19]. For one of these for which the use of radiant heat to accelerate setting is recommended by the makers, the effect on uptake will be compared with that on release [19].

2 Materials and methods

Two conventional GIC's were used GC Fuji IX (GC Dental, Japan) (FIX) and Amalgomer (Advanced Healthcare Ltd, UK) (AM) which is composed of AH2 glass powder and polyacrylic acid homopolymer. Glass Carbomer (Glass Carbomer, Holland) (GC) was a modified GIC. It contains fluorapatite as a secondary filler and the reactive glass has been treated with dialkyl siloxanes (described in European Patent 20040748628). All three GICs were in capsule presentations. LG30 is a "fluoride-free" glass developed at Limerick University.

The composition of the glasses determined by analysis (Ceram Research) are shown in Table 1.

2.1 Capsule mixing

After activation the capsule was placed in a rotating mixer, Rotomix (3M-Espe) for 10 s as per manufacturer's instructions. The mixed capsule was then loaded into the gun. A polyethylene mould of dimensions 3 mm diameter and 2 mm thick discs was placed on a sheet of acetate and the mixed cement was injected into the mould, then covered with acetate sheet. The acetate sheets were used to obtain a flat surface area of each specimen, therefore ensuring that the dimensions remained the same. The specimens were then left for 6 min to standard set.

Table 1 Weight percentage composition of GIC glasses (remainder oxygen)

Element	Si	Al	Ca	Na	F	P	Sr	La
FIX	13.7	17.9	0	1.0	10.2	2.2	19.9	0
AH2	18.7	15.8	7.1	5.5	12.9	1.6	0	0
GC	20.0	14.1	2.1	1.9	9.0	2.5	13.6	0
LG30	14.6	18.1	13.9	0.05	0.04	6.4	<0.01	<0.01

2.2 Ultrasonic curing

A further set of 18 specimens were prepared for all three materials and set using a flat tipped ultrasonic hand piece, the ultrasound was applied to the cement that was employed using EMS Piezon Master 400 Dental Scaler that was set on the maximum setting on the acetate sheet, and no coolant water was released. The flat tip of the scalar was moved continuously on the surface in a uniform manner over the acetate sheet where the ultrasonic waves penetrated through into the cement for 55 s until cement was set [19, 20].

2.3 Heat curing

The mixed GC cement was placed in the mould where an acetate sheet was placed on the surface. The heat was applied using a Flashlite 1400 (Discus Dental) light curing with an intensity of 1200 mW for 90 s. 18 cylinders were produced. Lamp and irradiation time were both as recommended by the manufacturer.

All samples were transferred to a 37°C air oven for 1 h. Eighteen cylinders were produced for each experimental condition and material. Three cylinders were dropped into 4 ml of 0.2% NaF providing $n = 6$ for each material/setting condition. They were stored stoppered in an incubator at 37°C for 24 h. The GIC cylinders were then removed.

The original NaF solution and the samples that had been in contact with the GIC cylinders were analysed for fluoride concentration using ion selective electrode potentiometry. TISAB IV was added to all samples including the calibration solutions as a decomplexing agent. The concentrations of F ion were determined by comparison with a series of decade control solutions. Uptake was calculated by difference between samples and original NaF solution.

3 Results

The uptake values are given in Table 2. Both conventional commercial glass ionomer AM & FIX show significantly reduced uptake for ultrasonic set compared to standard set. In contrast, GC and LG30 showed increased uptake. In contrast to the increase shown by GC with ultrasound the heat cured material showed almost no uptake. It was observed that the solutions were cloudy as contrasted to the SC and US solutions which were clear. These results for fluoride uptake and percentage change in uptake are shown in Table 2 and Fig. 1.

Table 2 Fluoride uptake (mg F/g cement) and percentage change in uptake

	GC	FIX	AM	LG30
Self cure	121.7	105.8	130.8	86.9
Ultrasound cure	161.0	96.8	108.1	104.8
Significance level of difference	0.01	0.05	0.02	0.01
% Change	+32.3	−8.5	−17.4	+20.6
Heat cure	1.23	–	–	–

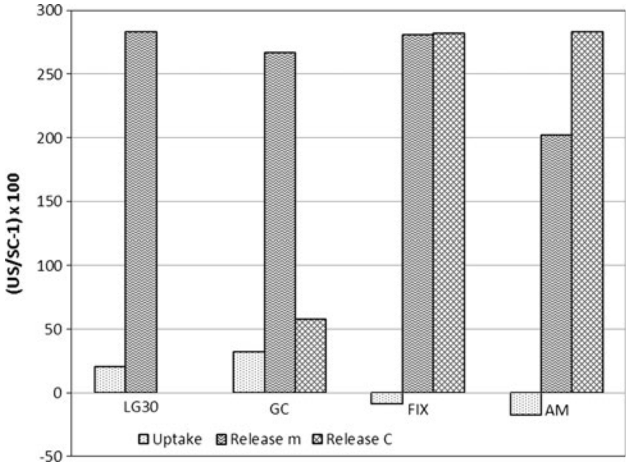

Fig. 1 Comparison of difference from self-cure to ultrasonic cure

4 Discussion

For the two conventional GICs FIX and AM the reduction in the F uptake by ultrasound is statistically significant with $P \leq 0.05$ (Student '*t*' test). In contrast the unconventional GC showed increased uptake as did the nominally fluoride free LG30 (both significant $P = 0.01$). This differs from release, where not only are the levels from standard set samples similar, but so are the effects of ultrasound [19] as shown in Table 3. A comparison of the differing effect of US (compared SC) is shown in a bar chart Fig. 1. The fluoride release is characterised by the slope (m) and intercept (C) of the regression equation of cumulative F release versus $t^{1/2}$. The former characterising the steady long term rate of release and the latter an indication of the initial non-linear "wash-out" phase [21].

Table 3 Change in F release as function of US/SC for m and C of linear regression equation [19]

	GC	FIX	AM	LG30
SC m	0.212	0.083	0.125	0.212[a]
US m *HC*	0.345 *0.102*	0.316	0.378	0.812[a]
% Change m	+267	+281	+202	+283
SC C	0.064	0.112	0.076	–
US C *HC*	0.101 *0.036*	0.428	0.291	–
% Change C	+58	+281	+283	–

[a] The figures for other materials are mg F/g cement whereas these are in µg/g

The reduced uptake produced by ultrasound is unexpected in that the F release rate generally relates positively to uptake [21]. However, the exact mechanism by which glass ionomers take up such large quantities of fluoride ion is not fully understood. The level of F in the cement expressed as a ratio of concentration in immersing fluid to that in the water content in the cement range from 1:16 to 1:56 [22]. These high internal concentrations exceed the solubility product of the fluoride source used [NaF]. It is therefore clear that the F ions are also taken up into other parts of the cement structure. Previous dynamic SIMS shows the F concentration to be greatest at the surface and to diminish with depth following an "error curve" relationship [23]. A more detailed study using XPS found that the F ion taken up was associated with Ca on a molecular level [24]. Presumably not as CaF_2 since this is insoluble whereas the F taken up is re-released from LG30 completely in 100 days [22]. From both studies it is clear that F ion taken up is differently distributed in the cement to its alkali metal counter ion, although taken up in roughly equal amounts. The cations are distributed throughout the cement, presumably in the polycarboxylate cement matrix. In contrast Jones et al. [24] postulate "…the reaction is heterogeneous across the surface, possibly as a result of enhanced reaction in the vicinity of agglomerates of residual glass particles within the polymer matrix". A more recent study showed that particles of the glass component of the cement can take up equivalent quantities of F ion to cements [25]. It therefore seems that the association of F is with Ca within the structure of the glass (or the depleted zone surrounding it in GICs). This would explain the ability of the cements to re-release F ion as contrasted to CaF_2 which does not enhance F release when added to an F-free GIC [26].

The effect of ultrasound on the set of GICs is not precisely understood. In general, the effect of ultrasonic radiation in enhancing chemical reactions has been widely reported for the last 70 years. The enhancement is produced in liquid or solid/liquid systems. Micro-cavitation occurs in the liquid and the collapse of these microscopic "bubbles" produces very high temperatures (2,000–4,600 K) [27] but these are extremely localised. The effects of these are to produce actions such rupture of covalent bonds in molecules that are stable at "bulk" temperature of the system [28]. One paper does postulate the mechanism that may occur in the ultrasonic setting of GICs [29]. The ultrasound is thought to act by changing the particle size distribution either by breaking up aggregates or even fracturing glass particles. The authors demonstrate this by applying the low energy ultrasound of a particle size analyser to GIC glass for a prolonged period and measuring particle size at the start and finish of ultrasound application. The present authors repeated this with GIC glass and provided further support for the theory by showing a greater change in particle size with zinc polycarboxylate cement which is more sensitive to ultrasonic setting [30]. Since it appears that some or probably most of the F taken up goes into or onto the glass it would be expected that particle size reduction and consequent surface area increase would result in increase in uptake for all materials.

In addition to these changes affecting uptake *within the cement*; at the cement surface ultrasound might produce a different effect. It was established in 1986 that neutral fluoride solution adversely affected GIC surface [31]. This was quantified in terms of change in surface roughness (Ra) and found to only affect F-containing GICs [32]. In particular, LG30 was unaffected whereas GIC based on AH2 (as is AM) was significantly roughened. LG30 was included in this study and showed no effect. In previously unpublished tests (Table 4) the effect of ultrasound on this effect was found to reduce the roughening (compared to standard set) for GICs based AH2 and G338 (a similar glass to AH2, used in ChemFil products). The effect of US relative to SC for AH2 is a 13.9% reduction in Ra similar to the 17.9% reduction in uptake found for AM. The change in Ra is just statistically significant $P = 0.05$.

In attempting to explain the reduced uptake exhibited by AM and FIX the effect on the intercept of the F release kinetic plots [19] (given in Table 3) may also be relevant. AM and FIX show very great increases with ultrasound whereas GC does not and the levels of C in LG30 are very low indeed (due to its having only impurity level of F). Previously LG30 was used in a study of interactions of GICs with NaF solution. It was shown that adding NaF to this cement made it interact like GICs with F in their glass component except for uptake was reduced by 38% [32]. This contrasts to the increased uptake of 60% found when the F content was increased in the glass component [33]. A possible explanation of the reduction in uptake for AM and FIX is that ultrasound causes so much F release from glass into the polyacid cement matrix (as indicated by high C values, see Table 3) that uptake is reduced in the same way as found for NaF additions [32]. Although GC glass has similar F level to FIX it is possible that the siloxane coating of the glass particles referred to in the patent (European Patent 20040748628) may reduce this effect of ultrasound.

Table 4 Effect of ultrasound on the surface roughening (R_a values) of GIC by NaF ($n = 18$)

	AH2	G338
Self cure H_2O	0.881 s.d. 0.550	0.524 s.d. 0.142
Ultrasound H_2O	0.945 s.d. 0.517	1.039 s.d. 0.200
Self cure NaF	2.842 s.d. 0.715	2.287 s.d. 0.128
Ultrasound NaF	2.447 s.d. 0.346	2.086 s.d. 0.709

The effect of radiant heat on GC is very dramatic. Even greater than its changes in release [19] shown in Table 3. Only the makers of GC advocate the use of this method of accelerating cure. Future studies should evaluate the effect of radiant heat on other materials. It would also seem desirable to evaluate the effect on surface roughening since low uptake is usually associated with low levels of roughening.

5 Conclusions

Ultrasonic setting can influence uptake of F ions from solution but the changes are much less than those produced by ultrasound on F release. Whereas F release is increased the effect on uptake varies from material to material. Increased uptake is probably related to reduction in glass particle size. In GICs where considerable F ion is released into the cement matrix by the enhanced reaction caused by ultrasound this is apparently sufficient to reverse the former effect producing reduced uptake.

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