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The effect of ultrasound on the setting reaction of zinc polycarboxylate cements

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Abstract The set of glass ionomer cement (GIC) is accelerated by application of ultrasound. Although GIC has somewhat displaced zinc polycarboxylate cement (ZPC) in dental applications the latter is still extensively used. Like GIC, it provides direct adhesion to tooth and can provide F release, but is more radiopaque and biocompatible than GIC. The aim of this study is to examine the effect of ultrasound on the setting of ZPC using Fourier transform infra red spectroscopy and any interaction with SnF_2 addition. ZPC with and without SnF_2 addition (+/−S) at luting (L) 2:1 P/L ratio and restorative (R) 4:1 P/L ratio consistencies. Ultrasound is applied to the cement using Piezon-Master 400, EMS, Switzerland at 60 s from start of mixing for 15 s. The ratios of absorbance peak height at 1,400 cm^{-1} $–COO^-$ to that at 1,630 cm^{-1} –COOH were measured and compared those obtained for the cement not treated with US. These values were taken at the elapsed time at which no further change in spectrum [ratio] was observed at room temperature [10–20 min]. The US results are taken at 2 or 3 min. No US: R/+S (1.09), R/−S (1.2), L/+S (1.07), L/−S (1.04); US: R/+S (1.50), R/−S (1.64), L/+S (1.38), L/−S (1.05). The results show all four ZPC formulations are very sensitive to ultrasound whether with or without SnF_2. Reducing US to 10 s produces lower initial ratios but these increase up to 10 min when very high ratios (>2) are obtained. Previous studies with restorative GICs found that 40–55 s US was needed to produce the effect found with 15 s on ZPCs. ZPC powder is more basic than GIC glass; this may account for ZPC's greater sensitivity to US. Ultrasound may provide a useful adjunct to the clinical use of ZPC both as luting agent and temporary restorative.

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1 Introduction

Ultrasound has been extensively used in dentistry for many years. Its major uses rely on its ability to enhance cleaning; removal of plaque and tartar from tooth surfaces and the debridement of the root canal prior to root filling. In addition ultrasonic vibration has been used to facilitate removal of fixed postheses (crowns and bridges). Early uses in restorative dentistry relied on ultrasound's effects on viscosity and voids. One commercial resin cement (Sonocem, ESPE GmbH) which had viscosity for handling purposes was designed so that the viscosity decreased on application for ultrasound to allow for seating of the prosthesis. An additional attachment was provided for the Cavitron ultrasonic scaler which was designed to condense amalgam. Although this provided improved properties it was found to create a *spray* of mercury droplets and was discontinued.

The use of ultrasonic vibrations to change the setting of glass ionomer cements (GIC) was reported by Towler et al. [1]. GIC are one of the class of polyalkenoate acid–base cements in which the acid is a carboxylic acid polymer (normally polyacrylic acid or a copolymer of acrylic acid). Several studies have confirmed the effect of ultrasound on GIC; both in respect of effect on the initial setting reaction [2] and on the properties of the set cement [3, 4].

Glass ionomers are not the only polyalkenoate cements used in dentistry. Zinc polycarboxylate was introduced to the dentist's armamentarium some years before glass ionomer. The latter has advantages over the former in the

areas of strength, translucency, acid resistance, and inherent fluoride release. Zinc polycarboxylate has excellent biocompatibility, resistance to early exposure to moisture, higher radiopacity, easier removal and lower cost. These comparisons are particularly relevant to uses as a luting cement. Although zinc polycarboxylate has no inherent fluorine content the addition of stannous fluoride was patented by Foster and Dovey [5]. Since this addition not only enhances the compressive strength [5] but also reduces susceptibility to acid erosion [6] it is extensively utilised. This addition also provides appreciable and sustained fluoride ion release [7]. In view of these properties it was decided to investigate the effect of ultrasound the setting reaction of zinc polycarboxylate using FTIR-ATR as previously used to investigate the effect on glass ionomers [2]. Although the main use of zinc polycarboxylate is as a luting agent it is also used as a base and temporary filling so two cement consistencies were investigated. In addition, the effect of stannous fluoride addition was evaluated.

2 Materials and methods

As most commercial zinc polycarboxylate powders contain stannous fluoride, a zinc cement powder was used to which stannous fluoride could be added. This was SS White Improved No. 1 (B/N B1388930). Note both zinc cement powder and zinc polycarboxylate powder are 9:1 zinc oxide: magnesium oxide. Stannous fluoride was blended into form 5% of the powder by weight. The liquid used was a 35% solution of a homopolymer of acrylic acid (Advanced Healthcare Ltd B/N 020314-1). When mixed as at a base consistency the powder liquid ratio was 4:1 and 2:1 as a luting consistency. All materials were mixed for 30 s.

To produce reference spectra of zinc, magnesium, and tin (stannous) polyacrylate the polyacrylic acid was mixed with pure zinc, magnesium, or tin (II) oxide. Additionally it was mixed with stannous fluoride. The four spectra are shown in Figures 1, 2, 3, and 4 respectively.

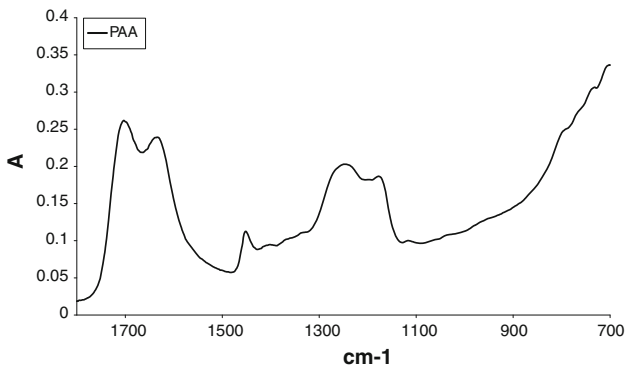

Fig. 1 FTIR spectrum of 40% PAA

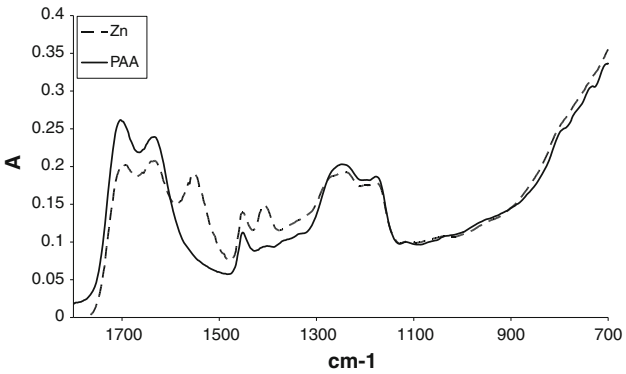

Fig. 2 FTIR spectra of 40% PAA and ZnO reacted with PAA

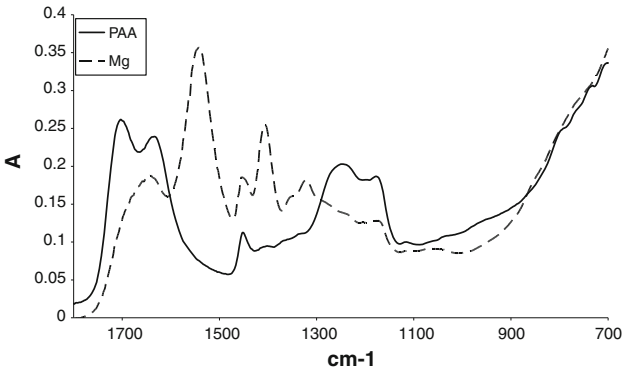

Fig. 3 FTIR spectra of 40% PAA and MgO reacted with PAA

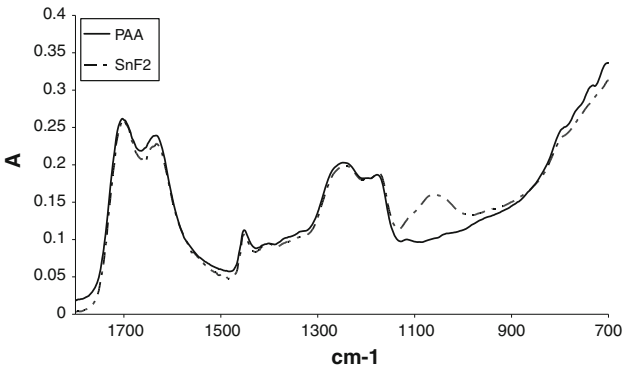

Fig. 4 FTIR spectra of 40% PAA and SnF_2 reacted with PAA

The ultrasound was applied to the mixed cement sandwiched between two sheets of plastic. The ultrasound was applied using a flat bladed scaler attachment of a Piezon-Master 400 (EMS Switzerland) shown in Fig. 5. The power setting used was that previously found to be optimal in setting glass ionomers [2]. Pilot studies found that whereas 55 s was optimal for setting restorative glass ionomers [2] only 15 s was required for zinc polycarboxylates.

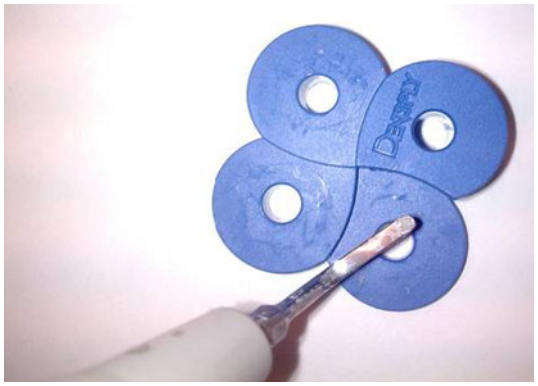

Fig. 5 Application of ultrasound to cement

The cement was transferred to the "Diamond Window" of a Spectrum GX infrared spectrometer. The FTIR-ATR spectra were recorded from 1,800 to 700 cm^{-1} the region in which the change from carboxylic acid to carboxylate salt groups is observed. As in the GIC this change is observed as a reduction of the –COOH peak at 1,700 cm^{-1} and an increase in the $–COO^-$ peak at 1,400 cm^{-1}. Spectra were recorded at times up to 1 h after the start of mixing.

3 Results

The ratio of peak heights is expressed as 1,400/1,700 cm^{-1}. These are shown in Table 1 at the time when no further increase is shown on subsequent spectra. For ultrasound (15 s duration) this was 10 min or less whereas without ultrasound times of up to 45 min were found before no further change in ratio was observed. (Note the ratio for PAA is 0.31.).

When ultrasound was applied for only 10 s the time to reach unchanged ratios was longer than with 15 s, but the ratios finally achieved were higher than 15 s ones being 2 or greater.

4 Discussion

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 to 4,600 K) [8] 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 [9].

Table 1 Ratio of peak heights expressed as 1,400/1,700 cm^{-1}

	Luting (without SnF_2)	Luting (with SnF_2)	Restorative (with SnF_2)	Restorative (without SnF_2)
No US	1.04	1.07	1.20	1.09
US	1.05	1.38	1.64	1.50

The effect of ultrasound on zinc polycarboxylate is similar to that produced on glass ionomer. The much shorter ultrasound duration compared to that needed for glass ionomer may possibly be due to disintegration of the powder particles creating a much larger surface area. This would be more likely with an effectively sintered particle compared to fused glass. The major effect of cement composition is that of powder/liquid ratio. In each case the restorative: luting ratio is greater than one. In contrast the presence of SnF_2 has no uniform effect.

The ratios obtained are very similar to those found with restorative glass ionomers without ultrasound of 1.07 and 1.20 (after 60 min). However with ultrasound the ratios obtained of 1.14 and 1.18 (respectively) are almost unchanged whereas ultrasound increases restorative zinc polycarboxylate by 37 and 38%.

The spectra of polyacrylic acid reacted with zinc oxide and magnesium oxide (Figs. 2, 3) show that magnesium polyacrylate has a peak at $\sim$1,320 cm^{-1} not observed on the zinc polyacrylate spectrum. (It should be noted that the reaction with ZnO is far less complete than that of MgO although both oxides were present in considerable excess).The presence of this peak in the spectra of set cements whether with or without ultrasound indicates that an appreciable amount of carboxylate groups are attached to Mg. In the restorative consistency there 4.9 mmol of PAA to 9.9 mmol of MgO and 44.2 mmol of ZnO. However at a luting powder liquid ratio the values for the oxides are halved. Although Smith states that inclusion of MgO in the powder gives water sensitive materials [10] because of non-specific binding to PAA [11] analysis of zinc polycarboxylate powders by Bertenshaw and Combe [12] show it to be present in commercial materials. The level of the peak at 1,310 cm^{-1} indicates that carboxylate groups are reacted with Mg as well as Zn (Fig. 6). In luting consistency the ratios of 1,310 cm^{-1} peak height to that 1,410 cm^{-1} is somewhat reduced compared to restorative as might be expected from the Mg:PAA molar ratios shown above.

No obvious spectral differences can be found between cements with and without SnF_2. Unsurprisingly adding SnF_2 to PAA produces no reduction in –COOH (Fig. 4). The additional peak at $\sim$1,050 cm^{-1} is not found in any of the $+SnF_2$ spectra. Attempts to produce a spectra of Sn polyacrylate by mixing PAA liquid with SnO showed no reduction of the –COOH peak.

The mechanism by which ultrasound enhances the setting speed of dental cements has been subject to some speculation. Although both ultrasound and heat increase

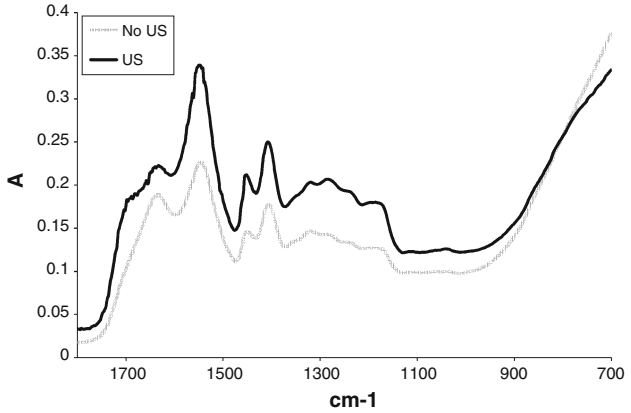

Fig. 6 FTIR spectra of ZPC with and without the application of ultrasound (taken at 5 min after start of mixing)

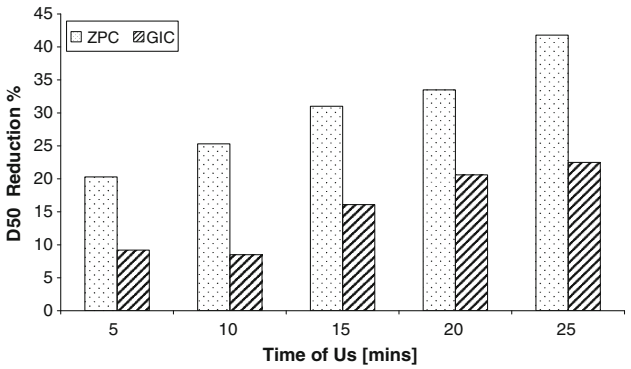

Fig. 7 Effect of ultrasound on particle size of GIC and ZPC

the speed of the setting reaction and ultrasound produces heat this is not sufficient to account for the increase observed. A recent study [13] on GICs showed that an effect produced by ultrasound (enhanced F release) was not produced by heat (F release was reduced).

The mechanism by which ultrasound enhances the setting rate of cements is not clearly established. Towler et al. [14] suggest that, in glass ionomers, ultrasound may increase powder surface area by breaking up aggregates or breaking down glass particles and this may account for increased reactivity. The powder of zinc polycarboxylate is produced by co-firing bricks of ZnO:MgO prior to comminuting these to a powder. These powder particles may be even more susceptible to such an effect and changes in particle size distribution when exposed to the much weaker ultrasound field in the particle size analyser (Fig. 7) provides some support for this hypothesis. The reduction in D_{50} (the point in the particle size distribution below which 50% of the particles lie) is almost twice that produced on glass of a GIC at all ultrasound duration. The effect on D_{10} was more variable.

The effect ultrasound on GICs enhances the bonding to tooth surfaces [4] and the release of fluoride [13]. It would seem sensible for further investigations to compare the effects of ultrasound on zinc polycarboxylates for the former and the ones containing SnF_2 for the latter.

This effect of ultrasound on the setting of ZPC can allow it to be used as a root end filling material, where it will accelerate the setting and improve the adaptation and sealing. Furthermore, since ultrasound will promote "command setting", ZPC could be used for bonding orthodontic brackets.

5 Conclusions

Ultrasound may provide a useful adjunct to the clinical use of ZPC both as luting agent and temporary restorative. The greater sensitivity of ZPCs to ultrasound as compared to GICs appears to be related to greater particle size reduction resulting in greater surface area for reaction accompanying the application of ultrasound.

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