01 Apr 2003

Investigation into the Ultrasound Setting of Glass Ionomer Cements. Part I. Postulated Modalities

Mark R. Towler
Missouri University of Science and Technology, mtowler@mst.edu

C. M. Crowley

R. G. Hill

Recommended Citation

M. R. Towler et al., "Investigation into the Ultrasound Setting of Glass Ionomer Cements. Part I. Postulated Modalities," *Journal of Materials Science Letters*, vol. 22, no. 7, pp. 539 - 541, Springer, Apr 2003.
The definitive version is available at https://doi.org/10.1023/A:1022946605523

JOURNAL OF MATERIALS SCIENCE LETTERS **22**, 2003, 539–541

Investigation into the ultrasonic setting of glass ionomer cements Part I *Postulated modalities*

M. R. TOWLER*
Materials and Surface Science Institute, University of Limerick, Ireland
E-mail: Mark.Towler@ul.ie

C. M. CROWLEY
Materials Ireland Research Centre, Plassey Park, Limerick, Ireland

R. G. HILL
Department of Materials, Imperial College, Prince Consort Road, London, UK

Glass ionomer cements (GICs) are formed by the reaction of an ion leachable alumino-silicate glass with an aqueous solution of poly (alkenoic acid). Water is used as the reaction medium [1]. An acid-base reaction occurs, whereby the acid attacks and degrades the glass structure, releasing metal cations which are then chelated by the carboxylate groups and serve to crosslink the polyacid chains. The cement consists of residual glass particles embedded in a hydrogel polysalt matrix [2]. The setting reaction in GICs is a continuous process evident by the increase in compressive strength of the cement with ageing time [3–5].

GICs undergo a two-step setting reaction. During the first step the material is susceptible to water uptake and during the second it is susceptible to dehydration. For example, when GICs are stored in water after an initial set of 15 min, a surface softening occurs, which may be caused by an inhibition of the setting reaction in a superficial layer of the cement [6]. This short-term relationship with water restricts the full potential of GICs for healthcare applications. It is for this reason that resin modified GICs (RMGICs) were developed. These materials, which are conventional GICs to which an organic, photo-polymerizable monomer has been incorporated [7], can be command set by the application of an intense light source. However, RMGICs have recognized drawbacks, related to the presence of both non-polymerized monomer and the resin itself [8, 9].

The authors have already shown that conventional GICs can be command set by ultrasonic excitation [10]. Ultrasound not only imparts an instant set to a GIC, but also imparts superior mechanical properties when compared to its chemically cured counterpart, particularly within the first 24 h after setting. The ultrasonically cured GIC does not require the incorporation of additional chemicals and therefore avoids the drawbacks associated with RMGICs.

In the previous study [10], nano-indentation testing was used to show that ultrasonically cured Fuji IX had hardness an order of magnitude greater than its chemically cured counterpart (Table I), while also exhibiting negligible creep, almost immediately after placement. This infers command setting of the surface area occurred due to the ultrasound.

The profound effect that ultrasound has been shown to have on the curing process is believed to be related, at least in part, to the way that the glass particles in the cement behave upon exposure to ultrasonic stimulation. To quantify this, Fuji IX was analyzed during exposure to different durations of ultrasound in an attempt to determine how the glass phase reacts. Cross sections of Fuji IX cement, set both conventionally and by ultrasound, were subsequently compared by microscopy.

All research was undertaken on one batch of Fuji IX (Lot No 0107165). The ultrasonic equipment employed was an EMS Piezon® Master 400 dental scaler (EMS, Nyon, Geneva, Switzerland). This equipment has a frequency of 25–30 kHz. The tip insert used (DS-003) was developed by EMS, for de-scaling applications. Comprehensive details of the ultrasonic procedure are available elsewhere [10].

Fuji IX glass is a low phosphate, low soda containing glass which has strontia incorporated as a radio-pacifier. The chemistry of the glass phase was determined by X-ray fluorescence (Ceram Research Ltd., Stoke-on-Trent, UK). This is shown in Table II.

Scanning electron microscopy (SEM) examination of the glass powder morphology was performed at magnifications of 1000 and 5000 using a Jeol JSM 840. All powders had been stored under vacuum and dried (10 h, 100 °C) prior to testing. The powders had been sputter coated with gold and were viewed using an accelerating voltage of 30 kV. From this it is evident that the larger glass particles are seen to have sub-micron particles "stuck" onto their surface, while smaller glass particles of approximately 1–2 μm coalesce.

The mean particle size, particle size distribution and specific surface area measurements of the glass phase of Fuji IX were determined using a Malvern Master Sizer 2000 (Malvern Instruments, Worcs, UK). Ultrasound was applied to the sample chamber for various

*Author to whom all correspondence should be addressed.

0261–8028

TABLE I Hardness values determined from nano-indentation cycles

	Hardness (GPa)		
Type of curing employed	Mean	Max	Min
Chemical curing	0.176	0.386	0.022
Ultrasonic curing	2.62	4.45	1.04

TABLE II Chemical analysis of the glass phase of Fuji IX

Compound	Fuji IX (wt%)
Silica	29.37
Titania	0.38
Alumina	27.91
Ferric oxide	0.08
Lime	0.06
Magnesia	<0.02
Potash	0.03
Soda	1.32
Phosphorus pentoxide	5.05
Chromium sesquioxide	<0.01
Manganic oxide	<0.01
Zirconia	<0.02
Hafnia	<0.01
Lead monoxide	<0.02
Zinc oxide	<0.01
Barium oxide	0.19
Strontia	24.67
Stannic oxide	<0.01
Cupric oxide	<0.01
Fluorine	10.20
Lanthanum oxide	<0.01

TABLE III Change in mean particle size and specific surface area of Fuji IX as a consequence of ultrasound of the aqueous dispersion

Time (minutes)	Obscuration (%)	S.S.A. (m^2/g)	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
0	8.25	1.24	2.249	6.777	19.235
3	8.36	1.39	1.977	6.605	19.14
5	8.49	1.48	1.846	6.49	19.374
7	8.63	1.52	1.835	6.448	18.615
10	8.54	1.56	1.771	6.426	19.170
14	9.04	2.47	1.355	6.199	20.079
17	8.98	2.73	1.197	5.963	18.798
21	8.98	3.4	0.960	5.520	17.156
25	8.89	3.19	0.994	5.771	19.164
29	9.14	3.14	1.092	6.746	28.632
32	9.22	6.32	0.342	5.171	17.889

durations and resultant changes were recorded (Table III and Fig. 3).

The sub-micron particles in Fuji IX would normally agglomerate or attach themselves to the larger particles, but ultrasound can facilitate their break up. This is evident from the particle size analysis, where the mean particle size decreases, and the specific surface area increases, by the appliance of ultrasound to the water bath during measurement. The breaking up of these agglomerates by ultrasound occurs in the sample chamber of the particle size analyser, even though the amount of powder to dispersant is very low and hence the adsorption/reflectance of the applied ultrasonic energy, by the glass, would be far less than in the cement system. The effect of the ultrasound on the setting reaction of the

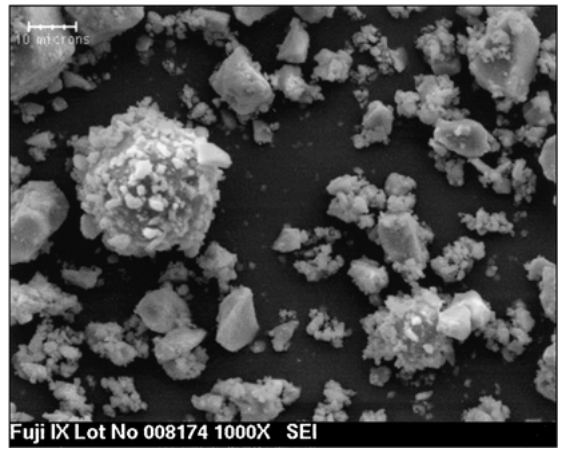

Figure 1 Fuji IX glass particles; 1000× magnification.

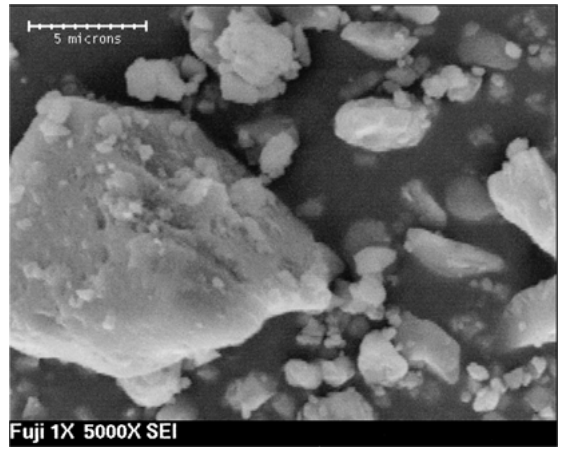

Figure 2 Fuji IX glass particles; 5000× magnification.

cement would be more marked, as the ratio of glass particles to dispersant in the cement itself is far higher. This breaking of the agglomerates offers a far greater surface area for reaction, thereby accelerating the set of the cement.

Cylindrical samples of Fuji IX (4 mm height by 3 mm∅) were produced by an accepted method [11]; three were left to set chemically and three were set by ultrasound. Images of the cross-section of the cylinders, when set conventionally and by ultrasound, were sourced using the microscope (Figs 4 and 5, respectively). The samples had been sputter coated with gold and were viewed using an accelerating voltage of 30 kV.

These micrographs suggest that fewer air bubbles are present in Fuji IX cement when set by ultrasound, than when left to set conventionally. This infers that the high frequency vibration of the cement by ultrasound results in better compaction of the final solid through improved packing of the residual glass particles and hence densification of the cement.

We can conclude that the mechanism of ultrasonic curing is heavily influenced by the make up of the glass phase in several ways:

1. The ultrasonic excitation is likely to promote more intimate mixing of the polyacid and glass powder,

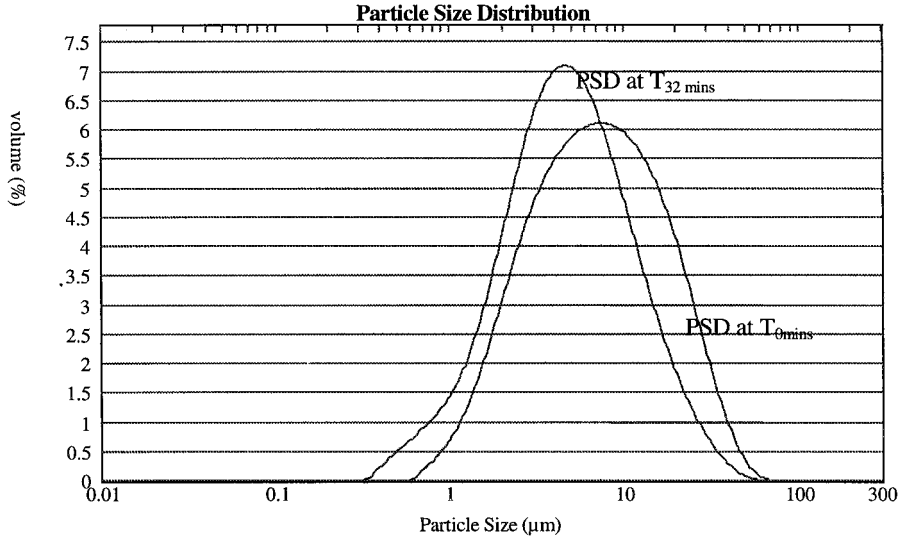

Figure 3 Change in particle size distribution of Fuji IX as a consequence of ultrasound of the aqueous dispersion.

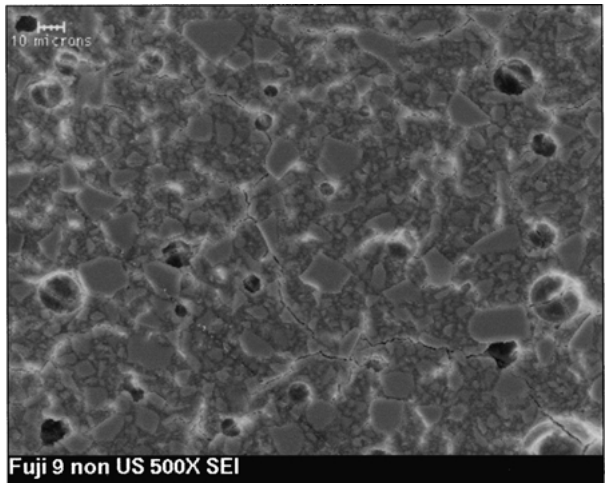

Figure 4 Cross section of Fuji IX set chemically (500× magnification).

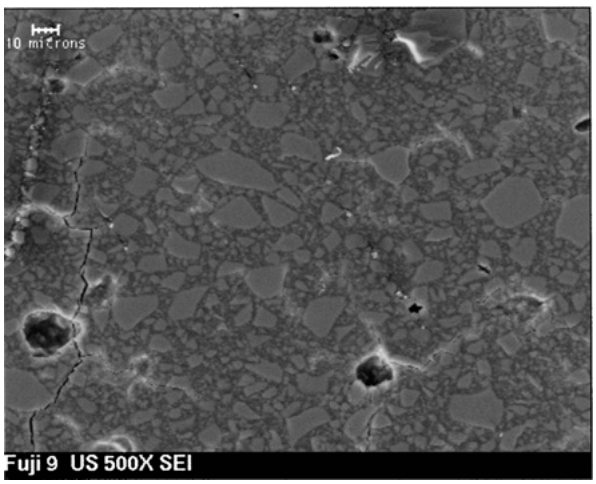

Figure 5 Cross section of Fuji IX set ultrasonically (500× magnification).

thereby allowing greater and more frequent contact between the glass and the acid.

2. Ultrasound decreases the mean particle size of the glass phase by breaking up agglomerates of particles. This offers a greater glass surface area for reaction with the acid.

3. The high frequency vibration of the material may result in better compaction of the final solid through improved packing arrangement of the residual glass particles and hence densification of the solid.

It is not possible to fully explain the mechanism of ultrasonic curing at this stage, but this work clearly shows that the breaking up of agglomerates of glass particles and densification of the cement by ultrasound are influential factors. Other factors such as the energy input and agitation of the polyacid chains during ultrasonic application may be important and will be the subject of further studies.

References

1. B. E. KENT and A. D. WILSON, *Br. Dent. J.* **135** (1973) 322.
2. S. CRISP and A. D. WILSON, *J. Dent. Res.* **53** (1974) 1408.
3. M. R. TOWLER, C. C. FRANCE and R. W. BILLINGTON, *ibid.* **77** (IADR Abstracts) (1998) Abs. #3117.
4. J. A. WILLIAMS and R. W. BILLINGTON, *J. Oral. Rehab.* **18** (1991) 163.
5. S. B. MITRA and B. L. KEDROWSKI, *Dent. Mater.* **10** (1994) 78.
6. R. J. G. D. E. MOOR and R. M. H. VERBEECK, *Biomaterials* **19** (1998) 2269.
7. S. B. MITRA, European Patent Application. No. 0323 120 A2, 1989.
8. J. W. NICHOLSON, and H. M. ANSTICE, *J. Mater. Sci.: Mater. Med.* **3** (1992) 447.
9. M. A. CATTANI-LORENTE, V. DUPUIS, J. PAYAN, F. MOYA and J. M. MEYER, *Dental Materials* **15**(1) (1999) 71.
10. M. R. TOWLER, A. J. BUSHBY, R. W. BILLINGTON and R. G. HILL, *Biomaterials* **22**(11) (2001) 1401.
11. M. R. TOWLER, C. C. FRANCE and R. W. BILLINGTON, *J Dent Res.* **77** (IADR Abstracts) (1998) Abs. #3117.

Received 20 November
and accepted 4 December 2002