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A preliminary comparison of the mechanical properties of chemically cured and ultrasonically cured glass ionomer cements, using nano-indentation techniques

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Abstract

There is a requirement for a dental cement with properties comparable or superior to conventional glass ionomer cements (GICs) but with the command set properties of the resin-modified GICs. The objective of this work was to show that the application of ultrasound to conventional Fuji IX commercial glass ionomer cement imparts a command set, whilst improving the short-term surface mechanical properties. Nano-indentation techniques were employed to highlight the improvements in hardness and creep resistance imparted to the cement through the application of ultrasound. The instant set imparted by the application of ultrasound provides improved surface hardness and creep, particularly within the first 24 h after setting. The surface hardness of the chemically cured Fuji IX (176 MPa) increased by an order of magnitude when set ultrasonically (2620 MPa), whilst creep reduced to a negligible amount. Rapid setting allows for shorter chair time and an improved clinical technique, making restorations more convenient for both the patient and clinician.

Keywords: Glass ionomer cement; Ultrasound; Nano-indentation; Mechanical properties; Setting

1. Introduction

Glass ionomer cements (GICs), developed in the late 1960s at the Laboratory of the Government Chemist in London, UK [1], are now used extensively in dental applications as luting cements and as colour-matched alternatives to amalgam restoratives. Subsequent research resulted in the release to market of the first commercial glass ionomer cements in the 1970s [2]. Whilst the GICs now available to the dentist are far superior to these early materials, they work on similar chemical principles. 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. 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 final cement consists of residual glass particles embedded in a hydrogel polysalt matrix [3]. The setting reaction in GICs is a continuous process evident by the increase in mechanical properties of the cement with ageing time [4–7]. Recent maturation studies using IR and NMR analysis [8] suggest that the initial increase in strength is mainly caused by gel formation and probably by silicate network formation. The silicate network reconstruction plays a significant part in the increase in strength after gel formation.

GICs can release clinically beneficial amounts of fluoride [9,10] and have acceptable handling properties and aesthetics [11,12] which make them suitable as dental restoratives. However, their relationship with water leads to some inherent drawbacks [13]. Glass ionomers go through two phases of setting reactions. During the first reaction, the material is very susceptible to water uptake and during the second, it is susceptible to dehydration. For example, when glass ionomer cements are stored in

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water after an initial setting of 15 min, a surface softening occurs, which is probably caused by an inhibition of the setting reaction in a superficial layer of the cement [14]. Although the strength of the cement increases when stored in water over time, probably from additional ionic cross linking [15], the short-term relationship with water currently restricts the full potential of GICs for healthcare applications.

More recent developments in GIC technology concern the production of command set materials. These are similar to the conventional GICs but benefit from the incorporation of an organic, photo-polymerisable monomer [16] allowing the command set by application of an intense light source. These materials retain most of the properties of conventional GICs, in that they adhere to enamel and dentine [17]. However, they also have some disadvantages, inherently related to the presence of the resin, in that polymerisation shrinkage occurs, they can swell in aqueous media [18] and they tend to have poorer long-term mechanical properties compared to conventional GICs [19,20] and there is a major toxicological problem with the release of the monomer. An alternative method of command set, which does not require the incorporation of photo-polymerisable monomers into the matrix, would be advantageous.

The aim of the work reported here was to demonstrate that GIC materials can be command set by the application of ultrasonic excitation. It is shown that the ultrasound not only imparts an instant set to the material, but also provides superior properties to the chemically cured counterparts, particularly within the first 24 h after setting. The ultrasonically cured GIC does not require the incorporation of any additional chemicals and, therefore, overcomes the drawbacks associated with resin-modified GICs.

Rapid setting and improvements in strength are important in providing resistance to attack by moisture and also in increasing wear resistance so that the material can be polished by the clinician. Rapid setting allows for shorter chair time and an improved clinical technique, making restorations more convenient for both the patient and clinician.

Anecdotal clinical results [21] with the ultrasonic apparatus had been very impressive and a method was set up which could quantify the improvement in mechanical properties in a simulation of clinical size restorations.

This new test procedure was developed using nanoindentation [22–24] to measure the surface mechanical properties of GIC at young ages. In this method, hardness and creep behaviour could be determined within minutes of the cement placement. Hardness gives an indication of wear resistance and creep behaviour is a measure of the viscous flow in the polymer and so gives an indication of the extent of crosslinking in the material. Whilst little work has been reported on the creep and stress relaxation of GICs [25–28] it is an important area as low creep resistance can lead to 'slumping' of the GIC, reducing marginal integrity

The objectives of this work were to; measure the surface mechanical properties of the cements, immediately after the initial set, to compare the hardness of the chemically set GIC with the ultrasonically set material within minutes of the ultra sonic exposure, and finally to compare the creep properties of chemically set GIC with the ultrasonically set material within minutes of the application of ultrasound.

2. Materials and methods

2.1. Materials and specimen preparation

The restorative glass ionomer cement used in this study was Fuji IX (GC Corporation, Tokyo, Japan), sourced from lot number 290587. The glass ionomer was supplied in an encapsulated form, designed for mechanical trituration. Samples of the material were activated and mixed in line with the directions supplied by the manufacturer.

Hardened steel stubs were machined with eight cavities, 2 mm in diameter and 2 mm deep to simulate clinical restoration size. Such a cavity should permit efficient transmission of the ultrasonic wave to the whole restoration. The mixed Fuji IX material was injected directly into these cavities. A freshly mixed capsule was used for each cavity.

The ultrasonic equipment employed was an EMS Piezon® Master 400 dental scaler (EMS, Nyon, Geneva, Switzerland). This equipment is used in dentistry for the removal of plaque from teeth. This equipment has a frequency of 25–30 kHz. The insert used (DS-003) was developed by EMS, for de-scaling applications.

Of the samples used for filling the cavities, four cavities on one stub were ultrasonically treated (USGIC) for 10 s. Testing was commenced 17 min from the end of the ultrasonic process and the procedure repeated on at least two samples. A further four samples on a second stub were left to set chemically (CHEMGIC) and covered with moist tissue paper, 5 min after placement, and maintained wet to prevent drying out. The samples were transferred to a water reservoir, at room temperature (23°C), 2 h before testing and maintained in the reservoir throughout the test as the method is sensitive to dehydration of the material surface.

The ultrasonically cured material (USGIC) was tested 17 min from the end of the ultrasonic process and at 3.5 min intervals thereafter. The chemically cured material (CHEMGIC) was tested 7.5 h after mixing and kept wet throughout the test period. At the end of the respective storage times, the surface response of the samples to displacement and creep was determined using the nanoindentation equipment.

2.2. Nano-indentation

Experiments were performed using a UMIS-2000 nano-indentation system (ASI, Canberra, Australia) fitted with a Berkovich indenter. The Berkovich three-sided pyramid geometry is preferred in nano-indentation because it provides a sharper tip, since the three faces must meet at a point, and this is an important consideration in nano-scale indentation experiments. The angle of the faces is arranged to give the same cross-sectional area as a Vicker's pyramid, at the same distance from the tip and so gives a directly comparable measure of hardness at considerably smaller loads.

All samples were subjected to the same indentation cycle using a 1 mN maximum force giving penetration depths in the range of 50–500 nm and corresponding contact areas of the order of a few μm^2. The test cycle time was approximately 2 min with a new test started approximately every 3.5 min for both types of sample. Some tests were held at maximum load (1 mN force) for 30 s to record the creep response. Testing was undertaken at room temperature. A typical load cycle is shown schematically in Fig. 1.

Hardness, H, is defined as

$$H = \frac{F}{A}, \tag{1}$$

where F is the force applied to the indenter and A is the projected area of the contact. In macroscopic indentation tests the area of contact is normally measured post facto using a metrological microscope to determine the size of the residual impression. In nano-indentation the residual impression has dimensions of a few microns and cannot be accurately measured by optical means. Instead, the projected area of contact is calculated from the geometry of the indenter and the measured depth of penetration in contact with the indenter, h_c, using [29],

$$A = kh_c^2, \tag{2}$$

where k is a constant equal to 24.5 for the Berkovich geometry. Eq. (2) gives the projected area for a given depth of contact for an ideal Berkovich indenter. However, in reality, the shape may vary from the ideal shape particularly in the first 50 nm of contact due to rounding of the tip. The true tip shape or *area function* of the specific indenter being used, A', is found by a calibration routine [30] in a separate experiment so that k is no longer a constant but some function of h_c.

The depth of penetration, h, under a given applied force, F, contains both a plastic (permanent deformation) component and an elastic component which is recovered on removal of the force, Fig. 2.

The depth of penetration in contact with the indenter contains the plastic component and part of the elastic component so that h_c is given by [31]

$$h_c = h_{max} - \left(0.75F_{max}\frac{dh}{dF}\right), \tag{3}$$

where dh/dF is the inverse of the slope of the initial unloading curve, as illustrated in Fig. 1.

Creep is the slow, continuous deformation with time in response to a force and normal takes a logarithmic form. In some tests the maximum force was maintained for 30 s and the creep deformation recorded as a function of time.

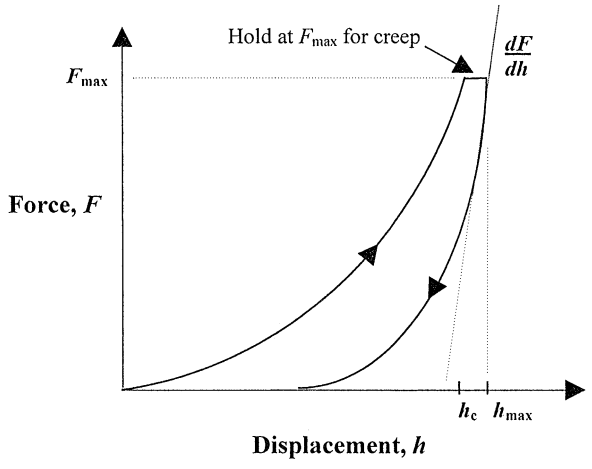

Fig. 1. Schematic diagram of force–displacement curve generated during nano-indentation.

3. Results

3.1. Comparison of force/displacement response

Force/displacement data from the UMIS test cycles, are plotted in Fig. 3 and include results from at least two samples in both cases. The data are plotted with the origin as contact with the solid surface and with the hold at maximum load (creep segment) removed for clarity. The results displayed are typical for the USGIC group and represent the stiffest responses from the chemically cured GIC group, the latter often showing extremely soft (polymeric) behaviour. The number of results plotted has been deliberately kept to a minimum in the interests of clarity. Both types of material often exhibited a soft surface layer (50% for CHEMGIC and 20% for USGIC) observed by a large offset in the force displacement curve before contacting solid material. However, this layer was significantly deeper for the chemically cured GIC (CHEMGIC average depth 4 μm, USGIC average depth 0.44 μm) implying there may be significant hydration at the surface in this case. Hardness results have been calculated for contact with the solid surface in all cases.

It was noted that no significant changes in the material response with time were observed for either material

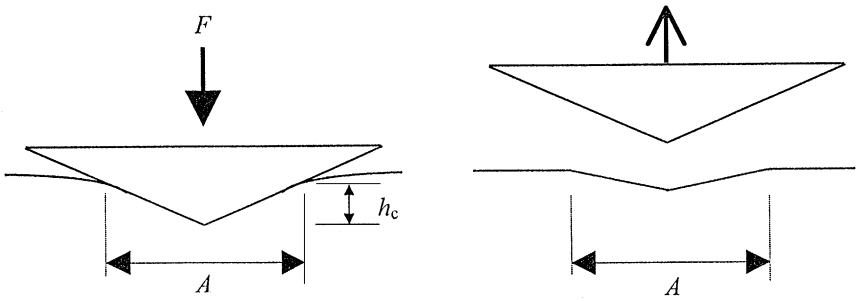

Fig. 2. Schematic illustration of the area of contact, A, and depth of penetration, h_c, for the Berkovich indenter.

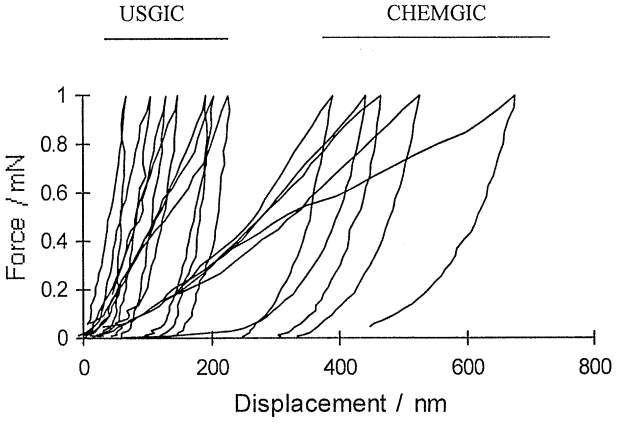

Fig. 3. Force–displacement curves from 1 mN nano-indentations using a Berkovich indenter.

throughout the duration of the testing, which was approximately 30 min in each case. That is, there was no systematic trend in any property that could be correlated with the order in which the tests were performed.

3.2. Comparison of recorded hardness values

Values for hardness were calculated from the force/displacement data using a minimum of 10 tests on each material and at least two samples of each type. Mean values are given in Table 1 for the two materials together with the maximum and minimum value to indicate the range of the data. The figures for the CHEMGIC are calculated from the seven highest hardness test results and so represent the best case. The figures for USGIC are calculated for the seven lowest hardness test results and so represent the worst case. The results indicate that there is an order of magnitude increase in hardness when Fuji IX GIC is ultrasonically cured, than when left to undergo chemical curing. The trend is followed not only of the mean values but also of the range of the data.

3.3. Comparison of creep response

The creep of the Fuji IX, when set by the two different methods, can be compared by analysing the displacement response when the sample is held under a 1 mN load for 30 s. The results displayed for the USGIC group are typical (mean displacement after 30 s, 9 nm). The results displayed for the chemically cured GIC group represent samples that exhibited the least creep (mean displacement after 30 s, 208 nm for all data, 80 nm for the group displayed). From Fig. 4, it can be seen that the chemically cured GIC exhibited appreciable creep over the 30 s period and shows the logarithmic time dependence of displacement, typical of creep behaviour. The ultrasonically cured GIC, however, exhibits negligible creep. The tendency to increase displacement with time is approximately linear and only just resolved above the noise in the data. The total displacement after 30 s is an order of magnitude smaller in the ultrasonically cured material than chemically cured material.

Table 1
Hardness values determined from nano-indentation cycles

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

4. Discussion

The force/displacement response from both the ultrasonically cured and chemically cured samples are plotted on the same axes in Figs. 3 and 4 to allow direct comparisons of the two methods. The two data sets are clearly distinguished from each other in terms of both the total penetration and the shape of the curves produced from the indentation cycle. The ultrasonically cured material has a hardness an order of magnitude greater than the chemically cured material and shows negligible creep, at a significantly short time after placement. There is a relatively large scatter in the results which might be expected from consideration of the scale of the test (contact area of the order of a few μm^2) and the in-homogeneity of the

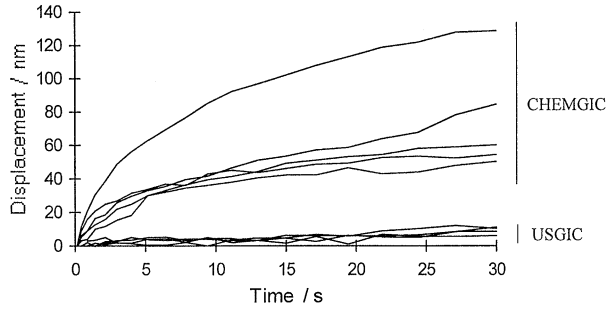

Fig. 4. Creep response at maximum load (1 mN) over hold period of 30 s.

microstructure. However, the results from the different curing methods unambiguously show two behaviours with no overlap between the data groups and an order of magnitude difference in the means in all cases. In this study, we have used a minimal number of test results and samples and clearly a greater number of tests would tend to reduce the scatter in results. Our purpose here, however, is merely to demonstrate that gross differences in behaviour are obtained when the material is exposed to ultrasonic excitation and are effective immediately after exposure.

The data for the chemically cured GIC in Figs. 3 and 4 represent the best mechanical performances from that group, i.e. the highest hardness, the least creep. This material showed a soft surface layer in the load/displacement response at more than half the sites tested. The depth of the layer was typically several microns, implying that surface hydration may take place due to the storage in water. The creep response also implies that significant amounts of uncured polymer remained in the chemically cured samples at the time of testing. Creep displacement would be expected to decrease as the polymer becomes increasingly cross-linked with time, i.e. as the curing process proceeds. The lack of creep in the ultrasonically cured material indicates that the curing process may be fully or at least substantially completed immediately after the application of the ultrasound. The soft surface layer is not absent but substantially reduced and the underlying (solid) material displays greatly enhanced rigidity.

The application of the ultrasound clearly has a profound effect on the curing process, as demonstrated by the results. We do not attempt to explain the mechanism of ultrasonic curing although several possible effects can be suggested: (i) the ultrasonic excitation is likely to promote more intimate mixing of the polyacid and glass powder, thereby, allowing greater and more frequent contact between the components and the liquid; (ii) the highly concentrated energy of the ultrasonic wave may accelerate the dissolution of the polyacid and the glass and allow more rapid diffusion of the ionic species through the liquid resulting in an acceleration of the cross-linking process and (iii) 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.

We have shown that the application of ultrasound can impart a command set to the surface of a conventional GIC material. The implications are that a command set GIC material is now available which eliminates the disadvantages associated with light cured GICs or amalgam restorations. Further benefits of the fast set technique will mean less chair time for the patient and the use of currently available de-scaling apparatus will require no additional financial outlay by the clinician. A further future possible application for the material/process is in the field of orthodontics, where the luting cement sandwiched between the tooth and the appliance can be set by the application of ultrasound through the metal brace.

5. Conclusions

The nano-indentation tests have shown that the application of ultrasound imparts a controllable set to glass ionomer cements compared to the same material which is left to chemically set. As a consequence of the improved set, the ultrasonically treated GIC also has superior surface mechanical properties to its chemically set counterpart, at a considerably shorter time after placement.

This research has highlighted several advantages of employing nano-indentation for determining the mechanical properties of dental materials, as the technique was able to undertake testing on similar sized samples to clinical restorations. Furthermore, it was possible to test the ultrasonically cured material within a few minutes of the application of the ultrasound.

The hardness of the ultrasonically cured GIC was approximately an order of magnitude higher than that of the chemically cured GIC, whilst also exhibiting negligible creep, implying the complete set of the material.

Applying ultrasound not only results in a command set but may also derive superior properties from more intimate mixing of the constituents and better compaction.

Most importantly, the ultrasonic treatment could have advantages for clinical practice in a range of dental and medical applications.

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