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Ultrasonically set novel NVC-containing glass-ionomer cements for applications in restorative dentistry

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Abstract The objective of this study is to investigate the effects of application of ultrasound on the physical properties of a novel NVC (*N*-vinylcaprolactam)-containing conventional glass-ionomer cement (GIC). Experimental GIC (EXP) samples were made from the acrylic acid (AA)–itaconic acid (IA)–NVC synthesized terpolymer with Fuji IX powder in a 3.6:1 P/L ratio as recommended by the manufacturer. Specimens were mixed and fabricated at room temperature and were conditioned in distilled water at 37°C for 1 day up to 4 week. Ultrasound (US) was applied 20 s after mixing by placing the dental scaler tip on the top of the cement and applying light hand pressure to ensure the tip remained in contact with cement without causing any deformation. Vickers hardness was determined using a microhardness tester. The working and setting times were determined using a Gillmore needle. Water sorption was also investigated. Commercial Fuji IX was used as control for comparison (CON). The data obtained for the EXP GIC set through conventional set (CS) and ultrasonically set (US) were compared with the CON group, using one-way ANOVA and the Tukey multiple range test at $\alpha = 0.05$. Not only ultrasonic (US) application accelerated the curing process of both EXP cement and CON group but also improved the surface hardness of all the specimens. US set samples showed significantly lower water sorption values ($P < 0.05$) due to improved acid–base reaction within the GIC matrix and accelerated maturation process. According to the statistical analysis of data, significant increase was observed in the surface hardness properties of CS and US specimens both in EXP samples and the CON groups. It was concluded that it is possible to command set GICs by the application of ultrasound, leading to GICs with enhanced physical and handling properties. US application might be a potential way to broaden the clinical applications of conventional GICs in restorative dentistry for procedures such as class V cavity restorations.

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1 Introduction

Glass ionomer cements (GIC) were invented by Wilson and Kent at the Laboratory of the Government Chemist in 1969 [1]. These materials are water-based cements, and are also known as polyalkenoate cements [2]. The glass ionomer name is derived from the formulation of the glass powder and the ionomer (ionic polymer) that comprise a carboxylic acid polymer, typically poly(acrylic acid). The cement formation arises from the acid–base reaction between the components. The matrix of the set cement is an inorganic–organic network with a highly cross-linked structure. The first GIC introduced had the acronym "ASPA", and comprised alumina-silicate glass as the powder and poly (acrylic acid) as the liquid. This product was first sold in

Europe (De Trey Company and Amalgamated Dental Company) and later in the USA [3–5]. GICs have unique properties, such as adhesion to moist tooth structure and anticarcinogenic effect due to fluoride release. In addition, the coefficient of thermal expansion for glass ionomers is close to that of tooth structure and they are biocompatible. Because of these unique properties, GICs are very useful and important as dental restorative materials [6–9]. In addition to their advantages, GICs suffer from the disadvantage of being brittle. Significant improvements have been made since the invention of GIC and are continuing to be made to enhance the physical properties of the cements. Although stronger and more aesthetic materials with improved handling characteristics are now available, lack of strength and toughness are still major problems [9, 10].

Many of these negative effects of GIC are due to the relatively slow setting of conventional GICs [11]. The setting reaction of GICs occurs in two phases: an initial set with the formation of mainly calcium polyacrylate and a subsequent hardening process with the formation of aluminum polyacrylate. During the initial setting stages, the loosely bound water causes some integrity problems. During the first reaction, the material is very susceptible to water uptake and to dehydration in the second phase. If the material is exposed to water during the first stages of setting, a superficial surface softening is observed [12, 13]. Development of the "set-on-command" glass-ionomer materials, based on light-curable hydrophilic resins is one method of reducing the dependence of early water uptake. The other solution to the slow setting is to enhance the setting rate of the cement may by the addition of energy during the setting of the cement by use of ultrasonic application [14, 15].

Recently, authors reported development of a novel *N*-vinylcaprolactam (NVC) containing polyelectrolytes in the formulation of a conventional glass-ionomer system [16]. This development was based on the fact that hydrophilic spacer groups such as NVC that does not co-ordinate ions increase chain mobility and allows more COOH availability, which allows for greater cross-link density and improved physical properties. The concept was found to be valid regarding the results of their recently published experimental (EXP) work [16, 17]. The new proposed system has exhibited significantly improved mechanical and enhanced surface properties. Thus, it was concluded that NVC-containing GIC is a promising restorative dental material [16, 17]. However, the handling properties of this system, namely working and setting time were still lengthy and not improved in comparison to commercially available products such as Fuji IX GIC.

Therefore, the purpose of this study was to investigate the effects of application of ultrasound on the physical properties of a novel NVC-containing conventional GIC. The null hypothesis of the study was that there would be no difference between the physical and handling properties (setting time, water sorption and microhardness) of NVC–GIC set by ultrasound application and NVC–GIC set by conventional mixing method.

2 Materials and Methods

2.1 Specimen preparation

The glass powders and polyacid from a commercially available GIC (Fuji IX, GC International, Tokyo, Japan) were used. Fuji IX is a fast setting, easy handling restorative material with good performance, which is widely used in the atraumatic restorative treatments (ART). AA (acrylic acid)–IA (itaconic acid)–NVC—which was synthesized previously by author [16]—terpolymer with 8:1:1 molar ratio used in this study for preparation of the EXP test samples. Synthesized terpolymer was dissolved in distilled water in a ratio of 1:1 (wt/wt). Fuji IX GIC glass powder and liquid were used, and the appropriate powder-to-liquid (P/L) ratio as recommended by the manufacturer was used. Specimens were prepared at room temperature following the manufacturers' instructions. EXP specimens were a mixture of the synthesized polymer and the Fuji IX powder. The control group (CON) was the mixture of the powder and liquid of the commercially available Fuji IX GIC. Ultrasound (US) at 25–30 kHz was applied 20 s after mixing by placing the dental scaler tip (Cavitron® Plus™ Dentsply) on the top of the cement and applying light hand pressure to ensure the tip remained in contact with cement without causing any deformation. In the following table (Table 1) different EXP groups of GICs and their abbreviation codes are mentioned.

For hardness testing specimens ($n = 6$) were made from each material for each storage time at 37°C (1 day and 1 week up to 4 weeks) (total sample size: $n = 48$). Cylindrical specimens, 6×3 mm, were prepared. The molds (PTFE (poly-tetrafluoroethene)) were filled with the cement mixture and covered with a piece of film and with a glass slide. Hand pressure was applied for 20 s while excess material was extruded from the top of the mold. The specimens were removed from the molds after 20 min and conditioned in distilled water at 37°C for 1 day up to 4 week. The specimens for the water sorption ($n = 6$) and setting time ($n = 6$) tests were prepared in the same manner as previously mentioned (6×3 mm) (total sample size for each test: $N = 48$). After storage in an oven at 37°C and 100% relative humidity for 1 h they were removed from the molds. Commercial Fuji IX was used as control for comparison (CON).

Table 1 Compositions and the abbreviations used for various EXP glass-ionomer samples in this study

GIC sample	Liquid composition	Powder composition	Setting method
EXP-CS	AA–IA–NVC (8:1:1)	Fuji IX glass powder	Conventional set
EXP-US	AA–IA–NVC (8:1:1)	Fuji IX glass powder	Ultrasound set
CON-CS	Fuji IX liquid	Fuji IX glass powder	Conventional set
CON-US	Fuji IX liquid	Fuji IX glass powder	Ultrasound set

2.2 Water sorption

It has been reported that GICs behave broadly in the same way in distilled water and saliva in terms of surface hardness and sorption. It was concluded that water is probably an acceptable storage medium for storing restorative dental materials in laboratory investigations [18]. Therefore, in this study, distilled water was used as the storage medium for hardness and sorption studies. The thickness and diameter of each specimen (which were prepared according to the abovementioned procedure) were determined at 3 points with a digital micrometer and the volume (V) was calculated in mm^3. The protocol described by Ito et al. [19] and Zhao et al. [20] was used in this study. Briefly, the specimens were conditioned in 100% humidity at 37°C for 20 min. Next, the freshly made specimens were weighed and conditioned individually in distilled water at 37°C before measurements. The specimens were removed from the distilled water (between 1 day up to 4 week). They were lightly dried with filter paper and weighed within 30 s to minimize the effect of dehydration. The mean values of 5 readings were reported for each material and formulation. The water sorption per unit volume (W_{sp}) was calculated using the equation [19]:

$$\text{Water sorption } \left(W_{sp}\right) = \frac{W_t - W_o}{W_o} \times 100$$

where V is the specimen volume (initial), W_t is the specimen weight at time t and W_o is the initial weight of the specimen. The percentage change in volume (ΔV) of the specimens was calculated using the following equation for each time interval from 1 day up to 1 month of storage in distilled water:

$$\Delta V = \frac{V_e - V_o}{V_o} \times 100$$

where V_e is the volume after immersion (mm^3) and V_o is the volume before immersion in distilled water (mm^3).

2.3 Microhardness measurements

The Vickers hardness values of the NVC-containing glass-ionomer and CON specimens with and without ultrasound set were determined according to the method reported by Gladys et al. [21] and more recently by Moshaverinia et al. [17] using a microhardness tester (Model MVK-E, M 400, Leco, St. Joseph, Mich). The specimens were stored in distilled water at 37°C for 1 day up to 1 month. A diamond indenter with a 0.98 N load and a dwell time of 10 s were used. All the specimens were indented and with the use of an optical microscope equipped with polarized light the indentations were measured. Subsequently, the Vickers hardness number (VHN) for each specimen was calculated according to the related formula. Only specimens with indentations on their surfaces that were sufficiently sharp to obtain accurate diagonal lengths were included in the analysis of data.

2.4 Setting time determination

The setting times were determined using a Gillmore Needle test according to the method published by Hurrell-Gillingham et al. [22] according to dental material standard. Briefly, a 1 mm diameter needle with 400 g weight was applied to the surface of the both the EXP and CON group and the time when this needle no longer indents the surface is designated as the setting time. This test was carried out at room temperature.

2.5 Statistical analysis

The data obtained for the EXP GIC set through conventional set (CS) and ultrasonically set (US) were compared with the CON group, using one-way and two-way ANOVA (factors: curing method and time) and the Tukey multiple range test at $\alpha = 0.05$ (Minitab version 15, Minitab Inc. State College, PA).

3 Results

Water sorption data for different materials are shown in Fig. 1. According to the statistical analysis of data, the EXT-US and CON-US cement samples showed significantly lower amounts in comparison to conventionally set samples EXT-CS and CON-CS, respectively. Additionally, significant difference found between EXP samples with US

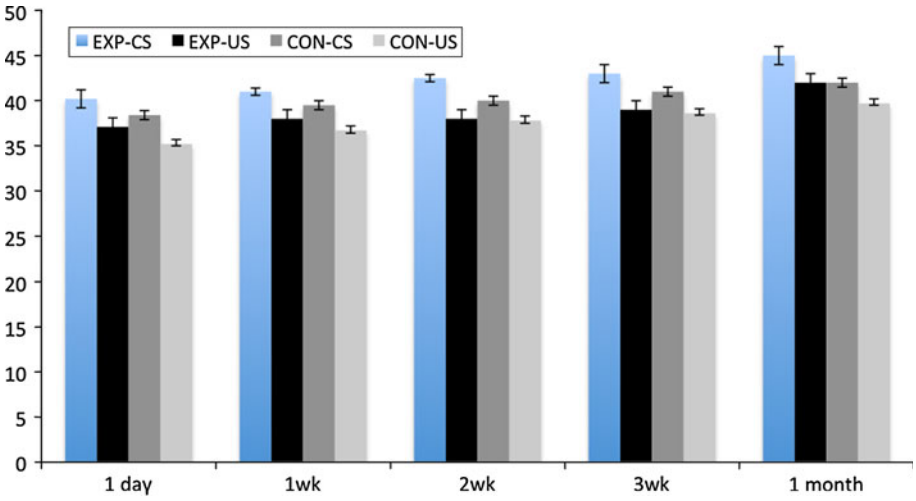

Fig. 1 Water sorption (W_{Se} = water sorption at equilibrium) results of EXP specimens and CON groups with US application and CS

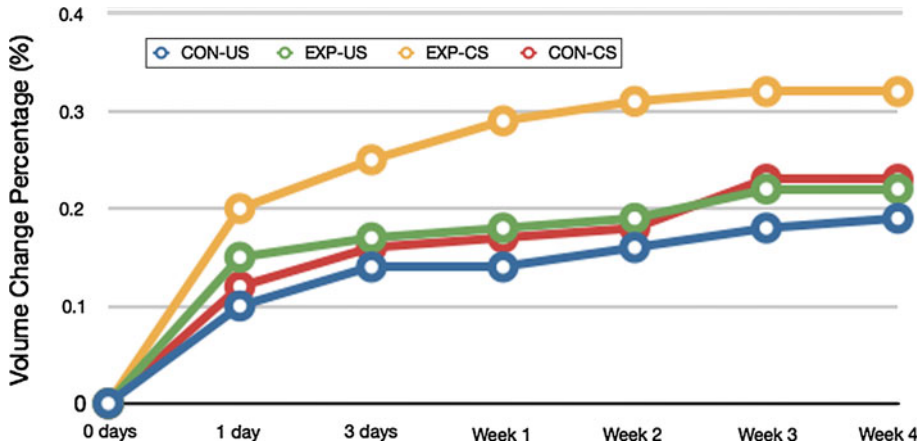

Fig. 2 Mean percentage change in volume over time in distilled water among EXP and CON with US and CS

set and CON samples with CS at all time intervals (P value <0.05).

Figure 2 shows the percentage changes in volume of the tested materials. The percentage changes in volume for EXP-CS specimens were the highest (statistically significant), followed by CON-CS EXP specimens before and after immersion in distilled water. A significant decrease (P value <0.05) was observed in the amounts of volumetric change after ultrasound application in both materials groups (EXP-US and EXP-US). The CON-US showed the lowest amount of volumetric changes followed by the EXP specimen with ultrasound application (EXP-US).

Values of Vickers hardness for the EXP and CON specimens after 1 day, 1 week up to 1 month of storage in distilled water are shown in Table 3. For each storage period, there was a significant increase (P value <0.05) in VHNs for the EXP-US and CON-US groups in comparison to EXP-CS and CON-CS specimens, respectively. According to statistical analysis of data there was a significant increase in the VHN of EXP-US samples in comparison to CON-US ones. Overall, after ultrasound application, a significant increase in surface hardness values of both EXP and CON was observed in comparison to specimen with CS (P value <0.05).

Table 2 Setting time characteristics of EXP and CON groups with CS and US setting

GIC Sample	Setting time (min)
EXP: NVC–GIC (CS)	3.0 ± 0.1
EXP: NVC–GIC (US)	<1.0[a]
CON: Fuji IX (CS)	2.5 ± 0.1
CON: Fuji IX (US)	<1.0[b]

CS conventional set, *US* ultrasonic set

[a, b] Results are significantly different

The setting time of the different GIC are given in Table 2. It is apparent from these results that ultrasound application significantly reduced the setting time of the resulting cement (P value <0.05). Ultrasonic (US) application accelerated the curing process of both EXP cement and CON group.

Table 3 Mean and SD of VHNs of EXP and CON GIC samples after 24 h and 1 week and 1 month of storage in distilled water at 37°C

GIC sample	1 Day	1 Week	1 Month
EXP-CS	$49.0 \pm 2.1^{a,A}$	$53.1 \pm 2.0^{a,B}$	$57.2 \pm 3.5^{a,C}$
EXP-US	$52.3 \pm 2.0^{b,A}$	$56.2 \pm 2.5^{b,B}$	$63.0 \pm 3.8^{b,C}$
CON-CS	$45.1 \pm 2.2^{c,A}$	$47.0 \pm 1.8^{c,B}$	$52.1 \pm 3.0^{c,C}$
CON-US	$47.4 \pm 2.0^{a,A}$	$50.6 \pm 2.3^{a,B}$	$55.9 \pm 3.3^{a,C}$

Results in each time interval with same superscript letters (*lowercase letters* in each column and *uppercase* in each row) are not significantly different ($P > 0.05$)

4 Discussion

The null hypothesis of the study that there would be no difference between the physical and handling properties (setting time, water sorption and microhardness) of NVC–GIC set by ultrasound application and NVC–GIC set by conventional mixing method, was rejected. Results are in good correlation with previously reported data [23–26]. Towler et al. [14] have reported that ultrasound application can impart a command set to the surface of a conventional GIC material. In their study, the results of nano-indentation test showed that the application of ultrasound passed on a controllable set to GICs compared to the CS counterparts [14]. In addition, cavitation has previously been observed in glass-ionomers where mean particle size was reduced after ultrasonic application leading to more collisions between particles [15]. Talal et al. [23] have reported in their studies that US application accelerated the setting reaction of glass-ionomers by accelerating the formation of the acid salts (acid neutralization). In another study, Thanjal et al. [24] showed that ultrasound application not only accelerated the setting reaction of glass-ionomers but also enhanced the fluoride releasing properties of GICs. Carvalho et al. [25] showed that ultrasound application made the conventional GIC command set and significantly increased their microhardness values. Additionally, Baloch et al. [26] found that surface microhardness of glass-ionomer samples set by ultrasound setting method was significantly higher than samples set by conventional method.

Tanner et al. in their work found that ultrasound can be passed on through the orthodontic brackets to command set glass-ionomers. They attributed this effect to a combination of cavitation, improved mixing of the constituents and better compaction of the GIC after ultrasound application. They concluded that application of ultrasound has resulted in both a command set and an improvement in the mechanical properties [27]. In the current study not only ultrasonic (US) application accelerated the curing process of both EXP (NVC containing GIC) cement and CON group (Fuji IX) but also improved the surface hardness of all the specimens. US set samples showed significantly lower water sorption values ($P < 0.05$) due to improved acid–base reaction within the GIC matrix and accelerated maturation process. According to the statistical analysis of data, significant increase was observed in the surface hardness properties of CS and US specimens both in EXP samples and the CON groups.

As demonstrated by the results of the present study, the application of the ultrasound has a significant effect on the curing process of the NVC-containing GIC. The possible mechanism of action of US could be due to the high energy of ultrasound waves transmitted to GIC material; which could be effective through one of the following mechanisms: (i) more intimate mixing of powder and liquid and thereby more complete setting reaction; (ii) acceleration of heterogeneous reaction between glass power and polyacrylic acid liquid due to formation of pressure wave which pass through the solid–liquid mixture resulting in an acceleration of the cross-linking process and [28]; (iii) better compaction of the final solid through improved packing arrangement of the residual glass particles (improved densification) [14].

Moshaverinia et al. [16, 17] reported that the presence of amide group in the structure of the NVC molecules resulted in hydrophilic domain formation, which leads to increased inter- and intramolecular (physiochemical) interactions within the cement matrix. In this study, it can be presumed that the application of ultrasound energy would accelerate the abovementioned physiochemical interactions within the NVC containing glass-ionomer matrix leading to significant improvement in the surface hardness of the material (Table 3).

Advantages of the current NVC-containing glass-ionomer system are enhanced mechanical properties and improved handling characteristics. Further benefits of the current NVC–GIC fast set system will mean less chair time for the patient and the clinician while using the currently available scaling devices with no additional cost to the clinician. In future work, we hope to be able to evaluate the effect of ultrasound application on the amount of fluoride release of the NVC–GIC system. We also will seek to optimize the proposed system for clinical applications such as class V cavity restorations, restoration of non-carious cervical lesions (NCCLs) and command-set luting cement.

The results of these endeavors will be reported in due course.

5 Conclusions

The ultrasonic treatment accelerated the setting reaction, enhanced surface hardness and water sorption of NVC containing GIC, As combined with their improved mechanical strength make this novel GIC formulation-technique a promising candidate for application in fixed and restorative dentistry**.** US application might be a potential way to broaden the clinical applications of conventional GICs in restorative dentistry for procedures such as class V cavity restorations.

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