Time dependence of the mechanical properties of GICs in simulated physiological conditions

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The mechanical properties of glass-ionomer cements (GICs) have been satisfactory for dental applications and have shown their potential in orthopedic surgery. Because the physiological environment in orthopedics is different from dentistry by unavoidable contamination with blood and other fluids such as normal saline used during an operation, the determination of GICs for orthopedic applications should be performed in an appropriate environment. The properties of a novel resin-modified GIC, S430, for orthopedic applications were evaluated in simulated orthopedic conditions by an early exposure to and long-term storage in normal saline. An early exposure to normal saline caused 20–60% reduction of its compressive and flexural properties, whereas long-term storage in normal saline showed slight changes of its mechanical properties. The effects were probably due to the disturbance of the cross-linking formation in the acid-base reaction and also the reduction of electrostatic interactions of the cross-linking polymeric chain of hydroxyethyl methacrylate (HEMA) in resin-modified GIC.
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1. Introduction

Glass-ionomer cements (GICs) were developed by Wilson and co-workers during the late 1960s [1]. These materials possess a significant number of attractive features including the release of fluoride to enhance caries resistance [2], good biocompatibility [3, 4], aesthetics, and also good adhesion to dental tissues [5]. GICs have mechanical properties, which are more than satisfactory for dental applications and have shown their potential in other medical areas, such as orthopedic surgery [6, 7]. However, the greater load-bearing applications under orthopedic conditions demand greater strength and toughness, and mechanical properties of GICs than required for dentistry. Attempts have been made to improve their properties by such means as; modification of the composition (glass and liquid compositions) [8–15], resin-modified GICs [16–18], and reinforced GICs (metal or fibers) [19–25].

The determination of GIC mechanical properties *in vitro* can be entirely different from the *in vivo* situations because of different environmental conditions. Exposure to aqueous environment has been shown to have deleterious effects on the mechanical properties of GICs [26–29]. In addition, Causton [26] and Cattani-Lorente *et al*. [29] showed more deleterious effects on the mechanical properties when the cements were exposed to water within 1 h after mixing. This observation raises serious concerns for using GICs in orthopedic surgery because of unavoidable contamination with blood and other fluids such as normal saline used during an operation. The larger, narrower and deeper cavity space in orthopedic arthroplasty also leads to difficulty ensuring and maintaining dry bone surface for cementing than the smaller and shallower space in dentistry. Therefore, in the determination of the mechanical properties of GICs for orthopedic usage, the preparation and storage of the cements for testing should simulate orthopedic conditions, that is, an early exposure to and storage in normal buffered saline.

The studies by Causton [26] and Cattani-Lorente *et al*. [29] revealed the effects of early exposure to water as GICs were mixed and were left to set for 10–15 min before exposure to water. For the comparison of the GICs' mechanical properties in dentistry by other investigations, the cements were left to set for 1 h before exposure to water [27, 28, 30–35]. There has been no systematic investigation determining the time for setting cement before exposure to an aqueous environment in orthopedic operation. Therefore, in this study, time dependence of the mechanical properties of the resin-modified GIC developed for orthopedic usage (S430) and the conventional GIC (Fuji IX), which were mixed and left to set for 10–15 min before exposure to normal buffered saline simulating orthopedic conditions, was investigated. The results were also compared with the earlier work by Higgs *et al*. [35] utilizing the same

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methodologies, thereby enabling the effects of an early exposure to normal buffered saline to be reliably quantified.

2. Materials and methods

2.1. Materials

The materials used were a high viscosity conventional GIC, Fuji IX, and the experimental resin-modified GIC used was S-430, which was incorporated with a 10% (by weight) hydroxyethyl methacrylate (HEMA) component (GC Corporation, Tokyo, Japan). The composition of both materials is shown in Table I. Both cement systems have been prepared according to manufacturer's instructions. The specimens were prepared by directly casting the prepared cement into a mold. To simulate clinical conditions, the mold was lightly pressurized for 10–15 min and was then stored in normal saline at 37 °C until further processing. The set cement was removed from the mold and polished, followed by storage in normal saline at 37 °C for one day, one week, two weeks, four weeks, and three months before testing. For the fracture toughness testing, the specimens were notched to approximately half the depth (2.5 mm) using the low-speed diamond blade saw and were pre-cracked using a razor blade prior to testing.

2.2. Testing machine compliance

Relatively few investigations pay significant attention to this issue in the determination of materials' properties, particularly, elastic modulus values [36–40]. Testing machine compliance is a measure of the force-displacement response of the testing machine itself [41]. Higgs *et al*. [42] demonstrated the significance of testing machine calibration for the accuracy of testing. Therefore, the testing machine was calibrated after testing for the correction of the results in this study.

2.3. Compressive test and flexural tests

In order to replace the conventional bone cement (polymethyl methacrylate, PMMA) by GICs in orthopedic surgery, their material properties have to be determined and compared. The material testing method needs to be precise and accurate and even better, to be standardized for comparison purposes. The testing method also needs to correlate well with the functioning environment of the material. The compression testing is widely used for evaluating brittle material such as glass ionomer cements, although the functioning nature of a typical dental restoration involves both tension and compression loading. Flexural tests in three-point bending have a role in testing brittle dental materials in that one side of the sample is placed in tension, which gives a measure of tensile strength. For these reasons, the compression testing is used in conjunction with the flexural testing to evaluate the mechanical properties of dental or other types of cements.

International Standard 9917 [43] was specifically designated for dental evaluation of GICs whereas International Standard 5833 [44] was specifically designated for the orthopedic PMMA cements. The fundamental differences between the two standards are the required specimen dimensions and the loading rate of mechanical testing. ISO 9917 [43] requires cements to be prepared as cylinders of dimension 6.0 ± 0.1 mm high and 4.0 ± 0.1 mm in diameter whilst ISO 5833 [44] requires 12.0 ± 0.1 mm high and 6.0 ± 0.1 mm in diameter. Specimens prepared for ISO 5833 [44] and ISO 9917 [43] were tested at crosshead speeds of 20 mm/min and 1 mm/min respectively. The compressive strength was calculated as the failure load divided by the measured cross-sectional area taken at the 2% strain offset for resin-modified GIC and as absolute maximum stress for conventional GIC.

The three-point bend test was used for the determination of flexural strength and modulus of elasticity. The flexural strength of cements was measured using beam-shaped specimens (size 25 mm × 5 mm × 2.5 mm). The three-point bending test was used with the specimen supporting rollers set at 20 mm apart. The load was applied to the mid-point of the specimen at a rate of 0.25 mm/min. The failure stress, σ_b, was determined from the following equation:

$$\sigma_b = \frac{3PL}{2bd^2}$$

where P is the force at fracture, L is the distance between outer rollers, b is the specimen breadth and d is the specimen height. The strain, ε, was calculated from the following equation:

$$\varepsilon = \frac{6d}{L^2}\Delta l$$

where Δl is the deflection of the beam at the point of loading making allowance for the machine compliance. The modulus of elasticity is obtained from the gradient of the stress strain curve.

2.4. Fracture toughness test

Failure characterization by means of fracture toughness gains more popularity as it more critically represents the

TABLE I Compositions of the glass ionomer cements used

Materials	Powder	Particle size	Liquid	Consistency	P/L ratio
Fuji IX	Fluoroalumino silicate glass 95% Powdered polyacrylic acid 5%	Less than 25 μm Water 45%	Polybasic carboxylic acid 10%	High	3.6/1.0 g
S430	Fluoroalumino silicate glass 100%	Less than 15 μm	Polyacrylic acid 30% HEMA 30% Methacrylate Resin 10% Water 30%	Low	1.8/1.0 g

TABLE II One-day properties of GICs with different exposure times to water

Properties\exposure to water	One-hour group	10-minute group
Fuji IX-Compressive strength	211.16 ± 27.92	151.98–169.72 (19.63%)
Fuji IX-Compressive modulus	14.34 ± 2.65	13.95–15.07
Fuji IX-Flexural strength	29.17 ± 7.56	17.48–17.31(40.08%)
Fuji IX-Flexural modulus	13.09 ± 2.93	4.72–4.79(63.41%)
Fuji IX-Stress intensity factor	0.63 ± 0.07	0.44 ± 0.10(30.16%)
S430-Compressive strength	113.72–163.37	76.50–93.66(40.67%)
S430-Compressive modulus	4.54–3.76	4.12–4.78
S430-Flexural strength	58.62 ± 6.73	25.54–29.62(49.47%)
S430-Flexural modulus	6.47 ± 0.21	2.06–2.21(65.84%)
S430-Stress intensity factor	0.91 ± 0.10	1.01 ± 0.09(10.99%)

intrinsic crack extension resistance of materials. The American Standard Test Method for determining the Plane-Strain Fracture Toughness of Materials (ASTM E399-83) [45], which is widely used to test brittle and/or quasi-brittle materials, has been used to determine the fracture properties of GICs and PMMA.

The standard specimen is a single edge notched beam loaded in three-point bending with a support span, S, nominally equal to four times the width. Calculation of K_c for each specimen was performed using the equation:

$$K_c = \frac{P_Q S}{BW^{3/2}} f(a/W)$$

where $f(a/W)$ is a dimensionless function of a/W, where

$$f(a/W) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W) \times (2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}}$$

The test was carried out in three-point bending using a Shimadzu materials testing machine. To minimize non-linear effects, the specimens were loaded at the crosshead rate of 0.25 mm/min. The critical load, P_Q, which was determined from the load cell of the material-testing machine, was used to calculate the fracture toughness, K_c, according to ASTM standard.

3. Results

Firstly, the results of this study are compared with the results by Higgs *et al*. (2001) [35] in Table II in determining the effects of simulated orthopedic conditions on the mechanical properties of GICs. The results of this study were designated as a 10-minute group whereas the results by Higgs *et al*. (2001) [35] were designated as a one-hour group. Almost all the mechanical properties in the 10-minute group are lower than those of the one-hour group except the compressive modulus, which did not change and the stress intensity factor of the resin-modified GIC, which was higher. The reduction in the mechanical properties of the conventional and resin-modified GICs showed the same behavior in each property except for the compressive strength in which the resin-modified GIC showed a greater reduction (40% compared with 20% of the conventional GIC).

The changes of the mechanical properties in the 10-minute group with time are shown in Figs 1–5. The * and # symbols indicate the groups that show significant differences. The compressive tests' results show considerable scatter and exhibit only slight changes with time (Figs 1 and 2). From the flexural tests, the flexural modulus showed a slight but significant increase for periods up to three months (Fig. 4). Although the stress intensity factor or the fracture toughness values of both materials showed insignificant changes, there was a slight increase up to four weeks and then decline for S430, whereas for Fuji IX, it was stable at three months (Fig. 5).

4. Discussion

The results from this study have to be compared with the results of the studies by Causton (1981) [26] and Cattani-Lorente *et al*. (1999) [29], in which the cements were also left to set for 10–15 min before being stored in water.

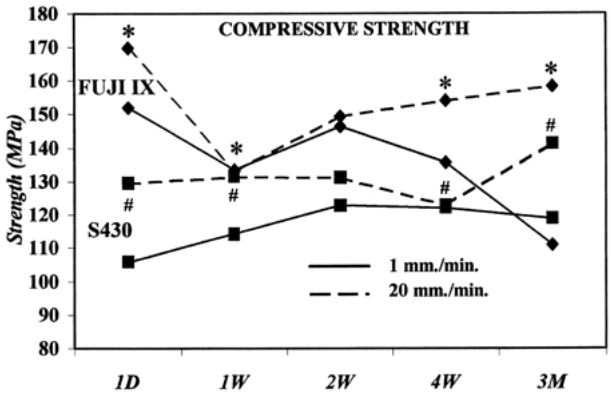

Figure 1 Compressive strength of Fuji IX and S430 storage in normal saline up to three months reveals an invariable strength towards aging time (* and # marks show statistical differences).

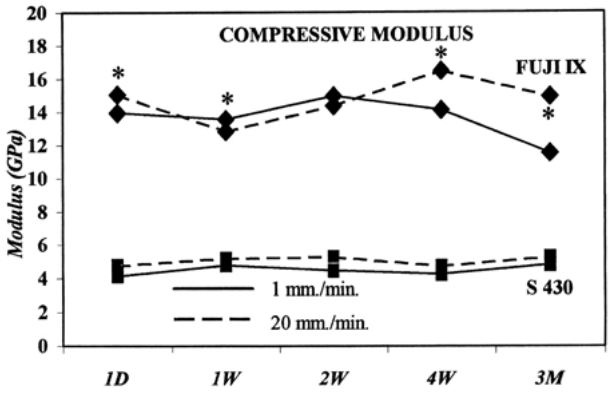

Figure 2 Compressive modulus of Fuji IX and S430 shows slight changes with time (* and # marks show statistical differences). Note that compressive modulus of Fuji IX is approximately 180% of S430.

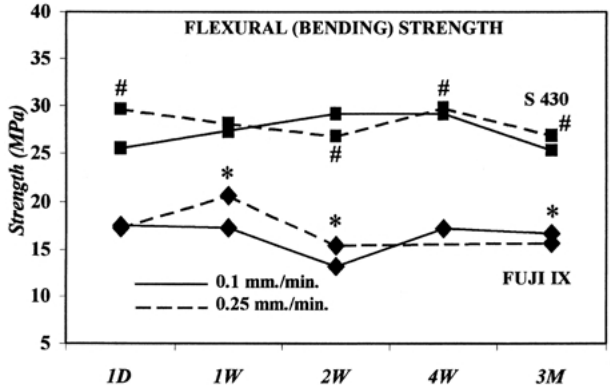

Figure 3 Flexural strength of Fuji IX and S430 also shows slight changes with time (* and # marks show statistical differences). However, S430 shows higher flexural strength (approximately 60% higher).

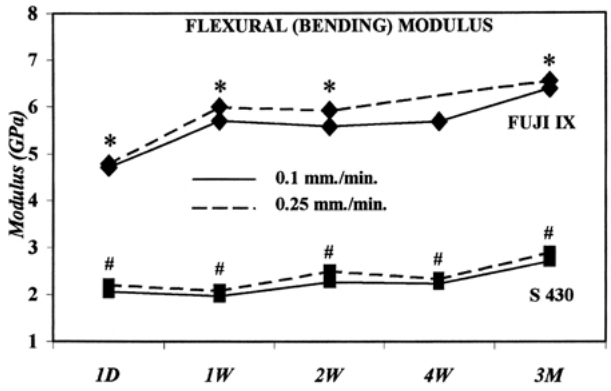

Figure 4 Flexural modulus of Fuji IX and S430 shows slight but significant increase with time (* and # marks show statistical differences). Note that flexural modulus of Fuji IX is approximately 160% of S430.

This condition is different from other previous investigations on mechanical properties of GICs in dentistry in which the cements were always left to set for 1 h before being stored in water [27, 28, 30–34]. Overall, the results showed that the effects of early exposure of GICs to water were detrimental. The reduction in compressive and flexural properties of GICs, except for the compressive modulus, was considerable, ranging from 20% to 60% in this study, which agrees with the results by Causton [26] and Cattani-Lorente *et al*. [29]. The result by Causton [26] showed a 34% reduction in compressive strength of the conventional GIC tested. Cattani-Lorente *et al*. [29] found the reduction in flexural strength of the resin-modified GIC ranged from 30% to 50% with different resin-modified GICs (for instance when wet and moist + wet conditions for 24 h were compared). However, the unchanged compressive moduli of both materials are difficult to interpret because compressive test is more a measure of internal shear failure [30] and therefore the external surfaces which dominate flexure properties are not as significantly affected [46]. Therefore the results may indicate that the internal structure of the specimens was not modified by the exposure to moisture, whereas the external surfaces were modified.

The reduction in the mechanical properties of the conventional GIC has been explained by the distribution of water and its influence on the crosslinking of the polymer matrix, which occurred mainly between 15 min and 1 h after mixing. In case of earlier exposure to water (less than 15 min), the disturbance of Al^{3+} ions activity, which play a major role in cross-linking polymerization of the polyacrylic acid, which shows its peak at $\sim$ 9 min [26], possibly causes a more detrimental effect. In addition, for the resin-modified GIC, the polar functional groups in the cross-linking polymeric chain of HEMA produce electrostatic interactions (hydrogen bonding), causing a reinforcement on the polymer system. Water reduces these electrostatic interactions, causing the reduction in the mechanical properties of resin-modified GIC [29].

On aging in normal saline, S430 and Fuji IX showed an invariant strength with aging time, despite the flexural moduli, which showed slight but significant increase up to three months. The study of the same cement setting condition by Causton (1981) [26] showed an increase in compressive strength of the GIC tested although his initial results revealed the reduction of compressive strength of the GIC group, exposed to water earlier (before 1 h). For cements, which were left to set for 1 h before exposure to water, Cattani-Lorente *et al*. [27] who investigated various commercial GICs, found four different pattern changes of the mechanical properties with time when they were stored in water. The four distinct patterns observed were: (1) an increase in strength to an upper limit value, (2) a gain in strength over a period of two or six months, followed by decrease, (3) a continuous decrease in strength with time, and (4) an invariable strength with aging time. They concluded that strengthening of GICs with time resulted from additional crosslinking and build-up of a silica gel phase, whereas weakening resulted from erosion and the plasticizing effect of water. Our results are comparable with the last pattern (4) of the four different patterns of mechanical properties of GICs with time observed by Cattani-Lorente *et al*. [29]. The different aging patterns of GICs of the study by Cattani-Lorente *et al*. [27] and this study were probably due to the wide variations in GICs' composition. The differences of GICs' microstructures have been shown to have significant effects on their mechanical properties and also the changes of the mechanical properties with aging [27, 34].

In this study, the compressive strength values of the conventional GIC (Fuji IX) were overall higher than

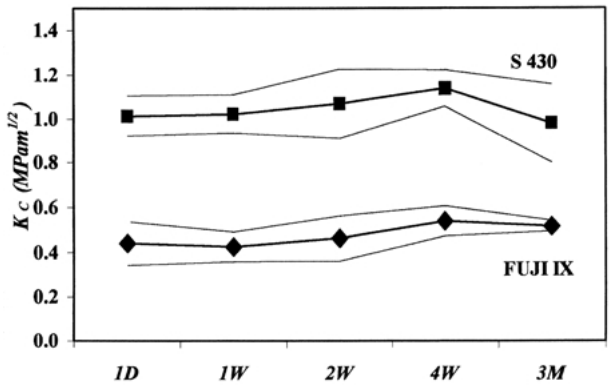

Figure 5 Fracture toughness of Fuji IX and S430 shows insignificant slight increase up to four weeks.

those of the resin-modified GIC (S430) (Figs 1 and 2) whereas the results by Xie *et al*. [34] showed no significant difference. The higher powder/liquid ratios may be responsible for this higher compressive strength and modulus of Fuji IX rather than the size of glass particles as conjectured by Xie *et al*. [34]. However, the flexural strength results were in agreement with the results by Xie *et al*. [34]. The flexural strength of S430 was much higher than Fuji IX (Fig. 3) and the plastic deformation and higher fracture toughness behavior of the resin-modified GICs is probably a major contributor for this higher flexural strength [34].

Failure property or fracture toughness is another distinct and important measure of a material's resistance to crack extension. The results revealed higher fracture toughness values of the resin-modified GIC than those of the conventional GIC as previously reported [47]. The weak organic-salt matrix of conventional GICs is strengthened by the cross-linked polymerization of introduced resin systems [48]. For conventional GICs, the toughness may increase or decrease with time depending on the resistance of the polymerized polyacrylate chains at the crack tip and the bonding to the glass particles; this will also influence the extent of the plastic zone formation about the crack tip which may be the dominant factors in determining the fracture properties (Hill, 1993), cited from Griffin and Hill [11]). The toughness may decrease by excessive crosslinking, restricting flow of the polyacrylate chains and reducing the plastic zone size at the crack tip. Surprisingly for the specimens exposed to water earlier, only the fracture toughness or the stress intensity factor of S430 increased, whereas other properties of both Fuji IX and S430 decreased (Table II). The increase of the fracture toughness of only S430 may possibly be explained by the water plasticizing the resin resulting in the appropriate amount of crosslinking. However, in combination with the results from compressive and flexural tests, this issue is rather complex and needs further investigation. By aging in saline, although the results showed no significant difference, the toughness of both Fuji IX and S430 increased with time up to four weeks, and thereafter showed little change for Fuji IX, but decreased for S430 at 3 months. The insignificant changes of the stress intensity factor of GICs on aging may also reflect the importance of external surface defects on bending test as the fracture toughness specimens were notched just before testing, and therefore exposed the same undisturbed material inside. This latter behavior was probably caused by hydrolysis and dissolution of some of the resin components after achieving their optimum toughness up to four weeks by maturation of the cross-linking reaction.

5. Conclusions

In orthopedic surgery, the unavoidable early exposure of GICs to an aqueous environment needs to be seriously considered, because this condition caused 20% to 60% reduction of the mechanical properties of the cements. The effects were probably due to the disturbance of the cross-linking formation in the acid-base reaction and also the reduction of electrostatic interactions of the cross-linking polymeric chain of HEMA in resin-modified GIC. For the resin-modified GIC (S430) tested in this study, long-term storage in normal saline showed slight changes in its mechanical properties. The results suggest a method to improve the compressive properties by means of an increase of the powder/liquid ratio (Figs 1 and 2). The current results support the suggestion by Xie *et al*. [34], namely to improve the flexural properties via the addition of polymer backbone, that is, a resin-modified GIC. Although the modification of GIC by resin also improves the failure properties, the fracture toughness of the resin-modified GIC is still lower than that of PMMA ($1.02 \pm 0.09\ \mathrm{MPam}^{1/2}$ for S430 compared with $1.66–1.74\ \mathrm{MPam}^{1/2}$ for PMMA [35]). A possible mechanism for further improvement of the toughness of resin-modified GIC is by fiber reinforcement [49].

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