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# The effects of heat treatment on selected properties of a conventional and a resin-modified glass ionomer cement

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**Abstract** This study investigated the effects of application of heat alone and heat & pressure on the compressive strength and modulus, the stress relaxation characteristics and the fluoride release of a conventional and a resin-modified glass ionomer cement. Cylindrical specimens were made from both materials and divided into 3 groups. One group was heat treated in an oven at 120 °C for 20 min, another group was subjected to heat & pressure at 120 °C for 20 min at 6-bar pressure. The third group acted as a control. The compressive strength and modulus, stress relaxation and fluoride release were tested over 56 days. The results of this investigation indicate that heat treatment had no significant effect on the conventional GIC used but significantly affected the resin modified GIC by increasing both the compressive strength and modulus and reducing the stress relaxation characteristics and the fluoride release. The use of GIC to produce inlay or onlay restorations that adhere to tooth tissue and release fluoride would be highly desirable. The results of this study indicate that it is possible to improve the strength of RMGIC with heat to a limited extent, but fluoride release may decrease.

## 1 Introduction

Glass ionomer cements (GICs) are water-based cements formed by an acid–base reaction of the acidic polymer and the basic ion leachable glass [1]. The structure of the set glass ionomer cement has been described as a matrix consisting of calcium and aluminium polyacrylates with glass particles embedded in it surrounded by a siliceous hydrogel [2–4]. More recent studies have found that large proportions of the silica are present in the matrix phase which suggests that there is a complete dissolution of part of the glass rather than an ion-exchange process on the surface [5, 6].The original model does not account for the presence of silica in this region and it has been suggested that a second reaction i.e. the formation of a silica matrix, is responsible for the increase in compressive strength with time [7]. It has also been proposed that the drop in mechanical properties at a later stage may due to increased cross-linking of the silica gel producing some embrittlement of the set cement [8].

Glass ionomer cement offers the advantages of adhesion to enamel and dentine [9] and has cariostatic properties due to sustained fluoride release [10]. Since being originally reported by Wilson and Kent in 1971 [11], further developments have led to their wide use as class V restorations for cervical abrasion and erosion lesions and root caries, luting cements, liners and bases, core build-up materials, fissure sealants, class III restorations, class I and II restorations in deciduous teeth [12], tunnel preparations, temporary repairs of fractured teeth or defective crown margins and luting agents for orthodontic brackets [13]. The greatest disadvantage of the glass ionomer cement is the initial lack of strength and unsuitability for restoration of incisal edges, marginal ridges or use as an inlay/onlay material like composite resins or porcelain.

A vast amount of research has been conducted in an effort to improve the strength of glass ionomer cements by modifying the chemical composition of both the glass and polyelectrolyte components [14] and also incorporating amalgam alloys but the resistance to abrasion was reduced

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[15]. The abrasion resistance and strength were improved by fusing silver particles onto the ionomer glass [16]. The addition of small amounts of water soluble resin, usually HEMA, has led to the development of restorative resin-modified glass ionomers (RMGICs) which have the ability to command set on application of visible light and develop strength more rapidly. The term "dual-cure" cement has also been used as the acid-base reaction of the glass and a light activated resin reaction both occur [17]. "Tri-cure" or "triple cure" cements describe another type of RMGIC, such as Vitremer, where the polymerization reaction of the resin is also initiated chemically in addition to the light activated reaction.

Other studies have investigated the influence of varying conditions such as humidity [18], temperature [19] and heat treatment [20] on the bond strength [21], setting reaction and strength of glass ionomer cements [22]. The use of heat to improve the mechanical properties of resin composites has been investigated by a number of workers [23–25]. Subsequently the use of radiant heat on a conventional GIC has investigated and concluded that the compressive strength of restorative GIC could be increased at temperatures above 37 °C [26]. Woolford [27] studied the effect of radiant heat on the surface hardness of a conventional glass polyalkenoate (ionomer) cement. The results showed that raising the temperature of the surface of the cement significantly improved the early surface hardness of the material. Another study has suggested that heat and pressure can increase strength particularly when the material is autoclaved [28]. Little work has been published on the effects of heat on the strength of newer conventional glass ionomers and none on those which are resin-modified.

The modulus of elasticity or Young's modulus represents the stiffness of a material. Within the elastic range, the higher the modulus the stiffer the material. It is desirable to match the modulus of the restorative material with the dental tissues, as the placement of restorative materials of different moduli will affect the overall modulus of the restored tooth and interfacial stresses generated.

For many dental materials visco-elasticity is an important factor in how the materials respond mechanically in vitro or in vivo. Visco-elastic behaviour denotes the tendency of a material to both flow and rebound when strained. It exhibits some time-dependence. This also depends on the temperature range, applied stress and applied strain. This may be measured in terms of stress relaxation or creep. Stress relaxation is the time dependent change of stress in a material held at constant strain. Creep is the time dependent change in strain under constant stress. Dental restorations are repeatedly subjected to transient pressures. The decay of stress after a specimen has been rapidly stressed gives a more realistic representation of the behaviour of the material in a clinical situation rather than the static creep test which is normally carried out on dental materials [29]. Stress relaxation is significant in dual-cured luting composites as relaxation may reduce the stress across the tooth restoration interface. This may also be significant in dual-cured glass ionomer cements [30]. Unconverted monomer is known to leach out of the set resin-modified cements at normal temperatures. A higher degree of conversion would be expected if heat is applied during the curing process and this would theoretically reduce the amount of leachable material. However, an improvement in the strength of the material but with a subsequent loss of the fluoride release would not be desirable. It would seem important in light of the foregoing review that attempts be made to overcome the deficiency in mechanical properties of both RMGICs and conventional GICs while maintaining the benefits of fluoride release and adhesion.

This study investigated the effects of application of heat alone and heat & pressure on the compressive strength of a conventional glass ionomer cement and a resin-modified glass ionomer cement while monitoring the fluoride release with respect to time. Furthermore, the stress relaxation characteristics and the modulus of elasticity of the materials when stored in water were observed over a period of 2 months.

## 2 Materials and methods

The materials used in this study were a conventional GIC (HiFi Shofu Dental products Advanced Healthcare Ltd., Tonbridge, UK) and a resin modified GIC (Vitremer 3M Dental Products Division, St. Paul, MN, USA). Both materials were supplied as a powder and liquid for hand mixing. HiFi was mixed at a powder: liquid ratio of 7:1. Vitremer was mixed in a powder to liquid ratio of 2.5:1. ISO standard cylindrical compression strength specimens 6 mm high by 4 mm diameter were constructed for both materials using stainless steel moulds. The materials were mixed according to the manufacturer's instructions. The mixed cement was then packed into the split metal mould which was resting on a polythene sheet and a metal slide. Once the mould had been packed with cement it was covered by another polythene sheet and metal slide and the excess cement was expelled using hand pressure. The resin-modified specimens were not light cured, as it was desirable to observe the effects of the treatment while the cement was in an immature state. The RMGIC sets in the absence of light by a redox reaction. Ninety specimens were prepared from each material. These were randomly divided into 3 groups,

Group 1: *heat (oven)*: The clamped moulds were placed in an oven (Esmadent, Div. of ESMA Chemicals, IL, USA) at a temperature of 120 °C for 20 min and then placed in an incubator (LEEC Colwick Industrial Estate, Nottingham, UK) at 37 °C.

Group 2: heat & pressure (Ivomat): The clamped moulds were placed in a heat & pressure vessel, (Ivomat Ivoclar AG, Schaan, Liechenstein ) and a cycle set at 120 °C for 20 min at 6-bar pressure. A small volume of water was also placed in the chamber to maintain humidity. The specimens were then placed in an incubator at 37 °C.

Group 3:control: The clamped moulds were placed in an incubator at 37 °C for 1 h.

After 1 h in the clamp, the specimens were demoulded and the excess flash removed. The specimens were then weighed (±0.0001 mg) and the length and diameter measured using calipers (Mitutuyo, Andover, Hampshire, UK) (±0.001 mm). All specimens were then placed in 20 mL deionized water and stored at 37 °C until required for testing. Six specimens of each material from each group were tested for stress relaxation and compressive strength after 1, 7, 14, 28 and 56 days in an Instron universal testing machine (Instron Ltd., High Wycombe, BUCKS, UK). Compressive moduli were calculated from the results.

### 2.1 Stress relaxation

The specimen was loaded to 37 MPa at 1 mm/min using the load cell of 1 KN. The stress relaxation of each specimen was then determined. The load was held for 45 s. Maximum load at 10, 12, 15, 20, 25, 30, 35, 40 and 45 s was noted. The stress relaxation of each of the specimens was then determined by calculating the slope of the line produced by plotting the graph of (Sm − St)/Sm against log time, where Sm = the maximum load and St = the load at time t. The median value of the 6 specimens was then used to compare the heat, heat & pressure and the control groups.

### 2.2 Compressive strength and compressive modulus

The same specimen was then subjected to a further compressive load until failure. From this data the compressive strength of the specimens could be determined by using the formula: Compressive strength = $P/\pi r^2$ where P is the load at failure and r is the radius of the specimen. The median value of the compressive strengths of the six specimens was calculated for the heat, heat & pressure, and control groups at the test intervals of 1, 7, 14, 28 and 56 days. The compressive modulus of the specimen was calculated from a straight line fit on the stress–strain curve below the proportional limit. The median value was also calculated.

### 2.3 Fluoride release

The deionized water used to store the compressive strength specimens was replaced every 7 days over the 56 day period and this was then used to calculate fluoride release. The fluoride ion concentration in the storage water was measured at intervals of 1, 7, 14, 28 and 56 days respectively using a differential electrode cell, comprising a fluoride ion electrode and a combination pH electrode connected to an Orion microprocessor Ionalyzer/901(Quadrachem Labs. Ltd. East Sussex, UK) based on the method originally described Tyler and Poole [31]. The machine was calibrated using standard fluoride solutions of 1, 10 and 100 ppm. Re-calibration was carried out at 2 h intervals. The fluoride release in mg per gm of cement was calculated from each of the 6 specimens in each group at each time The cumulative fluoride release could then be calculated for each specimen and the median cumulative fluoride released from the 6 specimens in each of the heat, heat & pressure and control groups was then obtained at these same time periods. The median cumulative fluoride released from the HiFi and Vitremer groups was then plotted with respect to time.

The data were entered onto spreadsheets (Microsoft Excel) and transferred onto a statistics programme (Minitab). Non-parametric Mann–Whitney statistical tests were used to compare the results for all evaluation.

## 3 Results

### 3.1 Fluoride release

The cumulative fluoride release from the HiFi and Vitremer specimens from the three groups up to day 56 is summarised in Figs. 1 and 2 respectively. Initially there was relatively rapid elution of fluoride from the conventional GIC over the first day, which was similar for all groups. Subsequently the fluoride release for the control and the heat & pressure specimens showed a reduction in the rate of release. The RMGIC control group showed the typical short-term rapid elution of fluoride but the pattern for the both the heat and heat & pressure treated groups showed a low rate of release with no apparent rapid elution. This resulted in a significantly reduced cumulative fluoride release from these specimens compared to the controls ($P < 0.05$) but no significant differences were found between the heat and heat & pressure treated groups.

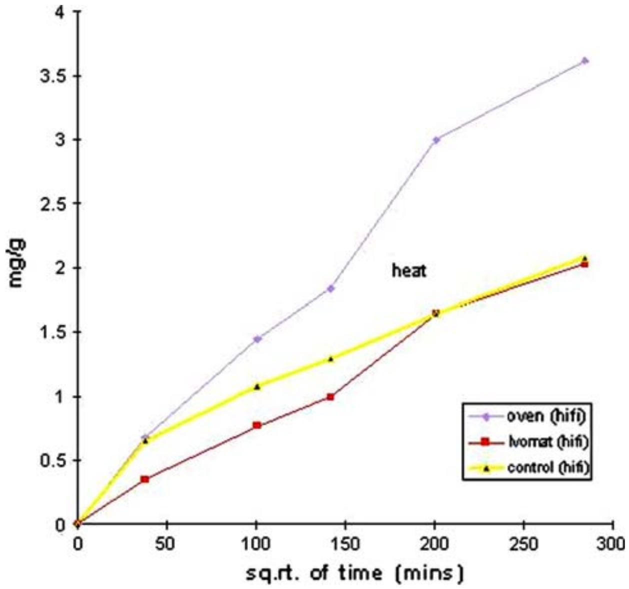

**Fig. 1** HiFi – cumulative fluoride release

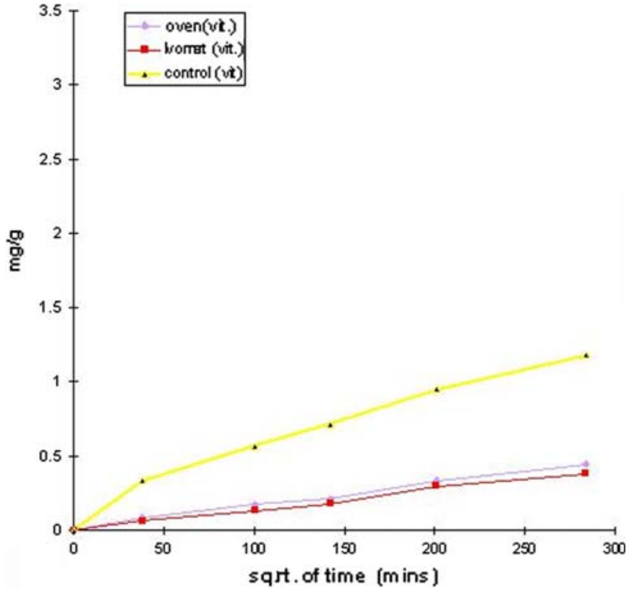

**Fig. 2** Vitremer – cumulative fluoride release

### 3.2 Compressive strength

The compressive strength values for each material are shown in Figs. 3 and 4. The median compressive strengths for all HiFi groups increased up to one month and then declined. There was no statistical difference between the control and the heat treated conventional GIC specimens. Both the heat and heat & pressure specimens of Vitremer showed a significantly higher ($P < 0.05$) compressive strength initially and this increased with respect to time.

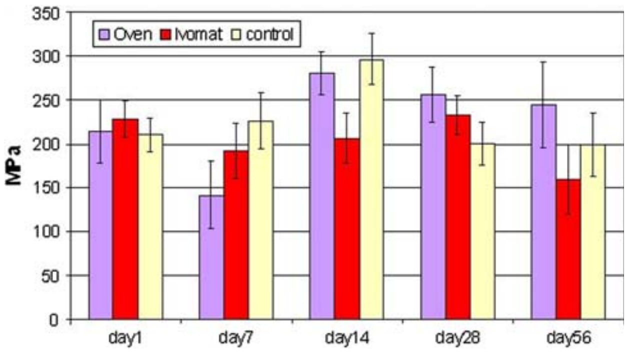

**Fig. 3** Compressive strength for HiFi (median)

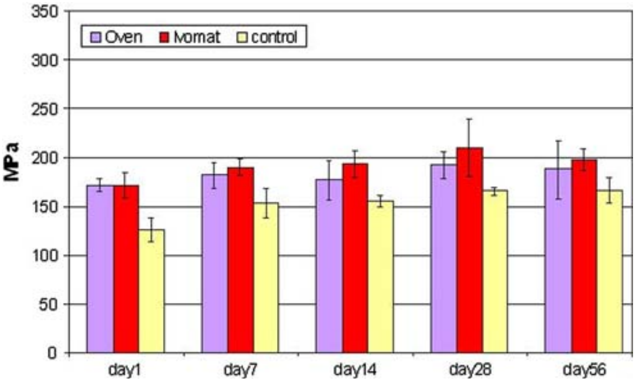

**Fig. 4** Compressive strength for Vitremer (median)

### 3.3 Compressive modulus

The compressive moduli of both the HiFi and Vitremer specimens are summarised in Table 1. The pattern of change of the modulus increasing over the first 2 weeks and then declining after this was similar for all groups of the conventional GIC. In the case of Vitremer the heat and heat & pressure treatment both caused an increase in the compressive modulus and this level was maintained over the experiment period. The modulus for the heat treated specimens was significantly higher than those subjected to heat & pressure at day 1 ($P < 0.01$) and day 7 ($P < 0.05$) but there were no significant differences thereafter.

### 3.4 Stress relaxation

Tan delta represents the relative rate of relaxation of the specimen. The tan delta values of the samples from HiFi and Vitremer groups are summarised in Table 2. In the control groups of both materials, the day 1 specimens have high relaxation rates that decrease sharply as the specimen ages. There was no significant change in the heat treated groups of the conventional GIC however, both the heat and heat & pressure groups had significantly decreased tan

**Table 1** Compressive moduli (GPa)

| HiFi | Heat | | | Heat & pressure | | | Control | | |
|---|---|---|---|---|---|---|---|---|---|
| | Median | Mean | (SD) | Median | Mean | (SD) | Median | Mean | (SD) |
| Day 1 | 7.05 | 6.86 | (1.19) | 7.75 | 7.52 | (0.67) | 6.58 | 6.52 | (0.65) |
| Day 7 | 7.60 | 7.89 | (0.96) | 7.79 | 7.93 | (0.72) | 7.01 | 6.93 | (1.63) |
| Day 14 | 9.23 | 9.32 | (0.83) | 8.09 | 7.74 | (1.11) | 9.10 | 8.86 | (0.67) |
| Day 28 | 9.18 | 8.97 | (0.37) | 8.61 | 8.54 | (0.56) | 8.38 | 8.44 | (0.45) |
| Day 56 | 7.38 | 7.58 | (1.17) | 6.72 | 6.13 | (1.41) | 7.38 | 7.22 | (1.18) |
| *Vitremer* | | | | | | | | | |
| Day 1 | 3.96 | 3.94 | (0.08) | 3.32 | 3.30 | (0.37) | 3.21 | 3.11 | (0.48) |
| Day 7 | 4.68 | 4.59 | (0.24) | 4.24 | 4.21 | (0.15) | 4.05 | 3.95 | (0.41) |
| Day 14 | 4.37 | 4.21 | (0.45) | 4.31 | 4.21 | (0.29) | 4.26 | 4.25 | (0.20) |
| Day 28 | 4.95 | 4.83 | (0.48) | 4.74 | 4.21 | (0.96) | 4.69 | 4.58 | (0.27) |
| Day 56 | 4.81 | 4.69 | (0.58) | 4.45 | 4.40 | (0.42) | 3.60 | 3.55 | (0.27) |

**Table 2** Tan delta (stress relaxation)

| HiFi | Heat | | | Heat & pressure | | | Control | | |
|---|---|---|---|---|---|---|---|---|---|
| | Median | Mean | (SD) | Median | Mean | (SD) | Median | Mean | (SD) |
| Day 1 | 0.033 | 0.033 | (0.002) | 0.032 | 0.032 | (0.001) | 0.035 | 0.035 | (0.001) |
| Day 7 | 0.032 | 0.033 | (0.003) | 0.032 | 0.033 | (0.005) | 0.034 | 0.035 | (0.002) |
| Day 14 | 0.032 | 0.032 | (0.001) | 0.032 | 0.032 | (0.002) | 0.032 | 0.031 | (0.001) |
| Day 28 | 0.031 | 0.030 | (0.002) | 0.031 | 0.031 | (0.001) | 0.031 | 0.032 | (0.001) |
| Day 56 | 0.032 | 0.032 | (0.001) | 0.030 | 0.032 | (0.003) | 0.032 | 0.032 | (0.002) |
| *Vitremer* | | | | | | | | | |
| Day 1 | 0.043 | 0.043 | (0.001) | 0.045 | 0.046 | (0.003) | 0.047 | 0.047 | (0.003) |
| Day 7 | 0.037 | 0.037 | (0.003) | 0.041 | 0.040 | (0.002) | 0.037 | 0.038 | (0.003) |
| Day 14 | 0.035 | 0.035 | (0.002) | 0.036 | 0.037 | (0.001) | 0.035 | 0.034 | (0.001) |
| Day 28 | 0.034 | 0.034 | (0.001) | 0.036 | 0.038 | (0.004) | 0.035 | 0.034 | (0.001) |
| Day 56 | 0.033 | 0.033 | (0.001) | 0.036 | 0.036 | (0.001) | 0.035 | 0.035 | (0.001) |

delta values ($P < 0.05$) when compared to the control from day 1 for the RMGIC. The relaxation value remained at those lower levels over the duration of the experiment.

## 4 Discussion

Indirect composites for inlay and onlay systems have been commercially available since 1986 whereby heat and pressure has been used to supercure the composite and improve the physical properties. One such system is the SR-Isosit system using the Ivomat, which heats the material to 120 °C at 6-bar pressure. The Ivomat was used in this study at this temperature and pressure for 20 min. The specimen size chosen was 6 mm in height by 4 mm in diameter according to ISO 9917 for compressive strength testing. It was decided to use this test as it is considered to be appropriate only for materials under standard conditions using standard 6 mm by 4 mm specimens with a load rate of 1 mm/min [32]. Therefore the results obtained from the different groups in this study would be comparable with other data published on compressive strengths and compressive moduli. Sample size was selected to be large enough to allow simple analysis yet be small enough to avoid logistical problems during specimen fabrication and while undergoing testing. Inevitably this meant that the statistical analysis would probably be by non parametric methods.

### 4.1 Fluoride release

The release of fluoride from GICs has been studied using laboratory experiments in different techniques and using different specimen dimensions and the values obtained are frequently dependent on the methodology used and the shape and volume of the specimen. Periodic replacement of storage solutions were carried out and the volume selected in this case was 20 ml, similar to that reported to provide an infinite sink for fluoride release over periods up to three months [33]. It is not known for certain where the fluoride released from set cements originate but it is thought generally to be from the silica-gel phase covering the glass particles, the matrix salts where fluoride ions can be tightly bound or the pore liquid where it is loosely bound [34]. The conventional GIC control group showed the initial burst of fluoride from day 1 and the oven group followed a similar profile. This pattern is similar to that observed in other studies [35]. It is usually associated with surface washout. The surface washout has been attributed to disturbances of the maturation phase of the setting reaction. The oven treated group however continued to show a higher level of fluoride release. This was probably due to the physical breakdown and disintegration of the cement that was observed around the edges of the cylinders. The heat & pressure group showed a slower more linear release. This may be attributed to accelerated maturation promoted by the higher temperature so less fluoride would be released as the cement had matured faster.

The heat treatment caused a significant reduction in fluoride release from the Vitremer specimens. This may be attributed to a greater degree of conversion of the resin component and possibly increased rate of reaction of the acid-base phase which result in a reduction in the amount of fluoride available. RMGICs have been shown to release as much fluoride or more than conventional GICs [36]. The results from this study indicate that the RMGIC, Vitremer, released less fluoride than HiFi, a conventional GIC, as shown in the control specimens. This may be due to the regime used in the study.

## 4.2 Compressive strength

Williams and Billington [37] demonstrated that the compressive strength of conventional GICs progressively increased over 24 h and reached values between 170–220 MPa and in this study a mean of 212.7 MPa was achieved for 24 h specimens. The initial increase in compressive strength is due to the formation of the polyacrylate chains and subsequent cross-linking of the matrix salts. The sodium or silicate as a matrix forming reaction may also play a role in this increase in strength [7]. The decline in strength at a late stage has been reported previously both for compression and flexural strength [38, 39]. It has been proposed that the progressive slow maturation reaction as a result of high density cross-linking occur possibly with the silica gel phase such that the material becomes more brittle [8].

The application of heat with or without pressure certainly did not enhance the compressive strength. The compressive strength for the heat treated specimens was similar to the control group. This may be in part due to the heat being applied after the cement had begun to go through its initial set or due to loss of water from the cement when it is still in its unbound form. Previous work in this area [20, 22, 26] had suggested that heat and heat & pressure can increase strength and produce a mature cement. Further work may be indicated with a fully mature specimen and also using one where the initial set is substantially retarded.

The Vitremer control group showed a steady rise in compressive strength throughout the time period as expected. The values obtained in this study (mean compressive strengths: 123–164 MPa) were lower than the mean range 229–270 MPa reported [40]. This may be as a result of only partial activation of the light polymerization as the Vitremer specimens were not light cured. The heat treatment of both the oven and Ivomat groups significantly increased the compressive strength of Vitremer from day 1. This is probably the result of increased level of conversion of the resin component and increased cross-linking, and possibly an increase in the rate of maturation of the acid–base cement reaction. The effect of heat on an already light cured material would be appropriate for further investigation.

## 4.3 Compressive modulus

The modulus of elasticity in the conventional GIC control group increased by day 14 and is due to the increased cross-linking of polyacrylate chains [41]. The modulus then decreases in time probably due to the plasticizing effects of water or the buildup of cross linking in the silica phase. The heat and heat and pressure did not have any effects when compared to the control group for the conventional GIC. It may be that the initial reaction has gone too far to completion for the effect to be of benefit. It has been demonstrated for Vitremer that the modulus of elasticity increases but after storage in water for 1 month, it decreases significantly [42] and this was also demonstrated in this study. The heat or heat and pressure treatment however, caused an increase in the modulus with a higher modulus being maintained for longer. The material became stiffer. This may be a result of a greater conversion of the resin phase. Possibly because the acid–base reaction rate is retarded, the heat may also have enhanced this phase. Certainly the modulus does not appear to decline with time. The modulus of the conventional GIC, HiFi, was much higher in this study compared to the RMGIC, Vitremer. This is in agreement with the data published previously on these materials [43].

### 4.4 Stress relaxation

The one day old conventional GIC cement exhibits appreciable stress relaxation characteristics and some plastic behaviour, which decrease sharply as the cement ages in water. The 1-month-old specimens exhibit little plastic behaviour as rigid cross-linking develops [44]. This pattern was demonstrated with the conventional GIC control specimens but the heat treatment did not seem to have a significant effect on these characteristics with the conventional GIC. This is probably an indication that the heat treatment had less effect on the setting mechanism. This may be due to the time of application or that the heat may have led to a loss of water. The control specimens for the RMGIC exhibited initially high relaxation rates that decreased on ageing. The heat treatment had a significant effect on reducing the values for the day 1 specimens. This suggests that the material had indeed lost some plastic behavior and had tended to become more brittle. It also may be that in this case the reaction has gone to completion. There was a significant difference with the oven treatment causing the material to become more brittle than the heat & pressure treated group. The effect of the water in the heat & pressure group probably allowed the resin component to retain more water and plasticize the material to a certain degree.

Some of the limitations of this study include using specimens not related to the size or shape of inlays or onlays. The heat application carried out on the specimens was delayed and certainly the reaction that the materials undergo will have gone to completion. Some variability in the times of application of heat inevitably occurred. The water loss in the heat treated specimens of the oven may have caused a degradation of the physical properties. The heat applied for both treatments was at 120 °C only and the properties may be different at other temperatures. This will be very much dependent on the glass transition temperature of the components in particular the HEMA.

The use of GIC to produce inlay or onlay restorations that adhere to tooth tissue and release fluoride would be highly desirable clinically. The results of this study indicate that it is possible to improve the strength of RMGIC with heat to a limited extent, but fluoride release may decrease. Further research should include using a slower setting conventional GIC, a fully light activated RMGIC, heat treatments carried out over a range of temperatures to assess optimal characteristics and the use of flexural strength testing as a more sensitive indicator of mechanical changes.

## 5 Conclusions

Heat treatment of Vitremer resulted in an increase in compressive strength but the release of fluoride was significantly reduced. Heat treatment of Vitremer also resulted in an increased modulus and decreased stress relaxation characteristics producing a material that was more brittle and less plastic. However, heat treatment of HiFi seemed to have no significant effect on the compressive strength, fluoride release, and modulus or stress relaxation characteristics.

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## References

1. J. W. McLEAN, J. W. NICHOLSON and A. D. WILSON, *Quintessence Int.* **25** (1994) 587
2. T. I. BARRY, D. J. CLINTON and A. D. WILSON, *J. Dent. Res.* **58** (1979) 1072
3. D. BRUNE and D. C. SMITH, *Acta. Odontol. Scand.* **40** (1982) 389
4. A. D. WILSON and J. W. McLEAN, in "Glass ionomer cements" (Chicago: Quintessence Publishing Co. Inc., 1988)
5. E. A. WASSON and J. W. NICHOLSON, *Clin. Mater.* **7** (1991) 289
6. P. V. HATTON and I. M. BROOK, *Br. Dent. J.* **173** (1992) 275
7. E. A. WASSON and J. W. NICHOLSON, *J. Dent. Res.* **72** (1993) 481
8. J. W. NICHOLSON, *Biomaterials* **19** (1998) 485
9. A. D. WILSON, H. J. PROSSER and D. M. POWIS, *J.Dent. Res.* **62** (1983) 590
10. L. FORSTEN, *Scand. J. Dent. Res.* **99** (1991) 241
11. A. D. WILSON and B. E. KENT, *J. Appl. Chem. Biotechnol.* **21** (1971) 313
12. T. P. CROLL and C. M. KILLIAN, *Quintessence Int.* **24** (1993) 723
13. W. DASCH, D. S. TURNER and J. M. POWERS, *J. Dent. Res.* **72** (1993) 224
14. H. J. PROSSER, D. R. POWIS and A. D. WILSON, *J. Dent. Res.* **65** (1986) 146
15. B. K. MOORE, M. L. SWARTZ and R. W. PHILLIPS, *J. Dent. Res.* **64** (1985) 371
16. J. W. McLEAN and O. GASSER, *Quintessence Int.* **16** (1985) 333
17. S. B. MITRA, *J. Dent. Res.* **70** (1991) 72
18. W. KANCHANAVISTA, G. J. PEARSON and H. M. ANSTICE, *Biomaterials* **16** (1995) 921
19. J. FRICKER, K. HIROTA and Y. TAMIYA, *Aust. Dent. J.* **3** (1991) 240
20. D. BRUNE, *Scand. J. Dent. Res.* **90** (1982) 409
21. T. J. ALGERA, C. J. KLEVERLAAN, A. J. DE GEE, B. PRAHL-ANDERSON and A. J. FEILZER, *Eur. J. Orthod.* **5** (2005) 472
22. C. J. KLEVERLAAN, R. N. van DUINEN and A. J. FEILZER, *Dent Mater* **1** (2004) 45
23. J. R. BAUSCH, C. De LANGE and C. L. DAVIDSON, *J. Oral. Rehabil.* **8** (1981) 309
24. S. WENDT, *Quintessence Int.* **4** (1987) 265
25. N. TANOUE, H. MATSUMURA and M. ATSUTA, *J. Oral. Rehabil.* **4** (2000) 288
26. J. A. WILLIAMS and R. W. BILLINGTON, *J Dent Res* **71** (1992) 525

27. M. J. WOOLFORD, *J. Dent.* **22** (1994) 360
28. C. HENGTRAKOOL, H. M. ANSTICE, G. J. PEARSON and M. WILSON, *J. Dent. Res.* **77** (1998) 814
29. R. S. HERTERT, E. F. HUGET, L. B. De SIMON and J. H. COSGROVE, *J. Dent. Res.* **54** (1975) 1149
30. D. C. WATTS, *J. Dent.* **22** (1994) 154
31. J. E. TYLER and D. F. G. POOLE, *Arch. Oral. Biol.* 34 (1989) 995
32. H. M. ANSTICE, J. W. NICHOLSON and J. F. McCABE, *J. Dent. Res.* **71** (1992) 1871
33. A. T. KUHN, G. B. WINTER and W. K. TAN, *Biomaterials* 3 (1982) 136
34. R. M. VERBEECK, E. A. De MAEYER, L. A. M. MARKS, R. J. De MOOR, A. M. De WITTE and L. M. TRIMPENEERS, *Biomaterials* **19** (1998) 509
35. W. M. TAY and M. BRADEN, *Biomaterials* **9** (1988) 454
36. Y. MOMOI and J. F. McCABE, *Dent. Mater.* **9** (1993) 151
37. J. A. WILLIAMS and R. W. BILLINGTON, *J. Oral Rehabil.* **16** (1989) 475
38. J. A. WILLIAMS and R. W. BILLINGTON, *J. Oral Rehabil.* **18** (1991) 163
39. G. J. PEARSON and A. S. ATKINSON, *Biomaterials* **12** (1991) 658
40. S. B. MITRA and B. L. KEDROWSKI, *Dent. Mater.* 10 (1994) 78
41. E. De BARRA and R. G. HILL, *Biomaterials* **19** (1998) 495
42. M. BRAEM, P. LAMBRECHTS, S. GLADYS and G. VANHERLE, *Dent. Mater.* **11** (1995) 137
43. S. GLADYS, B. Van MEERBEEK, M. BRAEM, P. LAMBRECHTS and G. VANHERLE, *J. Dent. Res.* **76** (1997) 883
44. J. M. PADDON and A. D. WILSON, *J. Dent.* **4** (1976) 183