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The influence of microstructure on thermal response of glass ionomers

Zhuoqun Yan · Sharanbir K. Sidhu · John F. McCabe

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Abstract This study was designed to determine the dimensional changes caused by thermal stimuli of glass ionomers with different glass/matrix ratios. Four cylindrical specimens were made for each of four powder/liquid ratios (3:1, 2.5:1, 2:1 and 1.5:1) for a conventional luting glass ionomer, two high viscosity restorative glass ionomers and a restorative resin-modified glass ionomer. The thermal characteristics were determined using a thermal mechanical analyzer (TMA) by heating the samples from 25 °C to 70 °C at 10 °C per minute. All glass ionomers and the resin-modified glass ionomer lost water on heating. The results of the thermal response of these materials were explained in terms of the opposing effects of thermal expansion and desiccation on heating. The contraction on heating of glass ionomer and related materials was found to relate to the glass/matrix ratio but not directly proportional to it. Materials with lower P/L ratios contracted the most when heated to 70 °C. The water loss from conventional and resin-modified glass ionomer with different glass/matrix ratios compensated for their thermal expansion and led to a minimal dimensional change when heated up to 50 °C. This outcome may be interpreted as an example of smart behaviour of these materials.

Introduction

The thermal expansion and contraction behaviour of restorative materials has often been studied and compared with that of tooth structure to evaluate the potential for microleakage resulting from thermal stimuli in the oral environment [1, 2]. The thermal behaviour of glass ionomers is unique because they can interact with water from the environment. The contraction caused by water loss may compensate for the thermal expansion of glass ionomers and this may help to maintain their original dimensions [2]. The matrix of glass ionomers contains 'loosely' bound water as well as 'tightly' bound water [3] which may be affected by the original powder/liquid (P/L) ratio and the structure of the set cement. The amount of 'loosely' bound water is dependent upon the levels of moisture/humidity in the wet or dry environment.

A glass ionomer is a two part material, powder and liquid, which requires mixing in order to set. Therefore the ratio of the powder and liquid determines the ratio of the reinforced glass filler to salt matrix in the set cement [4]. Until now there has been no objective evaluation of the effect of glass-core/matrix ratio on the thermal behaviour of glass ionomers and related materials.

This study aimed to investigate the dimensional change of glass ionomers with different glass-core to matrix ratios on heating. The hypothesis tested was that during the heating of glass ionomers the thermal expansion may be compensated by a shrinkage caused by loss of 'loosely' bound water. If the process is reversible, the opposite may occur when glass ionomers are cooled. Hence, different P/L ratios of glass ionomers, producing differences in the content of

Z. Yan (✉) · S. K. Sidhu · J. F. McCabe
School of Dental Sciences, University of Newcastle,
Framlington Place, Newcastle upon Tyne NE2 4BW, UK
e-mail: zhuoqun.yan@gmail.com

'loosely' bound water, may affect the thermal response of glass ionomers when heated and this has very important clinical implication for the longevity of the restored tooth.

Materials and methods

The restorative materials used in this study were a conventional luting glass ionomer, Ketac^{TM} Cem μ (KC) (3M ESPE, Germany); two high viscosity restorative glass ionomers, Ketac^{TM} Molar (KM) (3M ESPE, Germany) and Fuji IX GP (F) (GC Corp, Japan); a resin-modified glass ionomer, Fuji II LC (FLC) (GC Corp, Japan) [Table 1]. All materials used were two part materials which required mixing by hand.

According to the manufacturers' instructions, the mixing of all materials was carried out on a mixing pad at room temperature using a plastic spatula. Different mixing ratios (1.5:1, 2:1, 2.5:1 and 3:1) were achieved by weighing the liquid and powder separately on an electronic balance. The manufacturer's recommended mixing ratio for each material is shown in Table 1. The mixing process was completed in 30 sec. Four cylindrical specimens (6 mm in length and 4 mm in diameter) of each mixing ratio for each material were prepared in an open-ended, two part, stainless steel mould which was clamped between two glass slides. The auto-cured glass ionomers, KC, KM, and F were allowed to set (30 min) before removal from the mould. The light-cured material, FLC, was cured by a 40 sec exposure of each flat surface to a visible light source (Visilux^{TM} 2, 3M, Germany) while in the mould. All samples were stored in distilled water at 37 °C for 24 h and each specimen was weighed before testing.

Dimensional changes on heating were determined using a thermal mechanical analyzer (TMA, Stanton Redcroft, UK). Each sample was held vertically in a chamber having an optically flat base. A quartz probe, controlled by a balanced beam, with constant but negligible load (approximate 1 gram) was placed on the sample. A displacement transducer was connected to the probe to detect the dimensional change of the sample caused by expansion or contraction. Each specimen was heated in the chamber from 25 °C to 70 °C at 10 °C min^{-1}. At the end of the heating process, each specimen was immediately weighed.

Statistical analysis of the results was performed using ANOVA and Tukey–Kramer test at a significant level of 0.05.

Results

All the glass ionomers tested in this study showed weight loss during the heating process as shown in Table 2. The weight loss decreased as the powder/liquid ratios increased for all the materials tested. Comparing different materials with the same mixing ratio showed that the luting cement, KC, always had the greatest percentage of weight loss ($p < 0.05$) and of the restorative materials, the resin-modified glass ionomer (FLC) had a greater weight loss than the high viscosity glass ionomers (KM and F). For each material, the greatest P/L ratios produced the lowest final weight loss.

The dimensional changes on heating of all materials determined by TMA are shown in Figs. 1–4. All the glass ionomer materials (at all P/L ratios) tested in this study showed an initial minimal expansion followed by a contraction when heated further. For each material, the lowest P/L ratio produced the greatest overall contraction after heating to 70 °C.

Table 1 Materials used in this study and their composition

Product	Type of materials	Composition (manufacturer' data)	Batch No.
Ketac Cem Maxicap (KC)	Conventional luting glass ionomer	Powder: fluoroaluminosilicate glass. Liquid: aqueous polyacrylic acid. Manufacturers' P/L ratio: 3.8:1	151394
Ketac Molar Aplicap (KM)	High viscosity restorative glass ionomer	Powder: fluoroaluminosilicate glass. Liquid: aqueous polyacrylic acid. Manufacturers' P/L ratio: 2.9:1	164009
Fuji IX (F)	High viscosity restorative glass ionomer	Powder: strontium fluoroaluminosilicate glass. Liquid: aqueous polyacrylic acid. Manufacturers' P/L ratio: 3.6:1	0209102
Fuji II LC (FLC)	Resin-modified restorative glass ionomer	Powder: fluoroaluminosilicate glass. Liquid: aqueous solution of polyacrylic acid, TEGDMA and HEMA Manufacturers' P/L ratio: 3.2:1	0302151

HEMA = Hydroxyethylmethacrylate, TEGDMA = Triethyleneglycol demethacrylate

Table 2 Weight loss (% of original weight) following heating to 70 °C for samples of different P/L ratio

Material	P/L ratio			
	1.5:1	2:1	2.5:1	3:1
KC	$11.12^{a,1}$ (0.30)	$4.22^{b,1}$ (0.29)	$3.76^{c,1}$ (0.06)	$2.78^{d,1}$ (0.12)
KM	$1.89^{a,2}$ (0.47)	$1.18^{a,b,2}$ (0.04)	$1.06^{b,2}$ (0.02)	$0.82^{c,2}$ (0.03)
F	$2.06^{a,2}$ (0.24)	$1.52^{a,b,3}$ (0.17)	$1.40^{b,2,3}$ (0.20)	$1.01^{c,2,3}$ (0.06)
FLC	$2.22^{a,2}$ (0.26)	$1.82^{a,b,3}$ (0.27)	$1.42^{b,c,3}$ (0.18)	$1.10^{c,3}$ (0.06)

Mean (SD) values in the same row assigned the same letter (superscripts) are not significantly different; values within the same column with the same number (superscripts) indicate no significant difference ($p > 0.05$). In general, each glass ionomer at lower P/L ratios showed greater weight change (weight loss) on heating ($n = 4$). Statistical analysis of the results was performed using ANOVA Two-way and Tukey–Kramer test at a significant level of 0.05

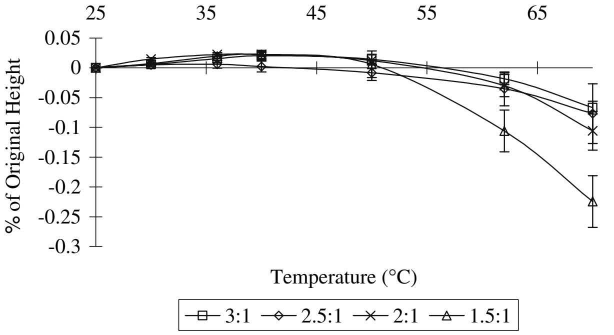

Fig. 1 Dimensional changes of KC with different P/L mixing ratios ($n = 4$, ± standard deviation). Each specimen was heated from 25 °C to 70 °C at 10 °C min^{-1}

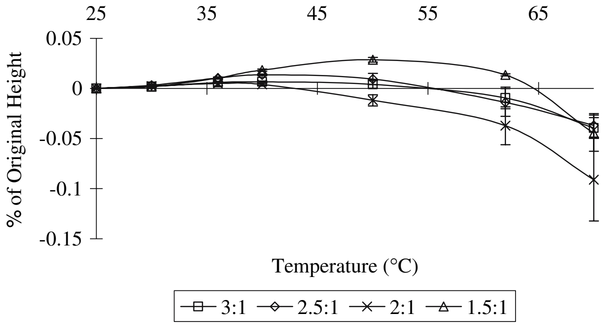

Fig. 2 Dimensional changes of KM with different P/L mixing ratios ($n = 4$, ± standard deviation). Each specimen was heated from 25 °C to 70 °C at 10 °C min^{-1}

Discussion

Thermal behaviour of glass ionomers and related materials has been reported in a previous study [2] which observed that thermal expansion of these materials may be compensated by water loss when heated. The water content and its relative mobility in the glass ionomer matrix have been considered as major factors in determining the thermal response behaviour of these materials. In glass ionomers, the water content and especially the 'loosely' bound water will depend on the powder/liquid ratio and the storage method [3].

Glass ionomers are water-based materials which interact with water in the environment. Water diffusion through the material matrix may be affected by material composition [5]. The ratio of reinforcing glass-core and matrix will affect the diffusion of water in the glass ionomer matrix [6]. When glass ionomers are mixed at a high initial P/L ratio, the ratio of reinforcing glass core in the matured cement matrix is

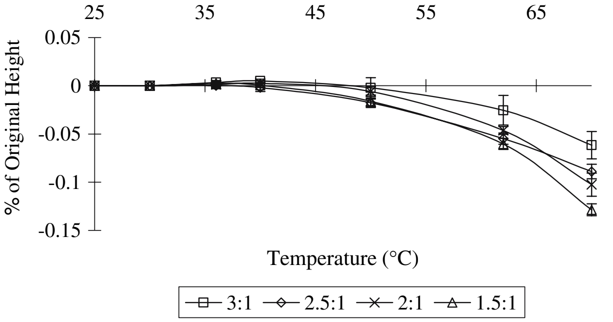

Fig. 3 Dimensional changes of *F* with different P/L mixing ratios ($n = 4$, ± standard deviation). Each specimen was heated from 25 °C to 70 °C at 10 °C min^{-1}

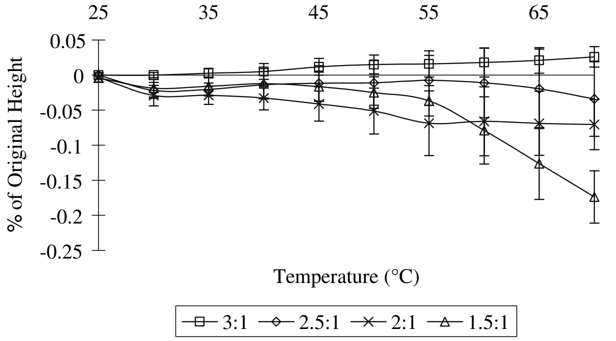

Fig. 4 Dimensional changes of FLC with different P/L mixing ratios ($n = 4$, ± standard deviation). Each specimen was heated from 25 °C to 70 °C at 10 °C min^{-1}

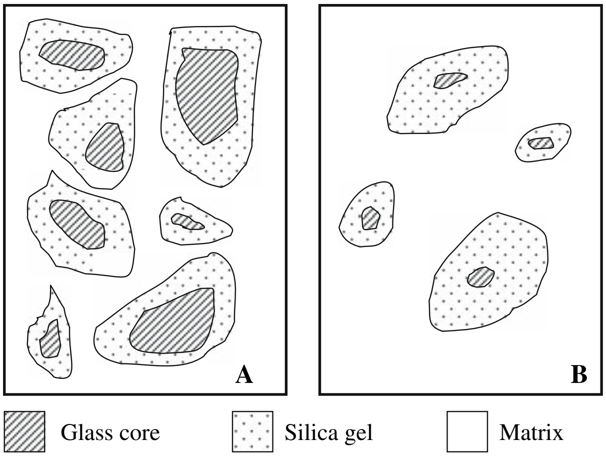

Fig. 5 Diagrammatic representation of the matrix of fully matured glass ionomer showing the matrix phrase and the structure of fillers (glass-core surrounded by silica gel). (**A**) High P/L ratio glass ionomer with large amount of glass filler in the matrix; (**B**) Low P/L ratio glass ionomer with small amount of filler in the matrix

increased (Fig. 5). Decreasing the P/L ratio reduces the amount of the reinforcing fillers in the matrix [4]. Decreasing the P/L ratio may introduce more porosity into the glass ionomer matrix [7] during the mixing process. The role of the water stored within the porosity of the cement is still not clear and the magnitude of contraction of a solid porous material which loses water depends on the mechanical properties of the material. Hence, a rigid material containing fluid within porosities may lose fluid without necessarily undergoing a significant dimensional change.

All the conventional glass ionomers tested in this study, including the luting cement KC and high viscosity restorative cements KM and F, showed a certain level of contraction on heating no matter what P/L ratio was used. The thermal dimensional curves of all the specimens were nonlinear over the temperature range observed. Coefficient of thermal expansion (CTE) which is normally used to describe the thermal expansion of materials was not a meaningful parameter for use in characterising these materials. Minimal dimensional changes were observed at the beginning of the heating process up to around 30 °C, after which a slight expansion process followed. No statistically significant differences were found in the initial expansion values among different P/L ratios of the same material ($p > 0.05$) in this range. At a temperature specific to each material, all products began to contract. The luting material, KC, showed the highest final contraction value compared to other materials with the same P/L mixing ratio. Luting glass ionomers, which have a lower P/L ratio and are relatively fluid, tend to have a high porosity [7]. The combination of a large acid-base cement component and a high porosity in the matrix may have combined to allow easy movement of water in and out of this type of material. For each material, the final contraction value was greater at lower P/L ratios.

FLC, a resin-modified glass ionomer, showed a significantly different behaviour to the conventional glass ionomers. The specimens prepared at the highest P/L ratio of 3:1 gave a thermal expansion over the whole heating range. An increase in the P/L ratio of these products produced an increase in the proportion of resin in the matrix of the set material and since resin matrix composites expand when heated [8] it was not surprising that these products behaved in a similar fashion. At lower P/L ratios, the behaviour of the resin-modified glass ionomer was similar to that of conventional glass ionomers i.e., they contracted upon heating to above mouth temperature.

The effect of changing the P/L ratio of GICs is in line with what is expected from their structure. However, the overall pattern was that dimensional changes were minimised by the opposing effects of thermal expansion and water loss.

In conclusion, the water loss from conventional and resin-modified glass ionomers with different P/L ratios compensated for thermal expansion and resulted in a minimal dimensional change on heating over the range of normal intra oral temperatures in dry ambient conditions which confirms the hypothesis. This finding suggests that glass ionomers are capable of ‘smart’ behaviour under conditions of varying temperature.

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