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Investigation of glass–ionomer cements using differential scanning calorimetry

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Six commercial glass–ionomer cements commonly used for various dental applications have been investigated using differential scanning calorimetry (DSC). The heat-flow behaviour and heat capacity of the cements were measured during isothermal (at 37 °C) setting reactions. The DSC results show that all materials undergo an exothermic setting process, but with different enthalpies of reactions and different heat capacities; there are no remaining endo- or exothermic reactions after the setting of the cement. All materials examined were found to be effective thermal insulators.

1. Introduction

Polymeric materials are being increasingly introduced and used in dentistry as cements, filling materials, dentine substitutes and treatment of early carious lesions. In recent years, glass–ionomer cements (GICs) have been a subject of interest as materials for dental applications, such as, restorative materials, filling of erosion cavities, general cementation purposes and cavity [1–6]. Conventional GICs are two-component systems, consisting of an ion-leachable flouroaluminosilicate glass powder and an aqueous solution of polycarboxylic acid. GICs set by means of an acid–base neutralization reaction, with the product of a hydrogel salt acting as a binding matrix. On mixing of the two-components, hydrogen ions liberated from the polymeric acid attack the glass, causing the release of metal ions such Al^{3+}, Ca^{2+}, etc. In turn, these cations cross-link the acid to form an insoluble matrix which subsequently bonds to the residual silicate structure formed on the glass surface.

The basic advantages of the conventional GICs are: fluoride-release, prevention of secondary caries, good adhesion to tooth structure and margin sealing, biocompatibility and thermal expansion coefficients matched to tooth structure. Also, the set cement is translucent and will shade similar to tooth colour. The surface of these cements resists mild acid attack and staining by certain agents, such as can occur in the mouth. The major defects of the GICs are moisture sensitivity in the initial stages of setting leading to crazing, lack of resistance to abrasion and susceptibility to fracture under high shear stresses. They are also porous and difficult to finish to a smooth surface [2, 4, 5, 7–11]. In order to overcome the disadvantages associated with conventional GICs, various efforts have been recently directed to the combination of methacrylate technology and conventional glass–ionomer chemistry in order to develop new types of GICs. These materials are referred to as “resin-modified” or “hybrid-GICs” or “resin-ionomers”, are curable by visible light activation (photoactivated polymerization) and have the advantages of early strength development, water resistance and command set. All light-cured systems suffer from the limited depth penetration of visible light. Hence, layering techniques are necessary which is a time-consuming procedure in many applications [5, 12–15]. We have investigated the setting reactions and thermal properties of some commercial GICs.

2. Materials and methods

The materials used in this study and their specifications are listed in Table I. A Perkin–Elmer DSC-7 instrument was used to measure the amount of heat flow of the GICs during isothermal setting reactions at 37 °C. A small portion of a freshly mixed cement, up to 60 mg, was placed in pre-weighed volatile sample aluminium pan. The unset cement-filled pan was inserted immediately into the DSC-7 sample holder (at 37 °C). The insertion produced a drop in the heat of the DSC-7 cell, because the sample was prepared at room temperature (20 ± 1 °C). Rapid transfer of heat from the apparatus returned the scan to the baseline position (sharp endothermic peak). After that the setting reaction produced an exothermic peak in all the materials investigated. The specific heats of materials under test were examined at 37 °C. A weighed sample of precured material was scanned between 20° and 60 °C at a heating rate of 10 °C min^{-1}. Each material was examined three times. The heat capacity, C_p, of

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TABLE I Details of glass–ionomer cements and resin–ionomers used in the study

Material	Code	Form	Polymer/Liquid (wt/wt)	Setting mechanism	Manufacturer
ChemFil Superior	CF	Powder/distilled water	7.3 : 1	Acid–base reaction	Dentsply Ltd, DeTrey Division, Weybridge, Surrey, UK
Ketac-Cem Radiopaque	KC	Powder/liquid	3.8 : 1	Acid–base reaction	ESPE, GmbH, Am Griesberg, Seefeld, Germany
Chelon-Silver	CS	Powder/liquid	3.8 : 1	Acid–base reaction	ESPE, GmbH, Seefeld Germany
Hi-Dense	HD	Powder/liquid	7.8 : 1	Acid–Base reaction	SHOFU Dental products Ltd, Tonbridge, Kent, UK
Fuji II LC	FJ	Powder/liquid	3 : 1	Acid-base, visible light-curing and chemical curing reactions	GC Corporation Tokyo, Japan
Dyract	D	Encapsulated one-component	–	Light-curing and acid–base reactions	Dentsply Ltd, Weybridge, Surrey, UK

the sample was calculated using the formula

$$C_{\mathrm{p}} = D/RW \qquad (1)$$

where R is the scanning rate ($^{\circ}\mathrm{C\,s^{-1}}$), D the sample displacement (mW) and W the sample weight (mg).

3. Results and discussion

The DSC scans for powder component, liquid component and the powder–liquid mix for each material, were recorded isothermally at 37 °C. The DSC scans for the powder and the liquid show the same general pattern, i.e. there is no heat flow, as illustrated in Fig. 1a. A typical DSC scan obtained at 37° C for the glass–ionomer cements is shown in Fig. 1b. Four points were taken from each curve as follows.

1. Point A: represents the working time at room temperature from start of mixing to insertion of the sample-containing pan into the DSC-7 cell.
2. Point B: the time taken to reach maximum rate of heat output, representing the clinical setting time [16].
3. Point C: the time taken for the heat flow to reach 5% of the maximum, representing the actual setting time [17].
4. Point D: the time taken for the heat flow to become constant. This point represents the absolute setting time as indicated by the completion of the exothermic reaction [16].

The values for each material are given in Table II.

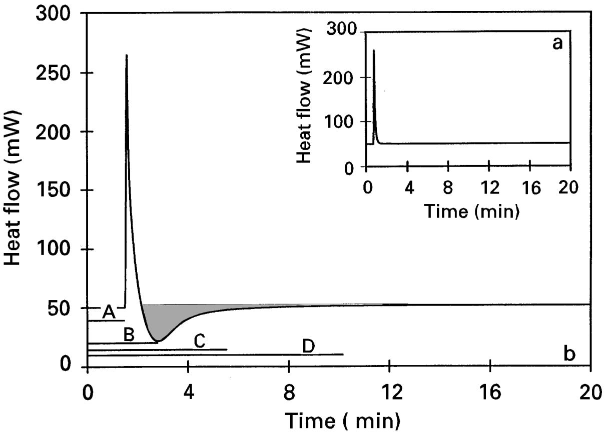

Figure 1 Representative DSC scan at 37 °C for (a) either the liquid or powder component of a glass–ionomer cement: (b) conventional glass–ionomer cement.

TABLE II Setting characteristics of materials investigated by DSC isothermally at 37 °C. Numbers in parentheses are standard deviations

Material	Working time (point A, min)	Peak maximum (point B, min)	Time to 5% of peak maximum (point C, min)	Time to constant heat flow (point D, min)
CF	1.83 (0.22)	3.32 (0.20)	8.90 (0.74)	10.33 (0.47)
KC	1.77 (0.10)	3.06 (0.26)	8.82 (0.38)	10.00 (0.82)
CS[a]	1.77 (0.30)	2.74 (0.43)	6.38 (1.31)	10.96 (1.42)
HD	2.15 (0.57)	3.29 (0.62)	7.89 (1.31)	10.00 (0.94)
FJ; dark-reaction	1.73 (0.21)	4.06 (0.09)	7.61 (0.67)	11.00 (0.00)

[a] 14 measurments.

A typical DSC trace obtained at 37° C for Fuji II LC setting reaction in the absence of light curing is shown in Fig. 2. It exhibits two distinct but overlapping peaks. They may be attributed to the two possible dark reactions: (1) the acid–base neutralization reaction; (2) the chemical polymerization reaction. Fuji II LC was also prepared as mentioned previously and the sample was exposed for 20 s to a visible light source (Visilux 2 light-curing unit, 420–500 nm) immediately before insertion into the DSC-7 cell. The light-cured cement exhibited no heat flow (e.g. like Fig. 1a). In the DSC trace for Dyract, no heat flow was

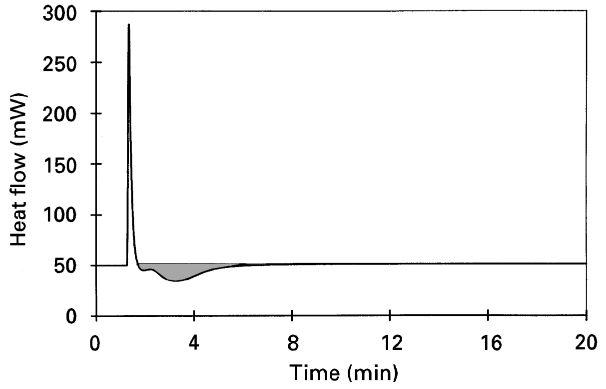

Figure 2 DSC scan at 37 °C for Fuji II LC glass–ionomer cement during dark reaction.

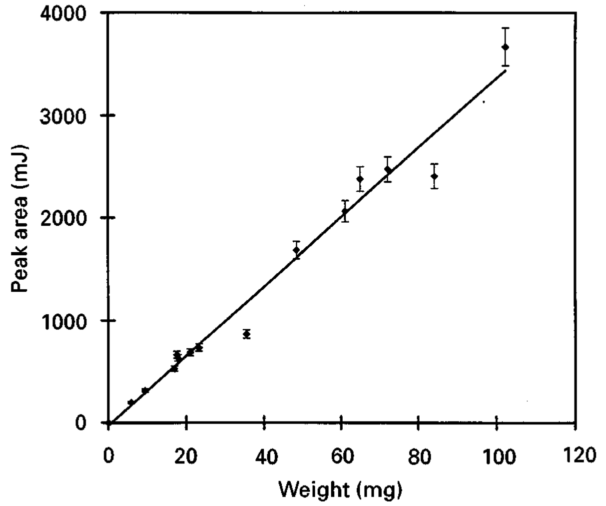

Figure 3 Relationship between the amount of material and the area under the exothemic peak of the GIC setting reaction.

measured for both dark and light-cured reactions. This material has no dark reaction at all, because it is an inert one-component system from the beginning and starts setting only after light-curing. It is likely that the light-curing produces a very fast setting; too fast to be detected by the DSC-7 instrument. Dyract has been reported by the manufacturer to exhibit the traditional glass–ionomer reaction over several months (Dyract Manual GB 2/94). Therefore, some of the light-cured cement samples of this product were soaked in distilled water at room temperature and their isothermal traces were recorded after different periods of time for up to 3 months. There was no evidence for such reaction, because in all cases, no peaks were observed.

Chelon-Silver was examined 14 times to investigate the relationship between the amount of material and the heat flow and to establish the reproducibility of the method. Fig. 3 shows that there is a linear relationship between the amount of material and the area lying under the exothermic reaction peak. There was no obvious correlation between the amount of material and maximum heat flow (peak height) as shown in Fig. 4. This result disagrees with that reported previously by McCabe and Wilson [16]. This may be due to the fact that the setting reaction starts rapidly and ends gradually, producing a rather broad peak.

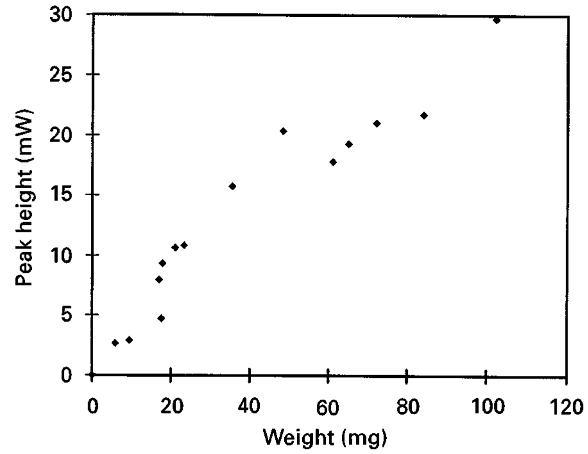

Figure 4 Relationship between the amount of material and the maximum heat flow of the GIC setting reaction.

TABLE III Thermal properties of glass–ionomers setting reactions determined at 37 °C by DSC. Number in parentheses are standard deviations

Material	Peak height $W g^{-1}$	Enthalpy of reaction (Jg^{-1})	Heat capacity (Jg^{-1} °C^{-1})
CF	0.152 (0.011)	25.722 (2.192)	1.183 (0.133)
KC	0.519 (0.042)	62.919 (3.113)	1.141 (0.175)
CS	0.380 (0.094)[a]	33.053 (3.329)[a]	0.857 (0.076)[b]
HD	0.128 (0.011)	16.289 (1.029)	1.033 (0.022)
FJ, dark reaction	0.248 (0.054)	40.096 (6.345)	1.267 (0.233)
FJ, light reaction	–	–	0.972 (0.029)
D, light reaction	–	–	0.898 (0.013)

[a] 14 measurements.
[b] 8 measurements.

The peak height, the amount of heat liberated during the reaction (enthalpy) and heat capacity of each material, are listed in Table III. The minimum value of the heat of reaction was obtained from Hi-Dense (16.289 J g^{-1}) and the maximum value was obtained from Ketac-Cem (62.919 J g^{-1}). When light-cured Fuji II LC was allowed to set in the dark (absence of exposure to the visible light source) it exhibited a very slow setting reaction. It reached its maximum heat flow at 4.06 (0.09) min, while the conventional GICs reached their maximum heat flow sooner. The quickest reaction was recorded by Chelon-Silver (point $B = 2.74$ min) and the slowest was recorded by ChemFil Superior (point $B = 3.32$ min). All materials showed an absolute setting after equal periods of time, approximately 10 min, except for Chelon-Silver and Fuji II LC dark reactions, which were 11 min each.

The dynamic DSC trace has been recorded for Chelon-Silver in order to detect any remaining reaction after the isothermal state. The temperature programme used was preset to keep the freshly prepared cement at 37 °C for 10 min, then heated to 250 °C and cooled to 37 °C, at a heating and cooling rate of 20 °C

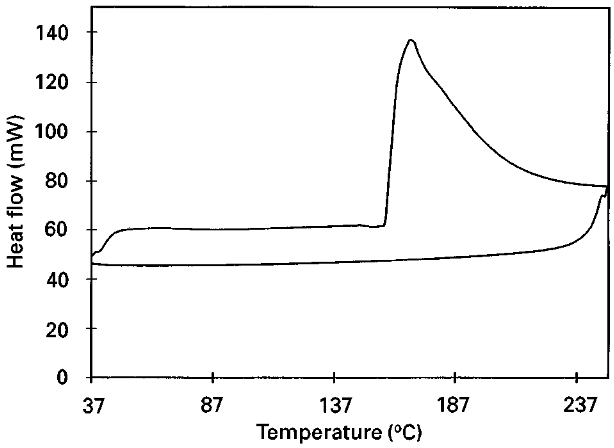

Figure 5 Dynamic trace for the Chelon-Silver glass–ionomer cement.

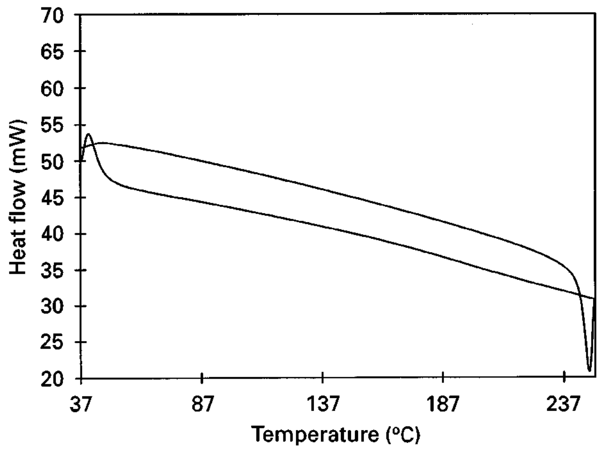

Figure 6 Dynamic trace for the powder component of Chelon-Silver glass–ionomer cement.

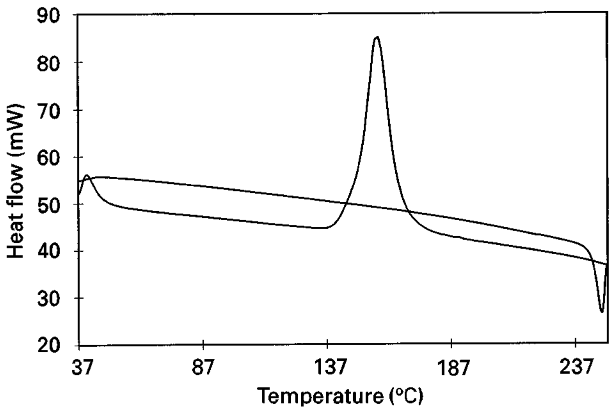

Figure 7 Dynamic trace for the liquid component of Chelon-Silver glass–ionomer cement.

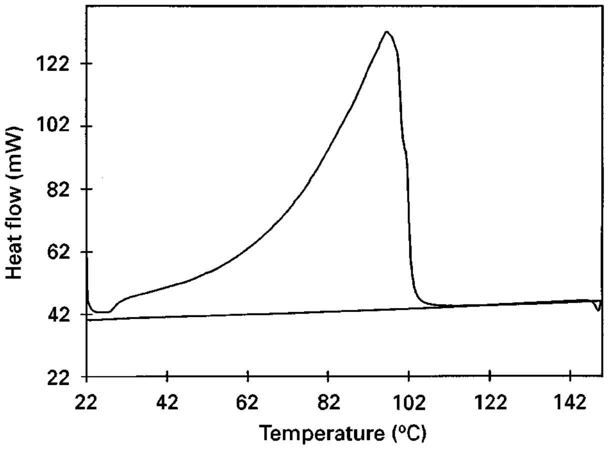

Figure 8 Dynamic trace for distilled water.

min^{-1}. The typical dynamic trace for Chelon-Silver is shown in Fig. 5. This figure shows that there is no remaining reaction after the isothermal stage, and this continued in the dynamic stage. The only endothermic peak obtained from this trace at 170 °C is probably due to the degradation temperature of the material. The dynamic traces for the powder and liquid components of this product were also recorded individually using the same temperature programme mentioned previously. Fig. 6 shows that the dynamic trace of the powder component has no peak in the temperature range covered. Fig. 7 exhibits an endothermic peak at 158 °C for the liquid component. This peak may be attributed to the degradation temperature of the polymeric constituent in the liquid. Comparing this peak value to that obtained from the cement, one can conclude that cross-linking of the polymer with the glass powder increased its degradation temperature by 12 °C or by 7.6%. In other words, the glass particles provide the polymer with more heat stability. Mueller *et al.* [18] reported that there was a dynamic reaction complementary to the isothermal reaction leading to an exothermic peak at 95° C, which is inconsistent with the results presented here. The peak, at 95° C can be attributed to the evaporation of the residual water contained in the materials used. This explanation has been confirmed by recording the dynamic DSC trace for a pan containing distilled water. A strong endothermic peak at 96.5° C is observed as shown in Fig. 8.

The heat capacity of Chelon-Silver was measured by two methods: direct and calibrant methods (Sapphire). The heat capacity of this material was found to be 0.857 (S.D. = 0.076) J g^{-1} °C^{-1} and 0.874 (S.D. = 0.077) J g^{-1} °C^{-1} for the direct and calibrant methods, respectively. The results show that there is no significant difference in the accuracy of either method. Thus, this comparison enabled us to use the straightforward direct method to determine the heat capacity for all materials under test with confidence.

The heat capacity of each material is listed in Table III. Generally, the light-cured cements exhibited heat-capacity values lower than those of auto-cured cements, except Chevlon-Silver which showed the lowest value of all (0.857 J g^{-1} °C^{-1}). When Fuji II LC was allowed to set without light-curing (dark reaction) it showed the highest value (1.267 J g^{-1} °C^{-1}). Because the heat capacity is an indicator of the thermal insulating property of a substance, the material would not then be an effective thermal insulator with a C_p value less than 0.1 J g^{-1} °C^{-1}. One can thus conclude that all materials examined are effective thermal insulators [16].

4. Conclusion

DSC traces for six glass–ionomer cements were examined and a correlation found between the area under the exothermic reaction peak and the amount of material used in the experiment. There was no correlation with peak height alone, contrary to previous reports. We believe this is because the reaction starts rapidly and ends rather slowly; thus peak areas must be measured. Our investigations show that a previously reported DSC peak at 95° C is attributed to the evaporation of residual water in the materials. We found that there was no difference in the values for the heat capacities when measured by either direct or calibrant methods.

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