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Investigation of the mechanical performance of young glass-ionomer cement using dynamic mechanical analysis

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Glass-ionomer (or more correctly, glass polyalkenoate) cements have wide applications in dentistry. This paper reports an investigation using dynamic mechanical analysis (DMA) on the setting of typical conventional glass-ionomer cements of varying age. Rectangular section cement samples were stored for four weeks in distilled water at 37 °C before being tested. The experimental procedure involved the clamping of the sample in tensile mode and heating through a 37–95 °C temperature range in water. A general behavioral trend was followed where all the samples showed increased flexibility with rise in temperature until a "threshold" temperature was reached, whereupon sudden tensile stiffening was observed. The temperature at which the stiffening took place was dependent on the age of the cement, and was interpreted in terms of the secondary cement forming reactions of silica and phosphate. The younger samples stiffened at significantly lower temperatures than the older ones. The activated nature of glass-ionomer setting chemistry meant that younger cements could be prematurely aged through heating.

Differential scanning calorimetry was used to study the effect of heating on the distribution of loosely bound water in the cements that had, and had not been exposed to a DMA cycle. Most notably, it was seen that the DMA process did not affect the water in the matrix. This leant further credence to the hypothesis that the stiffening observed during the DMA heating process was caused by accelerated network formation.
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1. Introduction

Glass-ionomer cements (GIC) consist of a powdered alumino-silicate glass that is mixed with a concentrated polyacrylic acid to form brittle white cement via an acid-base reaction. This process causes the partial reaction of the glass particles, which leads to formation of a hydrated polycarboxylate-metal ion matrix within which the alumino-silicate glass particles are bound. The current GICs have improved significantly since Wilson and Kent [1, 2] invented the original composition in 1971, yet the chemical processes that facilitate curing have remained largely unchanged. Since their inception, GIC has been most commonly used in dentistry.

In order for the mechanical performance of these cements to be improved to resist the type of loading conditions and environmental extremes that exist in the mouth, it is important to understand the detailed mechanisms by which the cements harden. Furthermore, the interaction between the cement and the mouth should be understood particularly for the period immediately post-placement while the setting chemistry occurs.

The early understanding of the setting chemistry of GIC involved the following steps [3]: Decomposition of the glass to allow the migration of Al^{3+} and Ca^{2+} ions into the aqueous phase of the cement. Followed by a gelation period where the liberated ions cross-link with the carboxylic acid group. The prolonged formation and hardening of the cement matrix was said to develop as the calcium and aluminum ions cross-link with the carboxylic acid group.

The last 10 years have seen continual development of the understanding of cement setting chemistry. Wasson and Nicholson challenged the original concepts and suggested that the formation of polysalt is not solely responsible for the cements' long-term mechanical performance. They instead suggested that the formation of polysalt is accompanied by an intertwined inorganic network of silicon and phosphorus [4]. Hatton and Brook [5] examined their theory further using X-ray micro-analysis. They found that the silicon and phosphorus are not confined to the unreacted glass, but are also present in the cement matrix itself. The revised concepts for the setting of GIC now acknowledge that in addition to the matrix forming calcium and aluminum polysalt, silica and aluminum phosphate gel are products of the cement forming reaction [6]. It is the inorganic network of these gels that account for the cements' insolubility and long term hardening [7].

The long term setting processes that include the formation of the inorganic and organic networks continue for up to six months after placement in the mouth. During this period the mechanical properties of the cement improve and the cements' solubility decreases.

This paper presents a series of tests using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) which focus on the mechanical properties of a typical GIC with respect to temperature and age. The behavior exhibited during these tests is explained with particular reference to the setting chemistry.

DMA was chosen because the process was the most suitable for investigating the mechanical properties of dental cement. It allowed small samples to be characterized in a temperature controlled aqueous environment.

2. Experimental

2.1. Materials and method

Acid washed kg 23 [Ex. First Scientific, Abertillery, Wales]; a typical, conventional acid washed GIC was used throughout this experimental with a powder: liquid ratio of 4 : 1. A stainless steel mould was used to fabricate the rectangular section rod cement samples of dimension 8 mm wide, 30 mm long and 2 mm deep. The mould was placed in an oven at 37 °C prior to being packed with wet cement. This allowed the mould to equilibrate with the cement storage temperature. The alumino-silicate glass powder and polyacrylic acid liquid were weighed on a balance to an accuracy of 0.01 g and hand-mixed. The cement was then packed to excess into the mould where its exposed edge was overlaid with a thin sheet of polycarbonate before being covered with a stainless steel plate and clamped with moderate pressure. It was then placed in an oven and maintained at 37 °C for 1 h before the mould was disassembled and the hardened cement removed and placed in a vessel containing distilled water at 37 °C. The aging cement was then stored under these controlled conditions until tested.

GIC contains a significant amount of water within its matrix in two forms, bound water and loosely bound water [8, 9]. Bound water is firmly held to the matrix of the cement and is said to be the by-product of the reaction between the silica gel and polysalt in addition to the original polyacrylic acid group [10]. Loosely bound water is responsible for the cement's susceptibility towards dehydration in a low humidity environment [10]. The storage medium is therefore critical to the strength of GIC.

2.2. Procedure

A conventional dynamic mechanical thermal analyzer (DMTA) (Polymer Laboratories MKII dynamic mechanical thermal analyzer) involves the clamping of a sample in air within a temperature-regulated chamber. To prevent desiccation and shrinkage of the cement sample, the apparatus was modified to incorporate a water bath in place of the oven unit. The GIC sample was clamped in the DMTA tensile testing head and supported with the beaker. The collared beaker was connected to a 5-litre heating vessel which regulated the temperature between 37 and 95 °C. Once installed, the dental cement sample was allowed to equilibrate at 37 °C with a 1 Hz sinusoidal tensile loading frequency. The temperature was then ramped and measurements of tensile $\tan\delta$, tensile storage modulus, and displacement were recorded at 4-second intervals until the water temperature reached its maximum. $\tan\delta$ is a measure of the phase angle between applied strain and the resultant stress. It follows the molecular relaxation which is responsible for the observed mechanical properties. A perfectly elastic material has a $\tan\delta$ equal to zero while a perfectly viscous material has a phase angle approaching 90° and hence a $\tan\delta$ tending to infinity.

Additional tests were carried out using a Stanton Redcroft STA 625 combined thermal gravimetric analyzer (TGA) and differential scanning calorimeter (DSC) on a 24 h and a 28-day-old GIC, comparing the mass loss (understood to be the manifestation of the desiccation of loosely bound water from the cement matrix) and the associated heat flow of the system at a temperature range of 37–200 °C. Cement was fabricated and stored in the same method as described earlier and once sufficient time had elapsed, a small piece of approximately 6 mg was removed from the sample and placed in the apparatus.

3. Results

3.1. Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis involved the testing of GIC of varied ages from 1 h to 4 weeks. A plot of storage modulus against water temperature was used as an illustration of the cement stiffness through a temperature range 37–95 °C. The tests were carried out to investigate and compare cement performance. In order for the optimal performances from each population to be compared, the graph displaying the highest storage modulus at each age was selected and is illustrated in Fig. 1.

On each of the plots (Fig. 1), an initial period of softening was shown; the storage modulus (stiffness) decreased with increased temperature. The negative gradient on each of the storage modulus plots suggested that the bonds linking the glass particles with the matrix and those actually within the matrix were softened as the temperature rose. At a certain temperature the stiffness of the cement stopped decreasing and began to increase with temperature. A trough was displayed at the point of minimum stiffness which represented that some permanent change had occurred in the cement. The temperature and shape of the trough was dependent on cement age. The younger cements exhibited an earlier more gradual trough than the older cements. The minimum stiffness for the 1 h cement occurred at approximately 65 °C while the four-week-old cement had a minimum stiffness at 92.3 °C.

Table I illustrates the variation of storage modulus with temperature for the complete range of cements. The results shown in Table I were taken from the data of Fig. 1.

In cases such as the 1- and 2-hour cements where the minimum stiffness occurred at a sufficiently low temperature, the stiffness that ensued could be seen to rise until it had regained its initial storage modulus value.

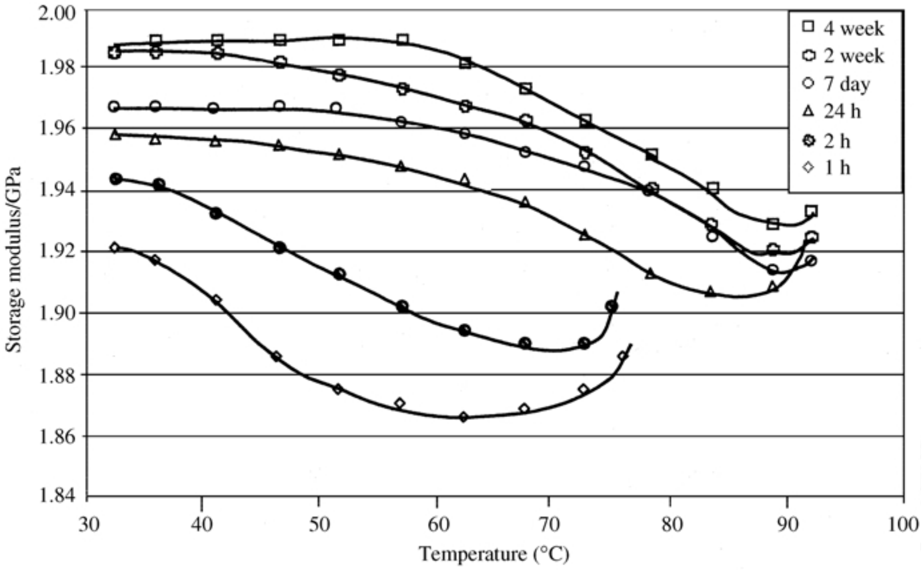

Figure 1 Comparison of storage modulus variation with temperature for cement at different ages.

TABLE I Storage modulus values

Cement age	Initial storage modulus/GPa	Minimum storage modulus/GPa	Position of minimum storage modulus/ °C
1 h	1.921	1.874	65.2
2 h	1.944	1.895	74.5
20 h	1.955	1.910	85.8
7 day	1.962	1.914	88.8
2 week	1.980	1.922	91.7
4 week	1.980	1.927	92.3

Fig. 2 confirms that permanent physical and chemical change of the sample had occurred to the sample during the DMA heat cycle. The cement underwent two consecutive thermal scans with the result of the first lying below the second. It is evident that the chemical change caused by the DMA cycle remained after its temperature had been returned to 37 °C. The second scan demonstrated the cement's enhanced stiffness, while the absence of a stiffness minimum suggested its reluctance to undergo further chemical change.

The mechanical performance of the re-tested cement could be likened to that of more mature cement because it exhibited enhanced storage modulus properties and the trace was shifted towards the right.

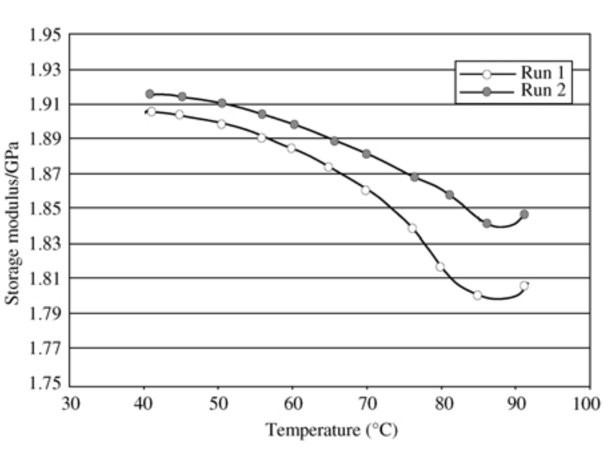

Figure 2 Storage modulus comparison for a 20-h-old cement subjected to two consecutive DMA cycles.

3.2. Combined thermal gravimetric analyzer (TGA) and differential scanning calorimetry (DSC)

The investigation involved the testing of 24 h and 28 day GIC samples in a combined TGA and DSC. Each sample was subjected to varied treatments and storage conditions as described in the list below. The aim was to observe the effect of each condition on the 24 h and 28 day cement and relate that to the cement's age. In every case, the cement was stored for the required time (either 24 h or 28 days) in distilled water at 37 °C before being exposed to one of the following conditions.

''Treated'' implies that the cement underwent DMA heating and a loading cycle as described in the materials and method section.

''Dry'' implies that the cement was stored under conditions of 20 °C air at 35% RH. While ''Wet'' implies storage in distilled water.

''200 °C'' refers to the heating of the sample in a vacuum from room temperature to 200 °C and storage for 1 h at the elevated temperature.

The plots of the results from these tests can be seen in (Figs. 3 and 4) below. Fig. 3 shows the TGA percentage mass loss comparisons for the eight samples and Fig. 4 shows the DSC relative heat flows for the same six cements.

The mass loss chart (Fig. 3) demonstrates most notably the stark difference between the samples that had been heat-treated to 200 °C (200 °C and treated) with the other two conditions. Both the ''24 h and 28 day 200 °C and treated'' cements were totally desiccated during the 200 °C bake and did not yield any more water during the DSC process.

As the cement matures, the network tightly, permanently binds a greater proportion of its water content. This rearrangement of water within the matrix reduces the cement's vulnerability to mass loss and volume change. However, the DSC mass loss chart reveals that the behaviour of a 1 day and a 28 day old sample are similar. The older sample gave up slightly more water during heating (approximately 2% of its overall mass). This is probably associated with the water of reaction that

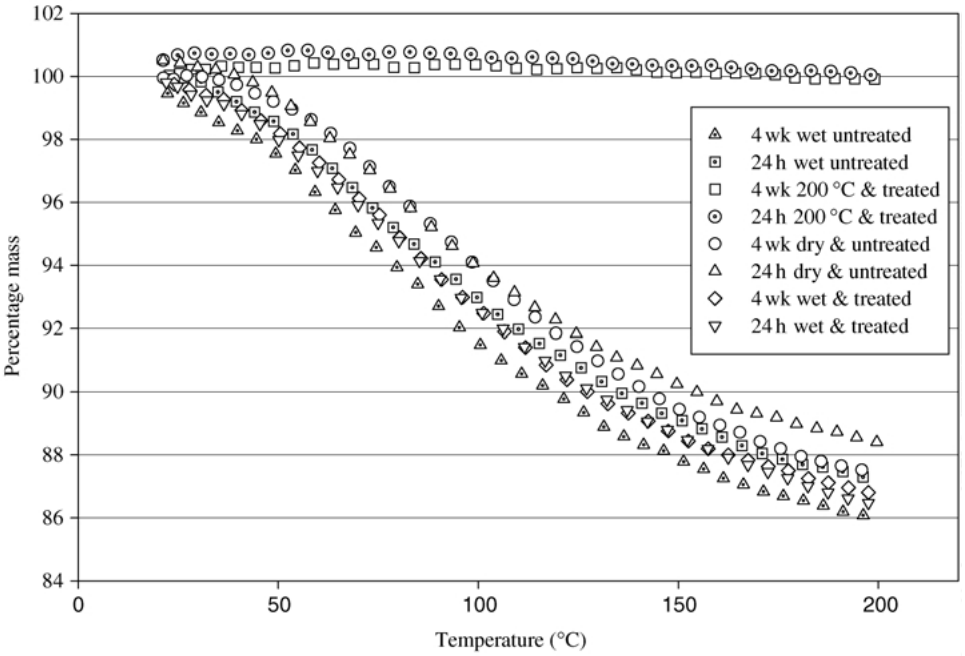

Figure 3 TGA mass loss comparisons for eight samples.

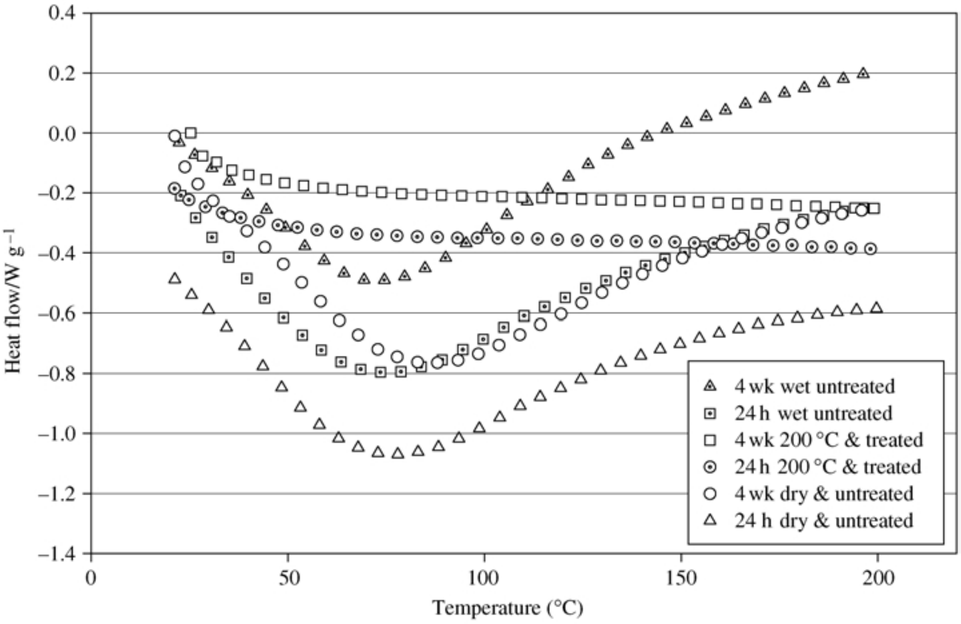

Figure 4 DSC energy comparison for six samples.

is produced as a by-product of cement formation which therefore exists in greater quantity in older cements.

The initial downward trend of the heat flow chart (Fig. 4) represents the endothermic region, the cement readily absorbed the energy from the system without itself increasing in temperature. The absorbed energy is equal to the energy required to free all the loosely held water from the cement matrix. As the ramped temperature increased further, the desiccated cement's temperature increased until it caught up with that of the furnace temperature.

The 24 h and 28 day 200 °C and Treated trace shows the behavior of desiccated cements. The initial curve within the first 10 °C of the plot is an artefact of the apparatus and is not a response from the material. The slight downward gradient shown on the plot was a trait of the apparatus and caused by a clockwise rotation of the chart data. All relative energy differential values along these two base lines are identical and all other results are measured from these datums.

4. Discussion

4.1. DMA

All the DMA traces exhibited the same basic pattern. The behavior of the four-week-cement sample, however, was slightly different from that of the 1-h sample. The younger sample had a more gradual increase in stiffness that was initiated at a lower temperature. The younger samples exhibited more prominent stiffening at their threshold point, which occurred at a correspondingly lower temperature.

Fig. 2 shows that a DMA heating cycle had an affect on the physical performance of GIC. The dual cycle, which incorporated the back-to-back, heated loading cycles caused further accelerated aging. The storage modulus was significantly higher for the re-tested cement and its stiffness minimum occurred at higher temperature; symptomatic of enhanced network formation. The excitation and heating caused by the DMA processing initiated a chemical change to the cement that facilitated its premature aging, confirming that the setting of GIC is an activated process.

Cements stiffen and harden naturally as they age because of the formation of organic and inorganic networks. Even after the initial 24-h setting period the cement continues to increase in hardness and strength [11]. The process can be accelerated through heating in an aqueous environment as is shown by the traces of Fig. 1. The amount by which the process can be accelerated is governed by the age of the cement; network formation of younger cements is more susceptible to environmentally induced acceleration.

The currently accepted concept for the setting of GIC involves the formation of two interpenetrated networks [11]. The original cement cross-linking explanation by Paddon and Wilson [12] was modified to include the formation of a second interpenetrated network of phosphorus and silicon [7]. It was initially thought that this mechanism of cross-linking was wholly responsible for the improved strength and modulus [12], but in contrast, it is now understood to be part of cement gelation. The process of cement hardening is instead achieved by the formation of a silica gel and where present, an aluminum phosphate gel network [6].

Fig. 2 confirms that the maturation of dental cement is also an activated process, which can be accelerated with increased temperature. The mechanical performance of run 2 is superior to run 1 because the heating process accelerated its setting chemistry above the normal rate.

4.2. TGA

The combined TGA and DSC study was carried out primarily to investigate the effect of a DMA thermal scan on the water content, and the energy of desiccation of young and matured GIC. It has been reported that a reduction in the amount of loosely held water in such cement could cause mild shrinkage, a tightening of the cement matrix and a resulting improvement in stiffness [10]. The TGA chart Fig. 3 at 95 °C (the maximum temperature range of the DMA process) shows relatively little difference between the loosely bound water content of samples that underwent the DMA thermal scan and those that did not. Therefore, the storage of typical GIC at 95 °C in an aqueous environment does not cause a significant movement of loosely bound water within the cement matrix. It therefore seems unlikely that the dog-leg upturn part of the traces in Fig. 1 was caused by this redistribution of loosely bound water.

The quantitative comparison for the percentage mass loss of the 24 h wet untreated and the 24 h wet treated sample at 95 °C are 6.2% and 6.3%, respectively. While the four-week wet untreated and the four-week wet treated at 95 °C are 8.0% and 6.8%, respectively. The DMA thermally ''treated'' process, which preceded the DSC scan in two of the four tests, did not cause significant dehydration and did not influence the cements' stiffness. The horizontal mass loss traces for the 24 h and four week 200 °C treated cements (Fig. 3) represent a datum from which the desiccation of the other cements can be compared. The contrast between the flat 200 °C traces with the steep gradient exhibited by all other TGA traces of Fig. 3 are stark. It shows that the DMA process did not cause notable redistribution of loosely bound water. Though slight desiccation can lead to an improved mechanical performance, it was not responsible for the increased stiffness of the GIC following the DMA thermal cycle.

4.3. DSC

The ''200 °C and Treated'' samples showed no variation throughout its DSC test. This complemented the results from the mass loss scan of Fig. 3 and it illustrated that energy change was implicitly related to the removal of loosely held water. The ''200 °C and treated'' sample contained no loosely bound water and therefore exhibited a flat energy scan.

The ''24 h and four week wet untreated'' samples reflected the typical behavior of cements that were allowed to mature in a conventional manner. The younger of the two samples had a lower trough, which was explained by the setting chemistry. Younger cements contain more loosely bound water in their matrix and desiccation consequently required more excitation; a greater input of energy.

The ''24 h and four week dry untreated'' results appeared in the same order as the ''24 h and four week wet untreated'' tests, however. The former were however positioned below and to the right on the heat flow trace. The difference was attributed to the dry condition prior to the DSC test where the samples suffered mild desiccation at their surface which subsequently acted as buffer, resisting any deeper water loss.

5. Conclusions

Dynamic mechanical thermal analysis in an aqueous environment can yield important information on processes occurring in the setting of GIC. The aqueous environment prevents water loss from the cement matrix and therefore prevents it from shrinking and cracking. It was shown that the physical properties of the cement changes most dramatically during the first 24 h of hardening. The cement underwent further significant change during the slow maturation phase. The rate of setting was found to be dependent on temperature; increasing the temperature accelerated the rate of setting and caused the cement's pronounced stiffening. The setting of GICs can therefore be described as an activated process. DMA traces showed that the stiffness of cement reduce with temperature until a threshold temperature is reached which causes the cement to stiffen. The TGA result revealed that the DMA testing process did not cause any redistribution of loosely bound water in the GIC. The stiffening was attributed solely to the formation of the silicate and phosphate networks. This matrix formation was induced more readily in younger samples where the capacity to form the inorganic network of silica gel and aluminum phosphate gel is greater.

The 24 h and four week old cement did not suffer significant desiccation when stored in 20 °C air at 35% RH. Loss of water was restricted to the exposed surface of the cement and the dried surface of the cement then acted as a buffer to resist cement desiccation from beneath the surface of the sample. Removal of the loosely bound water from below the surface occurred at a higher temperature and required a greater input of energy.

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