

NOVEL DENTAL CEMENTS CONTAINING COMBINATIONS OF CYANOACRYLATE RESIN, HYDROXYAPATITE, AND NEW ALUMINIUM-BASED FILLERS

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ABSTRACT

The setting characteristics of two novel cyanoacrylate-based cements, intended primarily for dental use, have been investigated using near-infrared spectroscopy and Vickers indentation. One cement was composed of cyanoacrylate and acid-coated hydroxyapatite filler particles, while the other was commercially available dental glass-ionomer cement (GIC) with incorporated cyanoacrylate. The two testing techniques have allowed the relationship between the extent of cyanoacrylate cure within the cements and their overall hardness development to be determined and discussed. In addition, preliminary rheological investigations have been carried out for a newly formulated Al-based GIC (AIGIC) to characterise its handling and setting behaviour.

1. INTRODUCTION

Although various acceptable types of white dental restorative cements are currently available, they far from satisfy all of the criteria required for an ideal restorative cement. In addition to the need for dental materials for repairing unhealthy, damaged teeth, there is also a growing need for new dental materials in cosmetic dentistry.

Due to their bacteriostatic and hemostatic properties, cyanoacrylates have found a large number of applications in medicine and dentistry. For example, in dentistry, cyanoacrylates have been used in periodontal therapy, as fissure and root canal sealants, and as adhesives for the bonding of orthodontic brackets [1, 2].

This paper discusses the setting mechanisms and the physical properties of two novel cyanoacrylate-based cements [3]: CAH – a cement composed of cyanoacrylate and acid-coated hydroxyapatite; and CAGIC – a cement incorporating cyanoacrylate into a commercially available dental glass-ionomer cement (GIC). Although these cements were mainly designed as dental restorative materials, and were investigated in this context, these types of composites could be used for many other general adhesive applications, for instance in the electronics and automotive industries. In addition to the cyanoacrylate-based cements, this paper will present preliminary results on the rheological properties of an aluminium-based GIC (AIGIC). The reactive aluminium fillers are expected to interact chemically with the surrounding matrix, thereby meaning that they play an active role in the curing mechanism of the cement.

The cyanoacrylate-based cements described herein represent new alternatives to the already available composite resins (CRs: typically glass-filled methacrylates) and resin-modified glass-ionomer cements (RMGICs: glass-ionomers modified by the addition of a resin component, typically hydroxyethyl methacrylate), but with several advantages. For example, they show enhanced adhesive properties due to the adhesive nature of the

cyanoacrylate in comparison to the (non-adhesive) methacrylate resins. Due to the basicity of the fillers and the nature of the polymerisation reaction, these cements will not suffer from incomplete polymerisation, a common problem for light-activated CRs/RMGICs. Also, the presence of the cyanoacrylate makes these cements less sensitive to desiccation and early moisture exposure, both well-known problems when using GICs and RMGICs [4]. Besides the aforementioned benefits of using cyanoacrylate, the hydroxyapatite and reactive aluminium fillers each contribute other valuable qualities to the proposed cement formulations. For instance, along with its biocompatibility, the use of hydroxyapatite increases the wear performance of the cement, its intrinsic radio-opaque response, and its polishability. Similarly, the significantly smaller and well-controlled particle size of the reactive species (0.2–0.3 μm), with its bond-enhancing coating, increases the cement compactability, which ultimately leads to an increase in the overall compressive strength and wear resistance [5].

The curing of CAH and CAGIC has been investigated using near-infrared (IR) spectroscopy and Vickers indentation, while that of AIGIC has been studied using rheology.

2. EXPERIMENTS

2.1 Materials

CAH and CAGIC

The hydroxyapatite powder used in this research was reagent-grade hydroxyapatite powder (Sigma-Aldrich). The mean and modal particle diameters of the powder were 9.59 ± 0.12 and 3.76 ± 0.12 μm , respectively, where the errors quoted are the standard error of the mean. Before use in the cement, the powder was coated with 5% TA and 5% PAA by a methanol deposition method. To a dry mixture of hydroxyapatite powder (90% by weight), TA (5% by weight), and PAA (5% by weight), a minimal amount of sieve-dried methanol was added to dissolve the acids. This slurry was then gently heated, with manual stirring, to aid methanol evaporation and to ensure an evenly coated powder. Once the methanol had evaporated, the powder “cake” was gently milled by hand using a pestle and mortar to separate the powder particles. The powder was then stored in a desiccator until required.

The glass powder used in this study was the commercially available Diamond Carve™ GIC powder (Kemdent, Associated Dental Products Ltd.). This powder is a blend of a strontium-based (calcium) fluoro-aluminosilicate glass, (+)-tartaric acid (TA), poly(acrylic acid) (PAA), and a copolymer of vinylphosphonic acid and acrylic acid P(VPA/AA). The mean and modal particle diameters of the powder were 9.10 ± 0.35 and 11.22 ± 0.37 μm , respectively. The powder was used as received.

The acid solution used in this study was Diamond Carve™ GIC liquid. This is an aqueous solution of TA and PAA. The material was used as received.

The cyanoacrylate adhesive (based on ethyl cyanoacrylate) used in this investigation was commercially obtained and is known under the trade name of Loctite Super Glue Control Liquid. The material was used as received.

AIGIC

Diamond™ capsules were used as the base material for incorporation of the reactive aluminium species. Diamond™ capsules contain the same ingredients as Diamond Carve™, but with a different powder to liquid ratio of 3.7:1. The reactive aluminium particles had an average particle diameter of 0.24 µm. The use of the capsules eliminated any variation caused by hand mixing, thereby ensuring repeatability.

2.2 Cement compositions and mixing methods

The following cyanoacrylate-based cement compositions were mixed (in parts by weight) for a total of one minute on dental wax paper, using a plastic spatula:

CAH: 10 parts of acid-coated hydroxyapatite powder were mixed with 13 parts of cyanoacrylate adhesive.

CAGIC: 5 parts of dental glass powder were mixed with 2.55 parts of cyanoacrylate adhesive. This paste was then mixed with 2.55 parts of acid solution followed by a further 5 parts of dental glass powder.

AIGIC: 2.5% (by weight) of the existing powder blend within the Diamond™ capsule was replaced with the reactive aluminum powder. AIGIC was mixed automatically using an amalgamator (see section 2.3 for extra details).

2.3 Cement sample preparations and storage

CAH and CAGIC

Near-IR spectroscopy was used to study the curing of the cyanoacrylate within cements CAH and CAGIC during the first 100 minutes after mixing. Samples for these studies were made by mixing the components of the cements as described previously, and then spreading them on Teflon plates for immediate study under room conditions. A total of 0.3 g of material was used for each sample.

The samples that were to be studied in the long term for Vickers hardness were made into disk-shaped samples. As will be clear from the near-IR spectroscopy results, the cyanoacrylate component of CAH was not fully cured after 100 minutes of ageing. Therefore, the CAH samples produced for Vickers hardness studies were also investigated using near-IR spectroscopy to monitor long-term curing. The materials were mixed as described above and the resulting paste was placed in a split-ring Teflon mould (3 mm (h) × 13 mm (d)) supported by a brass split-ring. In each case, Teflon plates were positioned above and below the mould and clamped down using a G clamp. For the CAH samples, before the top Teflon plate was clamped into place, the first infrared spectroscopy measurements of the cements were made. Samples were left clamped in their moulds for 45 minutes at room temperature. The next infrared and the first hardness measurements of the cements were made 45 minutes after the initial mixing, immediately after the removal of the samples from their moulds (prior to this, the cements would have not been sufficiently hard for the indentation tests or polishing to be possible). However, in the case of the CAH cement, due to the softness of the cement, the first measurable indentations could only be made 90 minutes after the initial mixing. All samples were polished to improve the visibility of the indentations. Between measurements, all samples were stored in an oven at 37 °C (to match human mouth temperature) and a relative humidity of approximately 30%.

AIGIC

The AIGIC capsules were stored at room temperature (22 ± 2 °C) prior to activation. The liquid sachet was broken and liquid was released into the mixing cavity within the capsule. The capsule was then mixed for 20 seconds at 3000 rotations per minute, using a Degussa Duomat 2 amalgamator. The amalgamator was used to ensure a consistent mixing between the reactive species and the existing ingredients of the DiamondTM capsule. After mixing, the cement was extruded from the capsule onto a shellac base plate and then loaded onto the rheometer plates. The unmodified DiamondTM capsules were mixed using the same method.

2.4 Hardness testing

A Future-tech FM-1e Microhardness tester (Future-Tech Corp., Tokyo, Japan) fitted with a Vickers indenter (square-based pyramidal diamond) was used for the hardness measurements. The indentation load was 200 g and the dwell time was 15 s. The 200 g load was chosen because it resulted in large indentations, meaning that a good representative area of cement was tested with each indentation.

Indentations were placed randomly on the sample surface but were spaced far enough apart for the indentations not to affect neighbouring indentations. Eight indentations were made on each sample composition at each time, except for data collected before two hours after initial mixing, where only three indentations were made.

In the case of the CAGIC sample, the first two hardness readings at 45 minutes and one hour were measured from unpolished samples and were therefore harder to define. As the CAH sample was too soft at this time for it to be possible to measure the indentations produced, all of the CAH hardness values were measured on polished cement. For the hardness studies, three samples of each composition were tested.

2.5 Near-IR spectroscopy

A Bruker Matrix-F FTIR Spectrometer (Bruker Optics Limited, United Kingdom) with a custom-made reflectance optical fibre probe was used for the tests. The spectrometer operated in the near-IR region of $4000\text{--}10000\text{ cm}^{-1}$ using a white light source and a TE-InGaAs detector, along with a CaF_2 beamsplitter. Diffuse reflectance spectra were collected at 4 cm^{-1} resolution.

The peak at 6207 cm^{-1} , associated with the C–H stretching vibration of $\text{H}_2\text{C}=\text{C}$, was chosen to quantify the extent of cyanoacrylate cure within the CAH and CAGIC samples. The peaks at 5810 cm^{-1} (in the case of CAH) and 5925 cm^{-1} (in the case of CAGIC), both corresponding to aliphatic C–H bond stretching vibrations, were used as internal standards. When studying the cement during the first 100 minutes of curing, one spectrum was collected every minute for 100 minutes. The room temperature that the samples were curing in was 23 °C and the relative humidity was 40–43%. The CAH samples were studied over a period of approximately one year. All near-IR studies were performed three times on three different samples.

2.6 Rheology

A TA Instruments Advanced Rheometer (AR2000) equipped with an environmental chamber using a parallel plate configuration was used to perform all of the rheological tests. The tests were carried out on 10 mm diameter aluminium flat-faced plates, using an oscillation stress of 2000 Pa, an oscillation frequency of 1 Hz and a distance of 1 mm

between the plates. The temperature during each rheological test was kept constant at 15 °C, in order to slow the onset of the reaction and allow the preparation and placement of the cement onto the plates. The acquisition of data for each experiment was started 1 minute 40 seconds from the moment the liquid sachet was broken and the liquid came into contact with the powder. Although all experiments were set up to run for 80 minutes, in the case of unmodified Diamond™ GIC, the data became extremely noisy after approximately 50 minutes. This is due to the fact that the oscillation stress set up at the beginning of the test becomes increasingly unsuitable as the cement sets and becomes more rigid.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 CAH and CAGIC

Figure 1 presents plots of the extent of cyanoacrylate cure within the cements during the first 100 minutes after mixing.

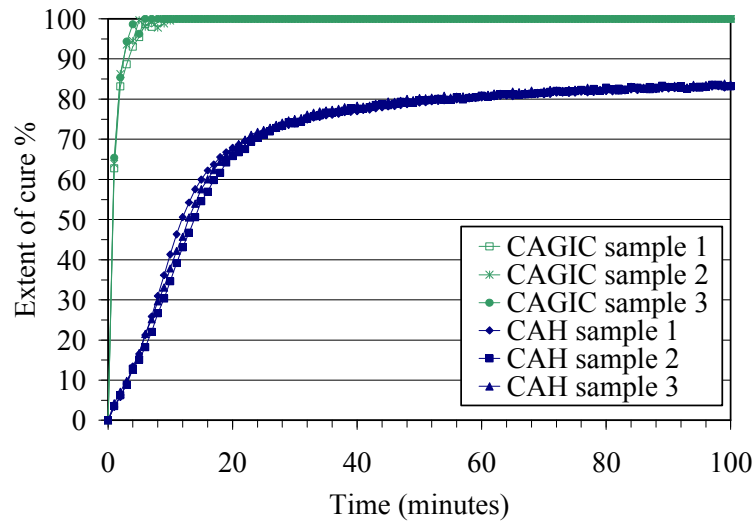


Figure 1: Extent of cure of the cyanoacrylate component within CAGIC and CAH (three samples of each) during the first 100 minutes after mixing.

The results in Figure 1 show that there is a clear difference between the curing profiles of the cyanoacrylate within the CAH and CAGIC samples. As water is known to initiate cyanoacrylate polymerisation [6], the water in the incorporated acid solution in CAGIC is the likely cause of this cement's rapid cyanoacrylate curing. Likewise, the slower curing of CAH's cyanoacrylate component can be explained by the fact that CAH has no water incorporated in its composition. Its curing is likely to be dependent on any water adsorbed on the surface of the filler powder and on the slow diffusion of water from the atmosphere into the cement. In addition, the hydroxyapatite powder is coated with dry PAA and TA. Acids are known to inhibit (anionic) cyanoacrylate polymerisation [6] and are therefore incorporated to allow adequate mixing of the cement by retarding the otherwise too rapid polymerisation of the cyanoacrylate. Once the acids are neutralised (*e.g.* by contact with water), polymerisation can take place.

The cyanoacrylate constitutes either part of (in CAGIC) or the entire (in CAH) matrix component of the cements. The matrix binds the filler particles together and therefore

the extent of cure of the matrix is likely to severely affect the mechanical properties of the cement (such as hardness, compressive strength, and wear). For this reason, the developing hardness of each cement was measured. The long-term hardness and extent of cyanoacrylate cure profiles for cements CAH and CAGIC have been plotted together in Figures 2 and 3, respectively.

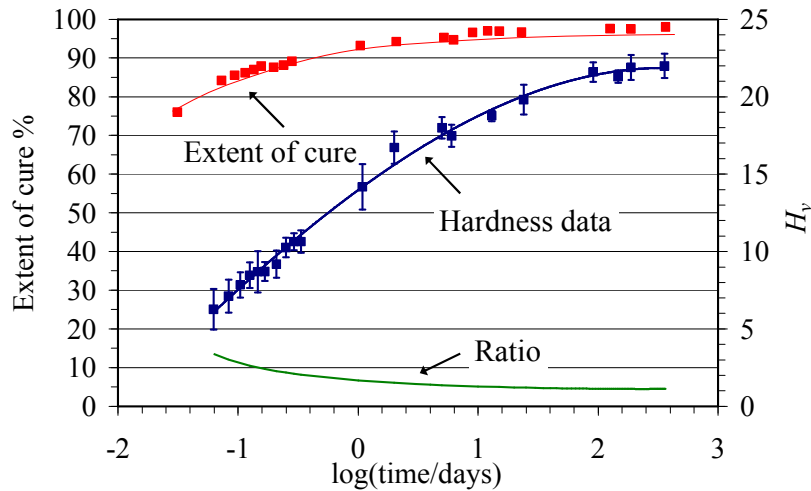


Figure 2: Long-term extent of cure (of the cyanoacrylate component) and Vickers hardness (H_v) vs. $\log(\text{time/days})$ for one single CAH sample. The ratio of the lines of best fit throughout curing is also plotted.

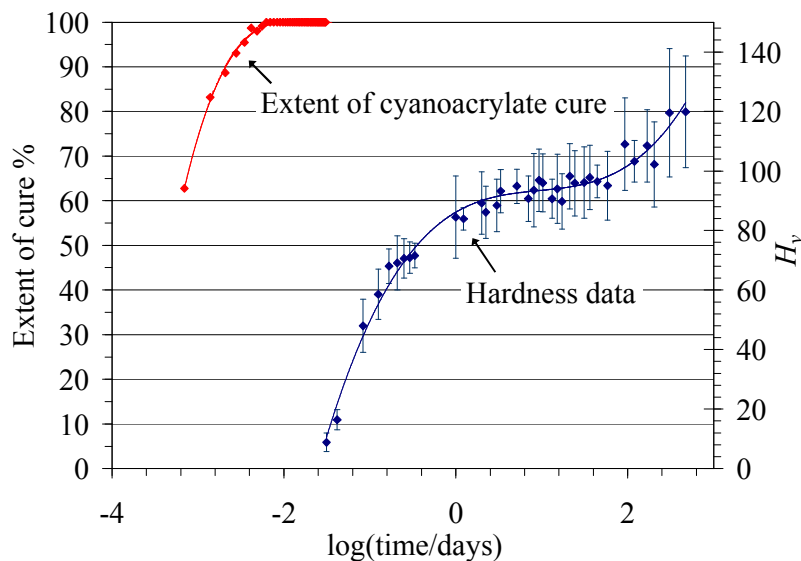
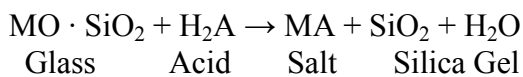


Figure 3: Long-term extent of cure (of the cyanoacrylate component) and Vickers hardness (H_v) vs. $\log(\text{time/days})$ for CAGIC.

As the setting of CAH should rely only on the cyanoacrylate polymerisation, the hardness of the cement is expected to be directly proportional to the extent of cyanoacrylate cure. To test for this, the ratio of the lines of best fit has been calculated throughout curing and is shown in Figure 2. If constant proportionality held, this ratio would be constant over time. Figure 2 shows that although the ratio changes at the start, it does approach a constant value in the long term. This indicates that the hardness and extent of cure are better correlated in the later stages of curing, possibly when the

monomer being consumed is involved in increasing the cyanoacrylate polymer chain lengths, although this is uncertain.

Figure 3 shows that, while the cyanoacrylate curing in CAGIC is complete after approximately 10 minutes, the cement undergoes the majority of its hardness development after this time. Therefore, the long term increasing hardness can mainly be attributed to the setting of the GIC component. GICs are well known to continually harden and strengthen due to the ongoing acid-base reaction (between the aqueous polyacid and the basic fluoride-containing aluminosilicate glass), which results in an increasingly cross-linked polysalt matrix [7]. A general chemical equation for this reaction [8] is as follows:



where M is a metal ion (*e.g.* Ca²⁺, Sr²⁺, or Al³⁺) within the glass, and A is the conjugate base of the acid (the acids being PAA and the P(VPA/AA) copolymer in this case).

Of the CAH and CAGIC samples, CAH attained a much lower final hardness than CAGIC (~22 *cf.* ~120). This has been attributed to several factors:

- (i) CAH has a much lower powder:liquid ratio than CAGIC.
- (ii) The hardness values of the hydroxyapatite fillers themselves are considerably lower than that of the glass fillers (the Knoop hardness values of hydroxyapatite and typical glass are 430 and 530, respectively) [9].
- (iii) The slightly lower final extent of cure of the cyanoacrylate in CAH.
- (iv) The strengthening polysalt matrix being present in CAGIC but not in CAH.

3.2 AIGIC

Understanding the visco-elastic behaviour of any new cement is critical as it defines the handling and setting characteristics, and dictates its potential for various applications. Firstly, the cement must remain sufficiently fluid long enough to allow careful placement and moulding within the tooth cavity (this time is known as the working time), after which it must rapidly set and develop a good degree of strength (referred to as the setting time).

In spite of the vast amount of information that can be provided by rheological studies, in dentistry, such investigations are treated in a very simplistic manner, using a Wilson rheometer to determine usually only the working and setting times [10,11]. In such tests, the amplitude of the oscillation is measured and the working and setting times are defined as the times at which the amplitude of oscillation is 95% and 5% of the original amplitude, respectively.

In the present study, the % strain and the storage modulus of the standard, unmodified DiamondTM GIC and AIGIC (both from capsule form) have been selected for further discussion and are presented in Figs. 4 and 5, respectively. The strain results were chosen as they provide the same information as that given by a Wilson rheometer. In addition, storage modulus findings are presented as they illustrate the actual setting profile of the cements and give an indication of their ultimate strength.

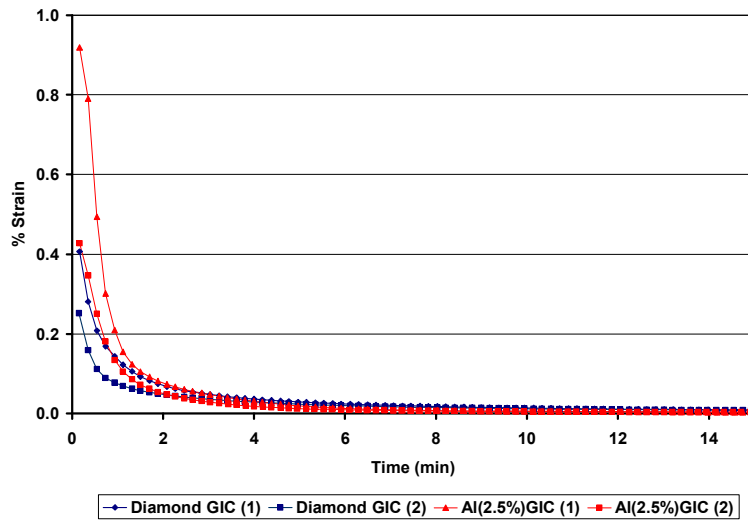


Figure 4: Strain of DiamondTM GIC and ALGIC during setting.

Figure 4 shows that the incorporation of the reactive aluminium species increases both the working and setting times. By applying the previous method [10,11] of determining the setting times of cements to the results in Figure 4, the ALGIC samples can be considered to be fully set after approximately 6 minutes, whereas the DiamondTM GIC samples are set after only 3 minutes. Taking into consideration the importance of the Ca^{2+} and Al^{3+} ions in the setting process of GICs (see Section 3.1), the addition of the reactive aluminium particles in the proposed formulation was expected to supplement the formation of salts and subsequently to speed up the setting mechanism, thereby increasing the strength of the cement from the early stages of curing.

When the ALGIC is activated, the reactive aluminium species are expected to dissolve and form solvated aluminium structures similar to those leached from the fluoro-aluminosilicate glass. The immediate availability of the aluminium structures was expected to lead to instant salt formation and therefore a rapid setting of the ALGIC cement. Surprisingly, the results in Figure 4 show that the incorporation of the reactive aluminium species slows down the setting reaction.

Several factors could be responsible for the slow development of the cement:

- (i) The immediate formation of aluminium salts and hence the gelation of the polymer matrix hinders the movement of the PAA and P(VPA/AA) chains and slows down the migration of solvated cations to the functional groups of the polymeric chains.
- (ii) The inclusion of submicron particle size fillers may be physically hindering the movement of the chains, thereby preventing fast salt formation.
- (iii) There may not be enough polymeric solution for the increased powder surface area (due to the incorporation of such small filler particles). Previous studies [12] have shown that at high powder:liquid ratios with small particle size fillers, the increased cohesion has a greater effect on the paste viscosity than the reaction kinetics. Therefore, the new formulation might require a change in the initial powder:liquid ratio.

Further investigations are required to fully understand the reaction mechanism(s) governing the setting of aluminium-based GICs and their mechanical properties.

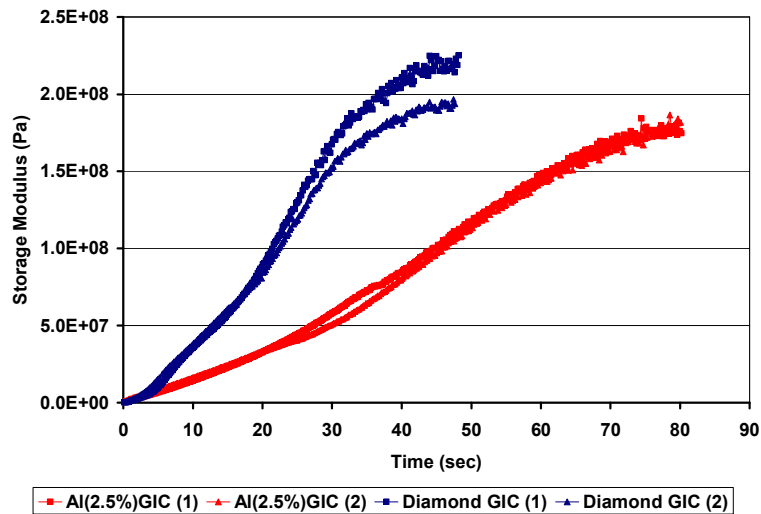


Figure 5: Storage modulus of Diamond™ GIC and AlGIC during setting.

The storage modulus profiles in Figure 5 reveal that the ultimate setting times of the Diamond™ GIC and AlGIC are ~50 and ~80 minutes, respectively. These setting times are much longer than those that would be obtained by applying the 5% oscillation amplitude principle (used for Wilson rheometry traces) to the results in Figure 4. These findings show that although the strain profiles give an indication of the network formation, they cannot be used as an ultimate measure of the setting mechanisms of cements. Changes in storage and loss modulus, as well as the phase difference between strain and stress, should be closely investigated to provide a much clearer indication of the cure kinetics. An early study [13] on visco-elastic behaviour of dental materials raised similar concerns for using the 95% and 5% oscillation amplitude principle to define the working and setting time.

In addition to Figure 5 showing a much slower setting mechanism for AlGIC than Diamond™ GIC (seen also from Figure 4), the lower final storage modulus values of the AlGIC samples suggest AlGIC to have a lower final strength than Diamond™ GIC. However, these values can be considered only as a comparative indication of the ultimate strength of the cements; hardness tests should be performed to validate the strength results.

4. CONCLUSIONS

The combination of infrared and hardness tests employed within this study proved to be well suited for determining the potential offered by CAH and CAGIC as new dental restorative materials. The results showed firstly that the cyanoacrylate curing is strongly affected by the rest of the cement's composition, and secondly that the two cements have very different hardness development profiles. For instance, the curing of the cyanoacrylate within CAH was much slower and reached only 98% conversion after one year. In addition, the hardness of the CAH was shown to be correlated with the extent of cyanoacrylate cure. In the case of CAGIC, although the cyanoacrylate component was fully cured after approximately 10 minutes, the cement continued to increase in hardness. This proved that the fully polymerized network of the

cyanoacrylate component did not prevent the acid-base reaction of the GIC component from continuing. On the other hand, the preliminary rheological results of AlGIC showed that the network formed by the readily available reactive aluminium species interacting with the acid hinders and delays the usual acid-base reaction of the Diamond™ GIC.

The advantages offered by a new stress controlled rotational rheometer (PC controlled) in comparison with a Wilson rheometer have also been demonstrated by comparing the strain and storage modulus results of AlGIC. Carefully designed tests using the new generation of rotation rheometers can provide greater insight into material behaviour by measuring the gel points, ultimate cure times, and strengths of the cements.

ACKNOWLEDGEMENTS

The authors would like to thank Kemdent – Associated Dental Materials for providing the Diamond™ and Diamond Carve™ materials and funding the project. Also, the authors duly acknowledge Alan Bennetts, Christopher Wilde, and Alan Wilson (ASPA Research Group) for their support throughout this investigation.

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