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Fourier transform infrared spectroscopy as a tool to study the setting reaction in glass-ionomer cements

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ABSTRACT

Glass ionomer cements (GICs) have been successfully used in dental applications for many decades, and new cement compositions are continuously being developed to expand the utility of GICs into broader applications including orthopaedics. To evaluate the clinical handling of GICs, two main measures of the setting reaction are currently used: working time and setting time. Attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) has potential as a powerful new tool for real-time characterization of these setting reactions, providing information on evolving chemical structure while allowing for greater sensitivity and reduced human variability. ATR-FTIR was used to examine the effect of calcium polyphosphate addition at 0–50 wt% to two GICs: a zinc-silicate cement and a germanium zinc-silicate cement. The slowing of the initial setting reaction with CPP addition to the germanium zinc silicate cements corresponded to a large increase in the injectability window, as demonstrated using a preliminary mechanically-based injectability test protocol, opening new possibilities for clinical applications. We propose that ATR-FTIR is a valuable tool for evaluating the setting reaction of glass ionomer cements to supplement existing measurements of working and setting time.

1. Introduction

Glass ionomer cements (GICs) have been used successfully in dental applications since the 1970s [1,2], but dental GICs are unsuitable for orthopaedic applications as they contain aluminum [3–7]. Al-free glass ionomer cements are under development; however, the change in the glass chemistry has significant effects on the setting reaction [8,9]. To examine the setting behavior of GICs, two tests are commonplace in the literature: working time and setting time [10]. Working time is defined as the length of time that the cement may be manipulated without having an adverse effect on its properties, while setting time signifies the time after which the cement can support the weight of a Vicat or Gillmore needle without making an indent [10]. These simple tests can be quickly performed, yet results can vary significantly, even between experienced researchers. Additionally, these tests provide limited information as they only define two points in the setting reaction.

While it is important that the setting behavior of a cement can be easily verified in the clinic, additional tools are needed for scientific evaluations of experimental cements. Real time analysis of the setting reaction is of particular importance when formulating cements for diverse orthopaedic applications. There are a number of tools that could be used, including: rheology [11–13], injection force and ATR-FTIR (attenuated total reflectance fourier transform infrared spectroscopy). Only ATR-FTIR allows for direct, real-time analysis of the chemical structure in the cement and changes in the bonding nature throughout the setting reaction. FTIR has a history of use with dental GICs, for examining (a) the chemical structure during setting [14,15] and (b) changes to setting chemistry due to the use of additives [16,17]. ATR-FTIR has the advantage over conventional FTIR as it allows a single wet cement to be monitored over time [18,19], whereby the sample is placed directly onto the ATR crystal, eliminating lengthy sample preparation. The characteristic bands in FTIR for the protonated and ionized forms of the carboxyl group on PAA have been well characterized [20–22]. We propose that this tool provides detailed information on the setting reaction with reduced human variability and increased precision.

ATR-FTIR was used to examine the setting behavior of two GIC formulations: a fast setting zinc-silicate cement and a slower setting germanium zinc-silicate cement with and without calcium polyphosphate (CPP) substitution for the glass component. CPP has been of particular interest for its capacity to extend the

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handling properties and to provide therapeutic ion release [23]. ATR-FTIR results were compared to the standard measures of setting and working times for both the zinc-silicate and the germanium zinc-silicate GIC, and followed by a newly developed injectability test protocol.

2. Material and methods

2.1. Glass synthesis

Melt-derived zinc silicate glass (4 mol% SrO, 12 mol% CaO, 36 mol% ZnO and 48 mol% SiO_2) was prepared as previously described, resulting in annealed glass powder <45 μm [23–26]. An experimental germanium zinc-silicate glass (4 mol% SrO, 9 mol% CaO, 36 mol% ZnO, 20.6 mol% SiO_2, 26.9 mol% GeO_2, 1.75 mol% ZrO_2 and 1.75 mol% Na_2O) was prepared by Ceradyne Inc. (Seattle, USA) according to the protocol by Dickey et al. [19]. The glass frit was ground in a planetary ball mill (Pulverisette 7, Fritsch, Germany) and sieved to obtain glass powder <45 μm, which was annealed at 593 °C for 3 h and then furnace cooled. Calcium polyphosphate glass was prepared by calcining calcium phosphate monobasic monohydrate at 500 °C for 10 h, melting at 1100 °C for 2 h, followed by grinding to particles <45 μm [23,27].

2.2. Cement formulation

Cements were prepared by mixing glass powder with 50 wt% PAA (M_w 12.7 kDa, Advanced Healthcare Limited, Tonbridge, UK) solution in deionized water with a powder to liquid ratio of 1:0.75 [23]. The cement composition was varied by substituting the silicate glass powders with CPP up to 50 wt%.

2.3. Handling properties

Working time and setting time were measured according to ISO 9917 [10] at room temperature and 37 °C respectively. All measurements were repeated 3 times (mean ± SD, n=3).

2.4. ATR-FTIR

The chemical structure of the GICs throughout the setting reaction was examined by ATR-FTIR (Tensor 27, Bruker) [19]. Cements were placed directly on the ATR crystal at ambient temperature. This allowed the measurement to occur at the bottom surface of the cement that was protected from air and the effects of water evaporation. Spectra were collected at a resolution of 4 cm^{-1} from a single sample for all timepoints, until after cement solidification was observed, corresponding to a total of 20 min for the zinc-silicate cements and 3 h for the germanium zinc-silicate cements. The conversion of free PAA to ionized PAA was monitored over time by calculating the absorbance ratio of the bands at *c.* 1550 cm^{-1} and *c.* 1700 cm^{-1} [20–22]. Three sets of cements were tested for each composition.

2.5. Injectability test

Cements were mixed and immediately loaded into four 1 mL syringes and manually primed through a 4-in. 12 G cannula. Four minutes after the start of mixing, the plunger of the syringe was advanced at 60 mm/min for 10 s every minute during the first 12 min and every second minute thereafter. The force applied to the syringe was measured using an Instron 3344 universal testing machine fitted with a 2 kN load cell. All materials were tested in triplicate.

Table 1
Working time and setting time with CPP addition to zinc-silicate and germanium zinc-silicate glass ionomer cements.

CPP substitution	Zinc-silicate cements		Germanium zinc-silicate cements	
	Working time	Setting time	Working time	Setting time
(wt%)	(s)	(min)	(s)	(min)
0	58 ± 5	2.1 ± 0.1	485 ± 38	40.8 ± 1.6
20	59 ± 2	2.8 ± 0.2	n/a	n/a
30	72 ± 3	3.2 ± 0.3	n/a	n/a
40	89 ± 3	4.6 ± 0.1	511 ± 17	49.0 ± 1.7

3. Results and discussion

CPP addition increased the working and setting times for both the zinc-silicate and germanium zinc-silicate cements (Table 1). The biggest increases were observed for the zinc-silicate cements, as CPP addition of 40% increased the working and setting times by 53% and 119% respectively, whereas the germanium containing cements saw smaller extensions of 17% and 25%.

FTIR spectra were successfully collected over 20 min for the zinc-silicate GIC with CPP incorporation. The chosen collection time was much longer than the measured setting time, as the setting reaction was slower at room temperature. The characteristic band for free PAA (not coordinated to a metal ion) was identified at *c.* 1700 cm^{-1}, as was the band for ionized PAA at *c.* 1550 cm^{-1} (Fig. 1a). As the setting reaction proceeded, the absorbance for the ionized PAA band increased and the absorbance for the free PAA band decreased from a clear peak into a shoulder. The setting profile was plotted as the ratio of the absorbance for the ionized PAA to free PAA over time, as described in Fig. 1b. For all CPP addition levels, the conversion ratio followed a smooth increase over time, with the rate of conversion decreasing with increasing CPP content. This trend was also observed for the final conversion ratio at 20 min, where 40 wt% CPP addition decreased the ratio by 53%. These FTIR results are consistent with noted increases in working and setting times with increasing CPP content.

The germanium containing cement followed a different setting profile (Fig. 2a and b). Initially, there was a smooth increase in the conversion ratio (Fig. 2c), followed by an inflection and an increase in conversion rate, resulting in an 's' shaped curve. The increased standard deviations at late time points may have been aggravated by fluctuations in the ambient conditions. This is one of the limitations of ATR-FTIR, that small changes in temperature may have affected the rate of setting and evaporation over the long duration of the study. The ionization ratio for the cement with 40 wt% CPP was 22% less than that of the cement containing no CPP at 3 h. This is a much smaller difference than was found for the zinc-silicate cements, and is consistent with the smaller increase in setting times observed for CPP addition in the germanium containing cements.

The 's' shaped reaction profile may be due to the formation of an intermediate complex, as was proposed by Dickey et al. [19] Increasing the germanium to silicate ratio in the glass resulted in faster Ge^{4+} and Zn^{2+} release, yet slower growth of the ionization ratio of PAA (measured by ATR-FTIR). Dickey et al. suggested that the germanium and zinc ions may form a temporary intermediate, similar to the proposed mechanism for the aluminosilicate system [1], which can delay the setting reaction of the GICs. Formation of this complex may cause the initial reduction in reaction rate, with the breakdown of these transient species resulting in a subsequent increase in reaction rate. This suggests that CPP incorporation does