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Characteristics of glass ionomer cements composed of glass powders in CaO–SrO–ZnO–SiO$_2$ system prepared by two different synthetic routes

Ill Yong Kim · Chikara Ohtsuki · Aisling Coughlan · Lana Placek · Anthony W. Wren · Mark R. Towler

Abstract Glass ionomer cements (GICs) are composed of an acid degradable glass, polyacrylic acid and water. Sol–gel processing to prepare the glass phase has certain advantages, such as the ability to employ lower synthesis temperatures than melt quenching and glasses that are reported to have higher purity. A previous study reported the effects of glass synthesis route on GIC fabrication. However, in that study, the sol–gel derived glass exhibited a reduced concentration of cations. This study investigates increasing the cation content of a sol–gel derived glass, 12CaO·4SrO·36ZnO·48SiO$_2$ (molar ratio) by heating before aging to reduce dissolution of cations. This glass was prepared by both sol–gel and melt-quenched routes. GICs were subsequently prepared using both glasses. The resultant cement based on the sol–gel derived glass had a shorter working time than the cement based on the melt-quenched one. Contrary to this, setting time was considerably longer for the cement based on the sol–gel derived glass than for the cement based on the melt-quenched one. The cements based on the sol–gel derived glass were stronger in both compression and biaxial flexure than the cements prepared from the melt-quenched glass. The differences in setting and mechanical properties were associated with both cation content in the glass phase and the different surface area of the resultant cements.

1 Introduction

Glass ionomer cements (GICs) have been used in dental applications for decades [1]. They have potential as bone cements because of their ability to adhere to both surgical metals and the mineral phase of human bone [2, 3], to set without shrinkage [4], or significant heat evolution [5] and to have comparable mechanical properties to human bone [6, 7]. GICs set by the reaction of an acid degradable glass with an aqueous solution of polyacrylic acid (PAA) or related water-soluble polymeric acids. The acid attacks the glass and cations are released into aqueous solution. Cations are then chelated by the carboxyl groups of PAA. The matrix sets by formation of crosslink between the polymer chains [2].

The glass phase in all commercial GICs is based on an alumino-silicate composition. The glass forms a cement by a chemical reaction between calcium and aluminum ions released from the glass surface and carboxyl groups in PAA in an aqueous environment. The release of aluminum ions from these cements has been reported to cause defective bone mineralization and has been implicated in the pathogenesis of degenerative brain diseases [8, 9]. To address this, a new glass phase free from aluminum and based on the CaO–SrO–ZnO–SiO$_2$ system was developed by the authors [10, 11]. Release of the zinc ion from GICs based on this glass phase shows an antibacterial effect and

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reduces bone resorption. The strontium ion reduces bone resorption and stimulates bone formation [12].

The glass phase of GICs has conventionally been prepared by the melt-quench method. Sol–gel processing shows some advantages for glass formation, such as the use of a lower processing temperature, and a glass resulting which has higher purity and homogeneity than a melt quench glass [13, 14]. A previous study reported the development of a sol–gel derived BT101 glass with a nominal composition of $12CaO \cdot 4SrO \cdot 36ZnO \cdot 48SiO_2$ molar ratio [15]. However, setting behavior and mechanical properties of the resultant cements formed from this glass did not compare with those reported from a GIC based on the melt-quenched version of the same glass. The reason is that the resultant sol–gel derived glass contained a lower cation concentration than expected from its starting composition, because the cations were dissolved into supernatant solution extracted from a gel during aging in sol–gel processing [16]. If the resultant composition of the sol–gel derived glass had have been comparable to the starting composition, the glass would have potential as a glass ionomer for cementation. In the study reported herein, we prepared the sol–gel derived glass by heating before aging to prevent dissolution of cations from the gel. The aim of this study was to investigate the potential as a glass ionomer synthesized by the sol–gel route. GICs with the glass prepared by both sol–gel processing and melt-quench routes were evaluated in terms of setting behavior and mechanical property.

2 Materials and methods

2.1 Sol–gel synthesis of glass ionomer

A glass [15], BT101 with nominal composition of $12CaO \cdot 4SrO \cdot 36ZnO \cdot 48SiO_2$ in molar ratio, was prepared by hydrolysis and polycondensation of tetraethoxysilane (TEOS, $Si(C_2H_5)_4$, Alfa Aesar, Massachusetts, USA) in an aqueous solution containing calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Sigma-Aldrich, Missouri, USA), strontium nitrate ($Sr(NO_3)_2$, Sigma-Aldrich, Missouri, USA) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich, Missouri, USA). All the nitrates were dissolved into distilled water and nitric acid (70 mass% HNO_3, Across Organic, New Jersey, USA) was added into the solution. Then TEOS was added to the solution under stirring. After 20 min, the solution was transferred into a polyethylene case with its top sealed tightly and kept in an oven for gelation at 40 °C. After gelation, the wet gel was heated at 600 °C for 2 h without aging. The heated gel was pulverized and sieved to obtain a powder with a maximum particle size of 45 μm.

2.2 Melt-quenching synthesis of glass ionomer

BT101 glass was also prepared at the same nominal composition for sol–gel derived one through a traditional melt-quenching method. For the glass preparation, analytical grade reagents (Sigma-Aldrich, Missouri, USA), calcium carbonate ($CaCO_3$), strontium carbonate ($SrCO_3$), zinc oxide ($ZnCO_3$) and silicon dioxide (SiO_2) were weighed out and ball-milled after mixing. The mixture was oven dried at 100 °C for 1 h and then heated at 1,480 °C for 1 h in a platinum crucible and quenched into water. The frit was dried, ground and sieved to retrieve a glass powder with a maximum particle size of 45 μm.

2.3 Characterization of glass powders

X-ray diffraction (XRD, SIEMENS D5000, Siemens, Karlsruhe, Germany) patterns of both the samples were collected after powder preparation. Powder samples were placed on stainless steel holders and analyzed using CuKα radiation. A generator voltage of 40 kV and a tube current of 20 mA were employed. The morphology of the glasses were observed by scanning electron microscopy (SEM, Philips 515, Philips, Eindhoven, Netherlands). Before SEM observation, the powder samples were coated with gold. The resultant composition of the glasses was determined by energy disperse X-ray (EDX) spectroscopy (Philips, Eindhoven, Netherlands). All the EDX spectra were collected at 20 kV. Particle size was measured by a particle size analyzer (Multisizer 4, Beckman Coulter, California, USA) after sieving. Surface area was measured by BET method (NOVA 1000e, Quantachrome Instruments, Florida, USA).

2.4 Cement preparation

Cements were prepared by mixing the glass powder (<45 μm) with E9 PAA, (Mw 80,800, <90 μm, Advanced Healthcare Limited, Kent, UK) and distilled water on a glass plate. The cements were formulated at a P:L ratio of 1:3.25, where 0.2 g of BT101 glass was mixed with 0.3 g of PAA and 0.45 cm^3 water. The mixture was undertaken within 20 s. Both the glasses prepared by sol–gel and melt-quenching methods were mixed with 40 mass% PAA.

2.5 Cement characterization

The setting times (T_s) of the cements were conducted by the method outlined in ISO9917; the standard for dental water based cements. The working time (T_w) of the cements was measured in ambient condition and was defined as the period of time from the start of mixing during which it was possible to manipulate the material

without having an adverse effects on its properties. Average T_s and T_w values and their standard deviation were calculated from the obtained data. The compressive strengths of the cements after maturation for 1 days were also evaluated in accordance with ISO9917. Cylindrical samples were tested after setting by a testing machine (Instron 5566 Universal Testing Machine, Instron, Massachusetts, USA) using a 5 kN load cell at a crosshead speed of 1 mm/min. Cement discs with 10 mm × 1 mm in diameter and thickness were tested after setting. Testing was carried out by the testing machine using a 1 kN load cell at a crosshead speed of 1 mm/min. For each testing, five specimens were used. Average strength values and their standard deviation were calculated from the obtained data.

3 Results

Figure 1 shows powder XRD patterns of the sol–gel derived and melt-quenched BT101 glass particles after sieving. All particles were amorphous regardless of synthesis method. Figure 2 shows SEM photographs of the BT101 particles. It was observed that the sol–gel derived particles were agglomerated with nano-sized particles, like granules. In the case of melt-quenched glass, the small particles were also agglomerated on bigger particles and had rectangular morphology. Table 1 gives average particle size and specific surface area of both glasses. Average particle sizes (d_{50}) of the sol–gel and melt-quenched glasses were 3.9 and 3.2 μm, respectively. The specific surface area of the sol–gel and melt-quenched glasses were 71 and 38 m^2/g, respectively.

Figure 3 shows EDX spectra of the sol–gel derived and melt-quenched BT101 glasses. The intensity of silicon (Si)
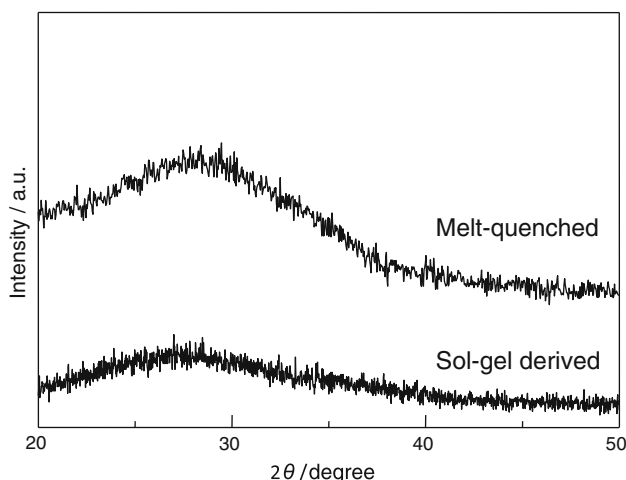
in the sol–gel derived BT101 was higher than that in the melt-quenched one. In the case of calcium (Ca) and zinc (Zn), the intensities of two elements in the sol–gel derived glass were smaller than those in the melt-quenched one. Table 2 gives the compositions of the sol–gel derived and melt-quenched BT101 glasses. The sol–gel derived glass contained 4.25 mol% of Ca while the melt-quenched one contained 4.88 mol%. Considering Zn content, the melt-quenched glass contained 19.51 mol% and the sol–gel derived one contained 9.31 mol%. In the case of strontium (Sr), the melt-quenched glass was containing 2.62 mol%, however, Sr was not detected on the sol–gel derived one.

Figure 4 shows working and setting times of the GICs prepared using the sol–gel derived and melt-quenched glasses. The working time of GICs prepared from the sol–gel derived and melt-quenched glasses were 3 min 50 s and 6 min 37 s, respectively. Setting time was determined as 76 min for a GIC prepared from the sol–gel derived glass and 20 min when prepared from the melt-quenched glass powder. The working time of GICs prepared from the sol–gel derived glass were shorter than from the melt-quenched one. The setting time of GICs prepared from the sol–gel derived glass were longer than from the melt-quenched one.

Table 3 gives the mechanical properties of GICs prepared from the sol–gel derived and the melt-quenched glasses. The compressive strength of GICs prepared from the sol–gel derived glass was 4.5 MPa, and from the melt-quenched glass was 1.8 MPa. The biaxial compressive strength of GICs prepared from the sol–gel derived glass was 0.3 MPa, while that of GICs prepared from the melt-quenched one was 0.1 MPa. The GICs prepared from sol–gel derived glass exhibited higher strength than when prepared from the melt-quenched glass.

4 Discussion

GIC are formulated by a crosslinking reaction of cations released from the glass and COO$^-$ groups of PAA during setting [2]. In the previous study, the prepared gel contained 0 mol% Ca^{2+} [15]. The low concentration of cations in the sol–gel derived glass inhibits formation of non-bridging oxygens (NBO) in the glass network. The lack of metal ions will influence the setting reaction. In this study, we prepared the sol–gel derived glass with calcium and zinc ions by heat-treatment before aging. The contents of the cations in the sol–gel derived glass were still lower than in the melt-quenched glass. During gelation and aging, supernatant solution was generated by shrinkage of gel [16]. Cations released from the surface of gel and, sometimes, crystallization of cations was occurred during aging and drying because of water vaporization [14]. In this

Fig. 1 Powder X-ray diffraction (XRD) patterns of the sol–gel derived and melt-quenched BT101 glasses

Fig. 2 Scanning electron microscopic (SEM) photographs of the BT101 glasses prepared by the sol–gel derived and melt-quenched routes
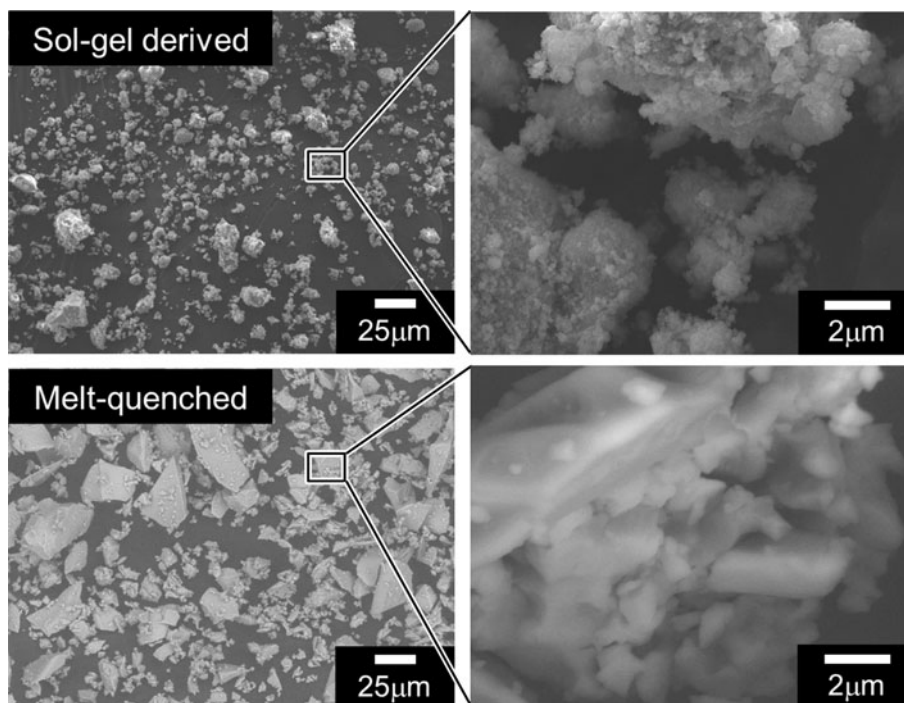

Table 1 Particle size and surface area of the BT101 glass prepared by the sol–gel derived and melt-quenched routes

Glass	Average particle size (d_{50}) (μm)	Specific surface area (m²/g)
Sol–gel derived	3.2	71
Melt-quenched	3.9	38

Table 2 Compositions determined from energy dispersive X-ray (EDX) spectra of the BT101 glass prepared by the sol–gel derived and melt-quenched routes

Glass	Composition (mol%)				
	O	Si	Ca	Zn	Sr
Sol–gel derived	64.69	21.75	4.25	9.31	–
Melt-quenched	54.46	18.53	4.88	19.51	2.62

– not detected

study, we could obtain the sol–gel derived glass without crystallization (see Fig. 1). To obtain this amorphous glass, the gel was heated before aging. The heated particles have a higher cation concentration than those reported in the previous study [15]. Sr was not detected by EDX spectra in the sol–gel glass. The Sr amount was below the detection limit of the EDX analysis.

The working and setting time may depend not only on the concentration of cations released from the glass but also the dissolution rate of these cations. Dissolution is affected by their compositions as well as surface area exposed to the PAA. The working time of GICs prepared from the sol–gel derived particles was shorter than those of GICs prepared from the melt-quenched one. The sol–gel derived glass had

Fig. 3 Energy dispersive X-ray (EDX) spectra of the BT101 glasses prepared by the sol–gel derived and melt-quenched routes
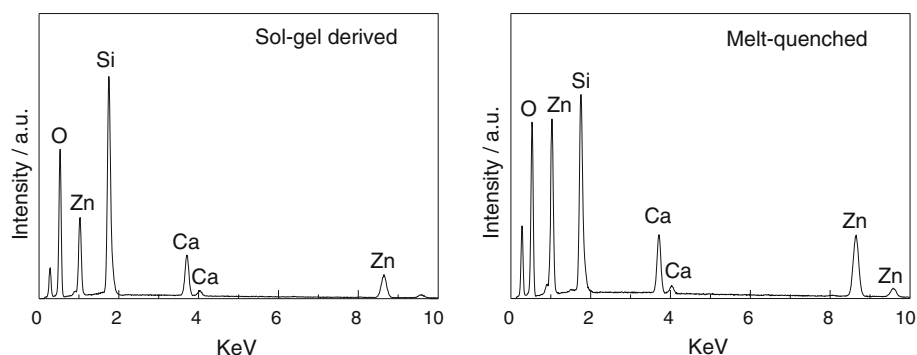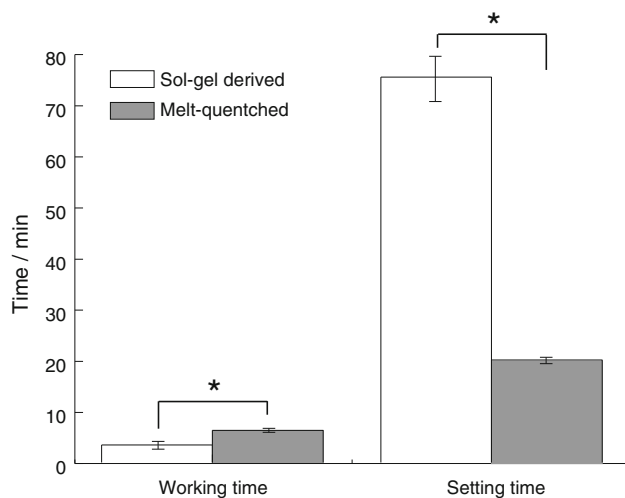
Fig. 4 Working time and setting time of the GICs using the BT101 glasses prepared by the sol–gel derived and melt-quenched routes. (* = $P < 0.05$)

Table 3 Compressive strength and biaxial compressive strength of the GICs using the BT101 glass prepared by sol–gel derived and melt-quenched routes

Glass	Compressive strength (MPa)	Biaxial compressive strength (MPa)
Sol–gel derived	4.50 ± 0.78	0.25 ± 0.13
Melt-quenched	1.81 ± 0.36	0.13 ± 0.07

larger specific surface area than that of the melt-quenched one. The average particle size (3.2 μm) of sol–gel derived particles was smaller than that (3.9 μm) of the melt-quenched analogue. In the early stages of the reaction after mixing, the difference in specific surface area of the two powders explains the difference in T_w, because the amounts of cations released from the surface of the sol–gel derived GIC were greater than from the melt-quenched glass.

The T_s of GICs based on the sol–gel derived glass were longer than those based on the melt-quenched glass. The total amount of cations released from the melt-quenched glass was much more than the sol–gel derived one. The resultant composition of melt-quenched glass contains a higher cation concentration than the sol–gel derived one. This suggests that T_w and T_s of GICs based on sol–gel derived glass resulted from larger specific surface area and lower cation content compared to those based on the melt-quenched glass.

Mechanical properties of the GICs based on both glasses were evaluated in both compression and biaxial flexure. The GIC based on the sol–gel derived glass recorded 4.50 and 0.25 MPa in compression and biaxial flexure, respectively. The GIC based on the melt-quenched glass recorded 1.81 and 0.13 MPa in compression and biaxial flexure, respectively. The cements based on the sol–gel derived

glass had higher strengths in both modalities. The difference might be caused by specific surface area and particle size of the glasses [17], because molecular weight and concentration of the PAA used to fabricate the cements were the same, and the particle size of the two glasses almost identical. It means that the effect of surface area is greater than that of particle size. The interfacial surface area between glass particles and PAA per unit volume increases using the sol–gel derived glass [18], because the sol–gel derived glass exhibited higher specific surface area than the melt-quenched one. However, the two types of cements showed low compressive strength values to be used in dental applications. The cements require further improvement by optimizing their composition, particle size and surface area of glass.

5 Conclusions

A glass composition, BT101 with a nominal composition of $4SrO \cdot 12CaO \cdot 36ZnO \cdot 48SiO_2$ in molar ratio was prepared by both sol–gel and melt-quench methods. The sol–gel derived BT101 had much higher specific surface area compared to the one prepared by melt-quench. The sol–gel derived BT101 had lower cation concentration than the prepared by melt-quench. The GICs prepared from the sol–gel derived glass set more slowly than those prepared from the melt-quenched glass. The GICs prepared from the sol–gel derived BT101 were stronger in both test modalities than those prepared from the melt-quenched BT101. The differences in setting behavior and mechanical properties of GICs can be associated by both cationic content and their dissolution rate from the surface of the glass as well as specific surface area.

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