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The effect of Mg^{2+} incorporation into the glass phase of zinc-based glass polyalkenoate cements

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ABSTRACT

The suitability of glass polyalkenoate cements (GPCs) as injectable adhesives in orthopedics has been compromised by the presence of aluminum (Al), a component in the glass phase of all commercial GPCs. There has been considerable work on the development of Al-free GPCs which can be formulated based on calcium (Ca) zinc (Zn) silicate (Si) glasses. These materials, in terms of biocompatibility and mechanical properties, have potential for orthopedics. However, many of these experimental Al-free GPCs have setting times shorter than 60 s, restricting clinical applications. Here, the authors incorporate Magnesium (Mg) into the glass phase of Al-free GPCs in an attempt to extend their handling properties without deleteriously influencing strength. Three Mg-Ca-Zn-Si glasses with increasing amounts of Mg (up to 12 mol%) substituting for Ca were synthesized and GPCs were subsequently produced by mixing each glass with aqueous polyacrylic acid (PAA). The results show that Mg substituted for Ca in the glasses did significantly affect the chemical structure of the glasses by increasing the bridging oxygen to non-bridging oxygen (BO:NBO) ratio. The resultant GPCs exhibited extended working times, in line with Mg content in the glass, combined with significant increases in both compressive and biaxial flexural strength with both cement maturation and molecular weight of the PAA phase. Mg-based GPCs recorded working times of up to 145 s, setting times of up to 191 s, and compressive strengths in excess of 58 MPa after 30 days maturation. Thus, we have shown that Mg incorporation into Al-free ionomer glasses can result in GPCs formulated from them that have handling and mechanical properties suitable for orthopedic applications.

1. Introduction

Magnesium (Mg) is an earth metal element present in the adult human body at approximately 24 g (1 mol) per 70 kg [1]; approximately 53% (12,720 mg) of which is found in the bones, 27% (6480 mg) in the muscles and 19% (4608 mg) in the soft tissues. < 1% of the body's Mg exists in serum and interstitial fluid [1–4]. The bones function as a reservoir for Mg facilitating, when necessary, the delivery of Mg ions into the bloodstream. Mg is also antibacterial [5] and is associated with the calcification process of bone [6–10]. Mg is involved in roughly 300 chemical reactions within the human body, such as activating phagocytosis, regulating active calcium transport [11], influencing wound healing and stabilizing bone metabolism [12,13].

Glass polyakenoate cements (GPCs) have been utilised in luting and restorative applications within dentistry [14–16]. GPCs form by the reaction of an ion-leachable glass and an aqueous solution of polyacrylic acid (PAA) [17]. When the acid attacks and the glass structure is degraded, cations are then released into the aqueous phase of the setting cement. As a result, the cations released are cross-linked by the polymer chains to create a cement with a microstructure composed of reacted and unreacted glass particles enclosed in a hydrated polysalt matrix [18, 19]. Outside of dentistry, GPCs have been utilised in ear, nose and throat (ENT) applications [20,21], partly as a result of the ability of GPCs to set without shrinkage [22] or significant heat evolution [23].

All commercial GPCs are based on alumino-silicate glass chemistry [19] and it is the reliance on the presence of aluminum (Al) that has restricted the use of such cements in orthopedics. Aluminum isomorphically replaces some SiO_4 tetrahedra in the glass structure, increasing the acid degradability of the glass [24]. However, the aluminum ion is a neuro-toxin which interrupts cellular homeostasis [25–27] and encourages cellular oxidation [28]. It has been associated with brain disorders such as Parkinson's and Alzheimer's disease [28–34] and there have been negative outcomes associated with the use of aluminum-containing GPCs for the purpose of reconstructive otoneurosurgery [35] and orthopedics [36]. Despite this, GPCs have potential as bone adhesives due to their ability to adhere to both surgical metals and the mineral phase of bone [37–39], but Al would need to be

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replaced with a component that influences glass chemistry in a similar way without the toxic concerns.

Boyd and Towler were the first to report that aluminum- free GPCs could be formulated using glasses from the ZnO-CaO-SiO_2 ternary system, since zinc oxide (ZnO) is capable of functioning as both a network modifier and a former similar to alumina [40,41]. Zn has the ability to increase DNA synthesis in osteoblastic cells [42], stimulate bone deposition [43] and is also antibacterial [44–46].

Mg^{2+} acts as both a network modifier and a former oxide in glass [11] in a similar fashion to Zn [47]. Incorporating Mg^{2+} into the glass structure as a substitute for Ca^{2+} is feasible as their ionic radii and chemical properties are almost identical [48].

Boyd et al. [47] developed the first zinc-based GPCs (Zn-GPCs). The resultant cements offered suitable biocompatibility and strength for orthopedic applications [41,46,49,50], but their setting times (< 1 min) were too short for injectable applications. Wren et al. [51] developed an ionomer glass, similar in composition to that of Boyd et al. [47] but with gallium oxide (Ga_2O_3) substituted for ZnO. Gallium ions have both chemotherapeutic and anti-inflammatory properties [52,53]. The setting times of the GPCs based on Wren's glasses were approximately 9 min; however, the cement suffered a significant decrease in compressive strength from 80 MPa to 6 MPa when Ga_2O_3 was added; postulated to be due to Ga^{3+} disrupting polyacrylate formation during the setting reaction. This demonstrates the challenge of balancing the handling and mechanical properties of Al-free GPCs [51]. Germanium (Ge) adopts the role of a network former when incorporated into an ionomer glass and is theoretically capable of isomorphically replacing Si in the network [54]. Germanium-based glasses have also been investigated by Dickey et al. [55–57] who reported that glass reactivity decreased with Ge incorporation, resulting in GPCs with extended working times of up to 10 min, setting times between 14 and 36 min, and compressive strengths in excess of 30 MPa after 30 days maturation [55]. However, compressive strengths significantly decreased from ~37 MPa to ~22 MPa after 180 days which may limit the applicability of these cements [55]. A further study by Kim et al. [58] considered GPCs based on magnesium/strontium (Mg/Sr) glasses (CaO-SiO_2-P_2O_5-ZnO-CaF_2). When increasing Sr up to 0.27 mol fraction, the setting time of the Mg/Sr glasses significantly increased up to 45 min while the compressive strengths significantly decreased to 13 MPa. Sr acts as a network modifier, thus disruption of the glass network can occur at a high Sr concentrations which then decrease mechanical properties of the resultant GPCs [58]. Efforts to extend the setting times of Al-free GPCs, then, are generally accompanied by a significant drop in strength [47,48,51,55,58–60].

When developing GPCs for orthopedic applications, certain criteria have been identified as pertinent for such cements [61, 55]:

- Injectability
- Ease of handling
- High radiopacity
- Adapted viscosity (not too low)
- Lasting, constant viscosity (around 5–10 min)
- Long setting time (≈15 min)
- Low curing temperature
- Adapted, lasting mechanical properties (> 30 MPa to withstand bone compression)
- Biocompatibility
- Low price
- Slow biodegradation

In line with these criteria, the purpose of the research was to develop a novel Zn-GPC containing Mg that have handling and mechanical properties suitable for fracture repair and stabilization by incrementally substituting MgO for CaO within the glass component of the cement.

Table 1
Glass formulations (mol%).

Glass formulations	SiO_2	CaO	ZnO	MgO
TK10	48	12	36	4
TK11	48	8	36	8
TK12	48	4	36	12

2. Materials and methods

2.1. Glass synthesis

A series of three glasses were synthesized (Table 1). Appropriate amounts of analytical grade silica, zinc oxide, calcium carbonate and magnesium oxide (MgO) (Sigma Aldrich, Ontario, Canada) were weighed out in a plastic tub and shaken by hand for 20 min. The glass batches were then transferred to platinum (Pt) crucibles for firing (1480 °C, 1 h). The melts were subsequently shock quenched into water and the resulting frits were dried, ground using a ball mill (420 RPM, 15 min) and sieved through a 45 μm mesh. The glass powders that passed through the sieve were subsequently used for characterization purposes and as reagents in a new series of GPCs named TK10, TK11 TK12 after the parent glasses.

2.2. Structural characterization of glasses

2.2.1. Network connectivity

The network connectivity (NC) of the glasses was calculated with Eq. (1) using the molar compositions of the glass (Table 1), where Si^{4+} is considered as a network former [19,20], Ca^{2+} as a network modifier [20]; and Zn^{2+} as an intermediate [52]. However, the authors assume that in this research Zn^{2+} takes on the role of a modifier and Mg^{2+} acts as an intermediate [11]. The authors assume two conditions for the network intermediate Mg^{2+}, a modifier (NC^1) and a former (NC^2).

$$NC = \frac{\text{No. BOs} - \text{No.NBOs}}{\text{Total No.Bridging}} \quad (1)$$

where: NC = network connectivity, BO = bridging oxygens, NBO = non-bridging oxygens.

2.2.2. X-ray diffraction (XRD)

XRD patterns were collected using an X'Pert PRO (PANanlytical Inc., St Laurent, QC, Canada). Glass powder samples were attached to a stainless steel disc. The powder compacts were then placed in the X-ray Diffractometer and scanned in the range $0^{\circ} < 2\theta < 100^{\circ}$ at scan step size 0.05° and step time of 10 s. A generator voltage of 45 kV and a tube current of 40 mA were employed using Cu kα X-ray source.

2.2.3. Particle size analysis (PSA)

Particle size analysis was performed using a Coulter Ls 100 Fluid module Particle size analyzer (Beckman Coulter, Fullerton, CA, USA). The glass powder samples were evaluated in the range of 2–60 μm with a run length of 60 s. The suspension fluid used in this case was glycerol maintained at a temperature of 37°C. The relevant volume statistics were calculated on each glass. The average diameters ($n = 5$) were recorded at 10%, 50%, and 90% of the cumulative volume distribution (d_{10}, d_{50}, and d_{90}, respectively).

2.2.4. Scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX)

Backscattered electron (BSE) images were taken on glass particles with a JEOL Co. JSM-6380LV (JEOL Ltd., Tokyo, Japan) Scanning Electron Microscope. Compositional analysis was performed with an EDX Genesis Energy-Dispersive Spectrometer (JEOL Co. JSM-6380LV, JEOL Ltd., Tokyo, Japan). All EDX spectra were collected at 20 kV using

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