Materials Chemistry and Physics 147 (2014) 360–364

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Materials science communication

Influence of gallium on the surface properties of zinc based glass polyalkenoate cements

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HIGHLIGHTS

- The addition of Ga^{3+} ions in a GPC result in a change in the surface charge.
- Increased surface hydrophilicity was shown using contact angle of water.
- Ion release profiling showed that Ga^{3+} release is amount dependent.
- Antibacterial properties were a result of the Zn^{2+} ion release, not Ga^{3+}.

ARTICLE INFO

Article history:
Received 9 December 2013
Received in revised form
26 May 2014
Accepted 8 June 2014
Available online 4 July 2014

Keywords:
Biomaterials
Glasses
Electrochemical properties
Surfaces

ABSTRACT

This study investigates the effect of gallium (Ga) additions, substituting for zinc (Zn), on the physio-chemical surface properties of aluminium-free glass polyalkenoate cements (GPCs). Substituting Zn with Ga resulted in a significant increase in hydrophilicity and thusly wettability, as shown by a decrease in water contact angle. Increasing Ga resulted in increased Zn release, irrespective of decreasing Zn content of the starting glass. This resulted in increased antibacterial efficiency, against *E*scherichia *coli*, but not *S*taphylococcus *epidermidis*. Ga was shown to have no effect on antibacterial efficiency.

1. Introduction

Glass polyalkenoate cements (GPCs) can be tailored for specific applications in the skeleton. The incorporation of ions into the glass phase may also impart therapeutic effects in the body [1,2]. However the incorporation of these ions may also have significant effects on glass chemistry, and contiguously, the characteristics of the cement [3,4]. Gallium ions (Ga^{3+}) are of interest with respect to mediating beneficial host responses to biomaterials [5,6]. Ga^{3+} is reported to have antibacterial [7–9], anti-inflammatory [10] and anti-cancerous effects [11] while also retarding bone resorption [12]. Ga^{3+} is also thought to ameliorate allograft rejection and reduce surface proliferation of infectious organisms such as syphilis, trypanosomiasis and tuberculosis [12–14], as well as fungi [15–17].

In studies conducted on Ga^{3+} ions and Ga-compounds against *P*seudomonas *aeruginosa* and *S*taphylococcus *aureus*, the mechanism of action has been described in the literature as being due to the Ga^{3+} ions ability to disrupt iron (Fe^{3+}) metabolism [15,18,19] in bacteria as it has a similar electric charge, ionic diameter and co-ordination number [16]. It has also been reported [20] that an improved bacterial adhesion to the substratum can be achieved with a decreased (more negatively charged) electrokinetic potential.

Synergistically with Ga^{3+}, zinc ions (Zn^{2+}) also have a number of positive therapeutic effects. Zn^{2+} has the ability to increase the deoxyribonucleic acid (DNA) of osteoblasts [21], resulting in increased bone mass [22]. In addition, Zn^{2+} is also antibacterial and

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http://dx.doi.org/10.1016/j.matchemphys.2014.06.020
0254-0584/

acts against *Streptococcus mutans* and *Actinomyces viscosus* due to Zn^{2+} ion migration [23]. Consequently, zinc based GPCs containing gallium are of significant practical interest for a variety of potential clinical applications [6]. With respect to including Ga^{3+} and Zn^{2+} in the glass phase of GPCs, it is believed that Ga^{3+} may act as either a glass modifier or former depending on the overall chemistry of the glass and each has been shown to augment the functionality of GPCs in a variety of ways [24,25].

Replacing an ion species in the glass phase of a GPC with an ion species of different valency will have an effect on the basic chemistry of the GPC, which in turn, influences working and setting times, mechanical properties and ion release. Previous work by the authors details how Ga^{3+} ion additions at the expense of Zn^{2+} ions affects the glass chemistry and properties [26].

Surface characteristics play an important role in the substratum-bacterial adhesion and are influenced by both the bacteria and the material [27–29] *via* surface chemistry, energy and/or topography [20,27,30]. The extent to which Ga^{3+} and Zn^{2+} in GPCs may alter surface characteristics is therefore of significant importance, but is largely unexplored for Ga containing cements. This study investigates the effects of Ga addition (as a substitute for Zn) on the surface properties of a GPC and evaluates the influence of such substitutions on the material antibacterial efficacy.

2. Experimental

2.1. Materials

Three glass compositions (L-Con, L-Ga1 and L-Ga2) were formulated (Table 1). Glasses were prepared by weighing out appropriate amounts of analytical grade reagents and ball milling (1 h). The mix was then oven dried (100 °C, 1 h), fired (1500 °C, 1 h) in a platinum (Pt) crucible and quenched in water. The resulting frit was dried, ground and sieved to retrieve a glass powder with a maximum particle size of 45 μm.

Cements were prepared by mixing glass powders (<45 μm) with poly(acrylic acid) (PAA-Mw, ~210,000 & <90 μm, Advanced Healthcare Limited, Kent, UK) and de-ionized (DI) water. Cements were formulated at a powder-liquid (P:L) ratio of 1:0.74 with 50 wt % addition of PAA. Mixing was undertaken within 25–30 s in ambient room temperature (23 ± 1 °C). The resultant cements are allocated with the same nomenclature (*L-Con*, *L-Ga*1 and *L-Ga*2) that were assigned to the glasses that they were fabricated from.

2.2. Determination of physio-chemical properties

2.2.1. Contact angle (CA)

GPC discs (1 mm high, 12 mm diameter, $n = 5$) were prepared from all glass compositions (Table 1). Contact angles were measured by a method described by Moshaverinia et al. [31]. Disc samples were tested after 1 day, post cement preparation. Measurements were taken using an OCA 20 optical contact angle measuring instrument (DataPhysics Instruments GmbH, 70,794 Filderstadt, Germany). The distilled water drops were deposited with a microsyringe (DataPhysics Instruments GmbH, 70,794 Filderstadt, Germany) on each sample. The contact (wetting) angle, which correlates the interfacial tension, can be measured according to Young's equation; Eq. 1 [32]. Where L = liquid, S = solid, V = vapour, θ = contact angle and γ is the corresponding interfacial tension.

Table 1
Glass compositions (mol%).

	SiO_2	Ga_2O_3	ZnO	CaO
L-Con	48	0	40	12
*L-Ga*1	48	8	32	12
*L-Ga*2	48	16	24	12

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \tag{1}$$

$$\theta = \cos^{-1}\left(\frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}\right) \tag{2}$$

Thus, if θ increases the total interfacial energy equation inside the bracket in Eq. 2 decreases. This implies less adhesive forces between the surface and water, giving a hydrophobic surface and a more defined water droplet on the surface.

The contact angles for each sample set ($n = 5$) at the specific days were calculated using the recorded images and the following equation, Eq. 3.

$$\text{Contact Angle Per Batch} = \frac{\sum_{n=1}^{5}\left(\frac{\text{Left Angle}+\text{Right Angle}}{2}\right)}{5} \tag{3}$$

2.2.2. Roughness

A single GPC disc (1 mm high, 15 mm diameter) was prepared from all glass compositions for roughness (R_a) analysis. Measurements were taken at 3 random sites on each sample. Samples were tested after 1 day, post cement preparation. R_a measurements were performed using an Ambios Q-Scope™ 250/400 Nomad™ Series Atomic Force Microscope (Ambios Technology Inc., Santa Cruz, CA, USA). Intermittent-contact (wave) mode imaging was performed using a silicon nitride cantilever probe. A typical scan rate of 1 Hz and a scan size of 10 μm were used at a resolution of 256–512 pixels/line.

2.2.3. Ion release

Ion release studies were performed according to a method described by Wren et al. [33]. Samples were tested after being aged in DI water (37 °C) for 1 day, post cement preparation. The ion release profiles of cement samples were measured using the Agilent 4100 (Agilent technologies, Inc., Santa Clara, CA, USA) Microwave Plasma–Atomic Emission Spectrometer (MP–AES).

2.3. Antibacterial testing

Three GPC discs (2 mm high, 9 mm diameter) were prepared from all glass compositions (L-Con, L-Ga1 and L-Ga2). Antibacterial activity of the cements was tested against *Escherichia coli* (*E. coli*) and *Staphylococcus epidermidis* (*S. epi*) using the agar diffusion method at 1 day, post cement preparation. Bacterial stocks were made by plating cells from frozen stores onto their respective agar (Table 2), and allowing for 24 h incubating in a 37 °C oven. One colony was then extracted from the plate, added to 5 mL of its respective broth, and allowed an additional 24 h to incubate. After 48 h of total incubation, the broth/cell mixture was diluted according to Table 3 before being used to swab sample plates. To prepare the sample plates, disks were placed spaced out in triplicate ($n = 3$) on empty petri dishes and 20 mL of agar was poured over them. Once the dishes solidified, sterile swabs were used to spread the diluted bacterial stocks over the surface. The plates were then incubated in a 37 °C oven for 36 h, and subsequently disk diameter and inhibition halo were measured and recorded using callipers. Eq. 4 was then used to compute the inhibition zone (IZ) of each disk, where θ represents diameter.

$$\text{Inhibition Zone (mm)} = \frac{\text{Halo}\theta - \text{Disc}\theta}{2} \tag{4}$$