29 Jun 2012

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Recommended Citation

L. Placek et al., "Gallium Containing Glass Polyalkenoate Bone Cements: Glass Characterization and Physical Properties," *2012 38th Annual Northeast Bioengineering Conference, NEBEC 2012*, pp. 225 - 226, article no. 6207045, Institute of Electrical and Electronics Engineers, Jun 2012.
The definitive version is available at https://doi.org/10.1109/NEBC.2012.6207045

Gallium Containing Glass Polyalkenoate Bone Cements: Glass Characterization and Physical Properties

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Abstract- Gallium (Ga) glasses were developed to formulate a Glass Polyalkenoate Cement (GPC) series with both E9 and E11 polyacrylic acid (PAA) at 50, 55 and 60wt% additions. Working times (T_w), setting times (T_s), compression (σ_c), and biaxial flexural (σ_f) strength testing were evaluated to determine the GPCs potential use in orthopedics.

I. Introduction

A degradable glass is one of the major components of a Glass Polyalkenoate Cement (GPC); these are traditionally dental materials used for restorative purposes such as filling cavities in teeth and luting applications [1, 2]. The use of these materials in orthopedic applications has been postulated. One of the most important changes in the glass composition for possible orthopedic use is the incorporation of ions that have a positive therapeutic effect on bone (Sr^{2+}, Zn^{2+}, Ca^{2+}), and the removal of aluminum (Al^{3+}) which is known to deleteriously influence bone metabolism [3] and has also been implicated in numerous neurological disorders [4, 5].

Gallium is known to have a therapeutic effect in treating bone cancer [6] and is currently used as a therapeutic agent in cancer treatment [7]. The gallium ion also has anti-inflammatory and immunosuppressive activity in animal models of human disease [7].

This research supports the development of a Ga-containing GPC that can be injected into bone cavities created by resection of a tumorous growth through the evaluation of handling and mechanical properties. These properties must be determined suitable for cementation in orthopedic applications. Potential gallium ion release from these cements may have a chemotherapeutic affect while also filling the cavity created by the surgical procedure.

II. Materials and Methods

A. Glass Preparation and Characterization

Three Ga containing glass compositions (*Lcon., LGa-1, LGa-2*) were formulated for this study and are listed in 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 (100ºC, 1 h) and fired (1500ºC, 1 h) in a platinum crucible and shock quenched into water. The resulting frit was dried, ground and sieved to retrieve a glass powder with a maximum particle size of 45μm.

TABLE I. Glass Compositions (mol fract.)

	Lcon.	LGa-1	LGa-2
SiO_2	0.48	0.48	0.48
Ga_2O_3	0.00	0.08	0.16
ZnO	0.40	0.32	0.24
CaO	0.12	0.12	0.12

Diffraction patterns were collected to confirm amorphous structure. A combined differential thermal analyzer-thermal gravimetric analyzer (DTA-TGA) was used to measure the glass transition temperature (T_g) and determine an appropriate annealing temperature. X-ray Photoelectron Spectroscopy (XPS) was performed to analyze the surface chemistry, as well as the chemical state of the top few nanometers of the samples (all data was normalized based on the C1s peak position of 284.8 eV).

B. GPC Preparation and Properties

Cements were prepared by thoroughly mixing the glass powders (<45μm) with E9 and E11 polyacrylic acid (PAA - M*w*, 80,800 and 210,000, <90μm) and distilled water on a glass plate. The cements were formulated in a P:L ratio of 2:1.5 with 50, 55 and 60wt% additions of PAA in order to determine the material with the most suitable handling and mechanical properties for cement purposes. Complete mixing was undertaken within 20 seconds.

The setting times (T_s) of the cement series were tested in accordance with ISO9917 which specifies the standard for dental water based cements [8]. The working time (T_w) of the cements was measured in ambient air using a stopwatch, 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 effect on its properties. The compressive strengths (σ_c) of the cements were evaluated in accordance with ISO9917 [8]. The flexural strengths (σ_f) of the cements were evaluated by a method described in [9]. Both the compressive cylindrical samples and the flexural discs were tested after 1, 7 and 30 days.

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III. RESULTS

XRD data showed no crystalline species resulted from firing the three glasses. DTA yielded T_g values that were within 6°C for all three glasses (655°C for Lcon., 649°C for LGa-1, 651°C for LGa-2) which is insignificant and indicates that the Ga acts as a network modifier with similar bond characteristics as the Zn it is replacing. XPS survey scans for the three glasses are shown in Fig. 1. The survey scans confirm the starting formulation of each glass in addition to carbon which is used in sample preparation.

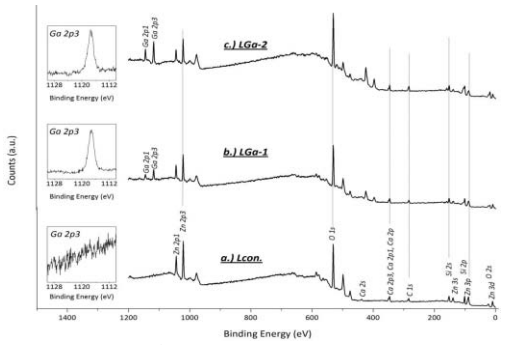

Fig. 1. XPS survey scan.

Working and setting times are shown in Figs. 2 and 3 respectively. Working times for the Control E9 and E11 containing cements decrease with increasing PAA concentration. This is due to the increase in $COOH^-$ groups available to crosslink the network. For both E9 and E11 there is an increase in T_w from the Lcon. to the Ga containing cements, but without significant difference between the Ga cements. T_s exhibited the same behavior as the T_w, however the E9 Ga containing cements exceed the setting time recommended for orthopedic applications. Seven day compression studies were conducted on the cement series, after which the E11, 50% cement was chosen as the best orthopedic candidate. The time dependent strength study results for this cement are shown in Fig. 4. For both the σ_c and σ_f the Lcon. cements were significantly stronger than the Ga cements, though no significant change occurred in the Lcon. values over time. The Ga cements showed significant strength increases over time for both σ_c and σ_f, but did not show significant differences between the two Ga contents at each respective time.

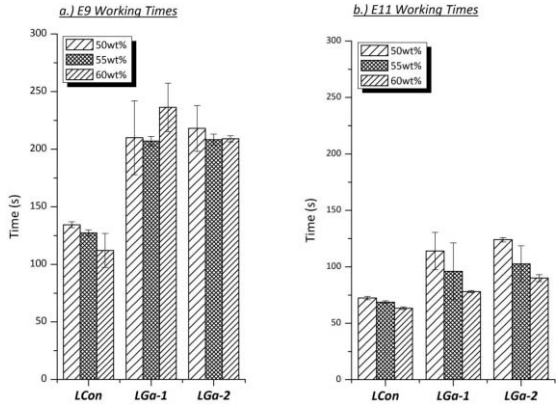

Fig. 2. Working times of E9 and E11 cement series.

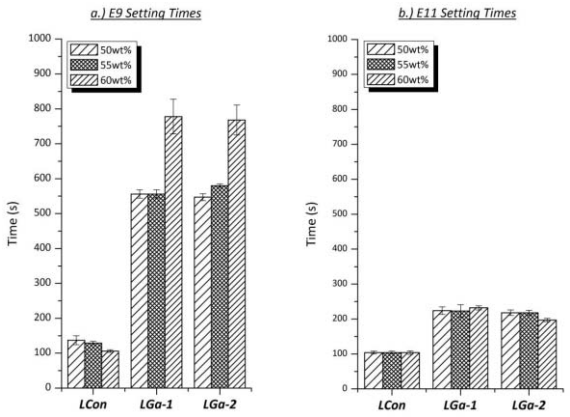

Fig. 3. Setting times of E9 and E11 series.

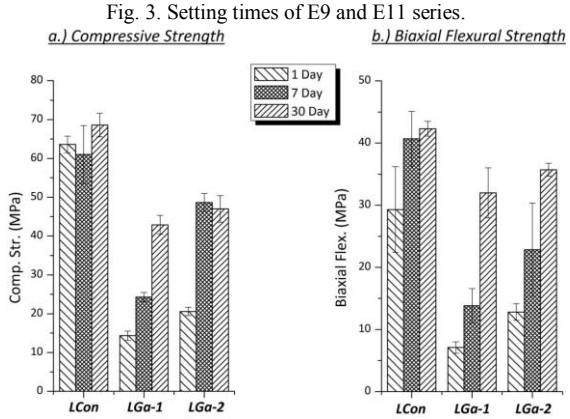

Fig. 4. Compressive and biaxial flexural strengths of E11 50% cements.

IV. CONCLUSION

The Ga cements LGa-1 and LGa-2 have suitable handling and mechanical properties for use as therapeutic bone cements. Future work to develop these cements will include ion release and cell culture studies to determine the concentrations and therapeutic effect of Ga release.

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