DENTAL MATERIALS XXX (2018) XXX–XXX

Available online at www.sciencedirect.com

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The influence of precursor addition order on the porosity of sol–gel bioactive glasses

Delihta Fernando[a], *Pierre Colon*[a,b], *Mark Cresswell*[c], *Catherine Journet*[a], *Nelly Pradelle-Plasse*[a,b], *Phil Jackson*[c], *Brigitte Grosgogeat*[a,d,e], *Nina Attik*[a,d,*]

[a] *Université de Lyon, Université Claude Bernard Lyon 1, CNRS UMR 5615, Laboratoire des Multimatériaux et Interfaces, Villeurbanne, France*
[b] *APHP, Hôpital Rothschild, Service d'Odontologie, Paris, France*
[c] *Lucideon Inc., Penkhull, Stoke-On-Trent ST4 7LQ, UK*
[d] *Faculté d'Odontologie, Université Claude Bernard Lyon 1, Lyon, France*
[e] *Service d'Odontologie, Hospices Civils de Lyon, Lyon, France*

ARTICLE INFO

Article history:
Received 21 December 2017
Received in revised form
29 April 2018
Accepted 5 June 2018
Available online xxx

Keywords:
Bioactive glass
Sol–gel
Porosity
Surface area
Mesoporous
Network modifiers
Precursors order

ABSTRACT

Objective. The superior textural properties of sol–gel derived bioactive glasses compared to conventional melt quench glasses accounts for their accelerated bioactivity *in vitro*. Several studies have explored ways to improve the surface properties of sol–gel glasses in order to maximise their efficiency for bone and tooth regeneration. In this study, we investigated the effect of order of network modifying precursor addition on the textural properties of sol–gel derived bioactive glasses.

Methods. The effect of precursor addition order on the glass characteristics was assessed by switching the order of network modifying precursor (calcium acetate monohydrate and sodium acetate anhydrous) addition for a fixed composition of bioactive glass ($75SiO_2$:5CaO:$10Na_2O$:$10P_2O_5$).

Results. The results of this study showed that the order of precursor addition does influence the porosity of these glasses. For the glasses of a fixed composition and preparation conditions we achieved a doubling of surface area, a 1.5 times increase in pore volume and a 1.2 times decrease in pore size just by the mixing the network modifying precursors and adding them together in the sol–gel preparation.

Significance. This simple and straightforward route adaptation to the preparation of bioactive glasses would allow us to enhance the textural properties of existing and novel composition of bioactive glasses and thus accelerate their bioactivity.

* *Corresponding author at*: Université de Lyon/Université Claude Bernard Lyon 1, CNRS (UMR 5615) LMI/Faculté d'Odontologie 11, Rue Guillaume Paradin, 69372 Lyon, France.
E-mail address: nina.attik@univ-lyon1.fr (N. Attik).

https://doi.org/10.1016/j.dental.2018.06.003
0109-5641/

1. Introduction

Bioactive glasses are well known materials researched for their application in bone and dental restoration/regeneration [1–5]. Thanks to the addition of dopants such as copper, zinc, strontium and magnesium to bioactive glasses, their potential for angiogenesis [6], enhanced antibacterial effects [7] and improved bioactivity [8–11] has been unveiled. Due to their impressive bioactivity and bone bonding ability bioactive glasses are used in clinical applications as bone graft, implant coating [12,13] and recently in dentifrices such as Sensodyne® and BioMin™ to treat dentin hypersensitivity and induce remineralization of dental tissues.

The conventional synthesis of bioactive glasses (melt–quench) involves melting oxide precursors at very high temperatures followed by rapid quenching in order to obtain an amorphous matrix [14]. The other dominant synthesis technique is sol–gel which represents a bottom up approach to making these glasses involving hydrolysis and condensation reactions of glass precursors to form a 3-dimensional polymeric glass network [15]. In contrast to the melt quench technique, sol–gel synthesis encompasses various process parameters that could be modulated to change the final glass characteristics. As such, sol–gel is a relatively more complex yet versatile route of making glasses. Furthermore, sol–gel bioactive glasses have earned significant interest due to their inherent porosity and improved surface area which allows for faster ion exchange translating into heightened bioactivity in comparison to traditional melt quenched glasses [16]. Besides bioactivity associated with apatite formation and cytocompatibility, porous bioactive glasses have the potential advantage of hosting drug molecules and growth factors thereby elevating the application of these glasses for therapeutic purposes [5,17,18].

Therefore, different optimization strategies of sol–gel processes have been reported in an attempt to improve the structural and textural properties of these glasses such as varying the composition [19], type of precursors [20–22], ageing temperature [20,23,24] catalyst [25], pH [26], surfactant type [27–29] and concentration [30,31]. However to the best of our knowledge, the influence of order of network modifying precursor addition on the textural properties of sol–gel glasses has never been assessed. Therefore, this study aimed to evaluate if the porosity of a given composition of sol–gel bioactive glasses can be improved by modulating the sequence of the network modifying precursor addition during the sol–gel process. The effect of precursor addition order on the glass characteristics was assessed by switching the order of network modifying precursor addition for a fixed composition of bioactive glass. This understanding could contribute to a simple and effective way of improving the textural characteristics of such glasses.

2. Materials and methods

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%), triethyl phosphate (TEP, 99%), calcium acetate monohydrate (Ca $(CH_3COO)_2.H_2O$, 99%), sodium acetate anhydrous (CH_3COONa), ethyl alcohol (EtOH, 99.7%), triblock copolymer $EO_{20}PO_{70}EO_{20}$ (P123,Mw = 5650) and glacial acetic acid (CH_3COOH) were used as supplied from Sigma Aldrich.

2.2. Sample preparation

The Mesoporous Bioactive Glasses (MBG's) with 1.8 wt% surfactant in the composition $75SiO_2$:5CaO:$10Na_2O$:$10P_2O_5$ have been synthesized by an acid catalysed sol–gel method assisted by evaporation induced self-assembly (EISA) process. Different glasses were create based purely on varying the order of network modifying precursor (Ca or Na) addition. Each step was performed at one hour intervals. Step 1 involved dissolving 2 g of P123 surfactant in 30 g ethanol. In step 2, 37.5 mL of de-ionised water and 214.5 mL of glacial acetic acid were added to the ethanol surfactant mixture. Each glass precursor was then added to the ongoing reaction in one hour intervals (step 3) in the order (a) TEOS, TEP, calcium acetate monohydrate followed by sodium acetate for *Ca before Na sample*, (b) TEOS, TEP, sodium acetate followed by calcium acetate monohydrate for *Na before Ca sample* and (c) TEOS, TEP followed by mixtures of sodium acetate and calcium acetate monohydrate *for mixed precursor sample*. Complete calcium (*15Ca/0Na MBG*) and sodium samples (*15Na/0Ca MBG*) were also prepared to provide reference compositions. The solution gelled in about one hour after adding the last precursor and was allowed to undergo EISA at room temperature (RT) for 4 days, followed by drying at 60 °C for 2 days. The dried gels were milled down and calcined at 340 °C at a ramp rate of 1 °C/min to reach the set temperature, held for 5 h at 340 °C and finally cooled to RT in 8 h.

2.3. Sample characterization

2.3.1. XRF

The glass composition of *Ca before Na, Na before Ca* and *mixed precursor* sample after 340 °C thermal treatment was determined by semi-quantitative X-ray fluorescence (XRF) method. A small quantity of material was smeared onto a filter paper and presented to the XRF spectrometer (Panalytical Axios) and run on the preinstalled semi quantitative XRF package.

2.3.2. XRD

The glass phase was characterized with X-ray diffractometer (XRD). XRD of samples after 340 °C calcination was performed using an X-ray diffractometer (XRD, X'Pert Philips, Netherlands) with Cu Kα radiation of wavelength 1.54 Å. The scans were recorded at 30 kV, 30 mA, 2θ ranges between 5°–60° and a step size of 0.02° and 90.17 s per step.

2.3.3. ATR-FTIR

The glass network was studied using Attenuated Total Reflection Fourier Transform Infra-Red spectroscopy (ATR-FTIR) on a Safas Monaco spectrometer. The spectra were collected in a wavelength range of 340–2000 cm^{-1} at a spectral resolution of 4 cm^{-1}.

Please cite this article in press as: Fernando D, et al. The influence of precursor addition order on the porosity of sol–gel bioactive glasses. Dent Mater (2018), https://doi.org/10.1016/j.dental.2018.06.003