Tailoring the viscoelastic properties of injectable biocomposites: A spectroscopic assessment of the interactions between organic carriers and bioactive glass particles

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ABSTRACT

Injectable bioglass (BG) pastes were produced using a melt-quenched glass based on $CaO–MgO–SiO_2–Na_2O–P_2O_5–CaF_2$ and two organic carriers, namely polyethylene glycol (PEG) and glycerol (Gly). The interactions between the organic carriers and the surface of the BG particles were assessed by spectroscopic methods (Fourier Transform Infrared, Raman, as well as 29Si and 13C solid-state NMR spectroscopy) in order to understand their effects on the viscoelastic properties of the biocomposites. While pure physical interactions were detected between PEG and the surface of the BG particles, chemical bonding was observed between glycerol and BG, enhancing the network cross-linking degree. Accordingly, the BG network of Gly-BG pastes was more condensed (higher fraction of Q[3] units detected by Raman spectroscopy) in comparison to that of PEG-BG and bare BG. Such chemical interactions between the organic carrier and BG were shown to negatively affect the viscoelastic behaviour of the resulting pastes. Thus, the PEG-based biocomposite exhibited improved flowability in comparison to its analogous Gly-BG biocomposite.

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1. Introduction

Biocomposites often consist of a biocompatible polymeric matrix reinforced by an inorganic phase [1–3]. The interactions between the organic and inorganic phases in biocomposites create materials that exhibit synergistically enhanced properties as compared to their individual components. Typically, two classes of organic/inorganic composites (hybrid materials) have been defined: class I hybrids represent composites in which there is a weak interaction between the organic and the inorganic phases, such as van der Waals or hydrogen-bond forces; whereas class II hybrids consist of composites showing covalent or iono-covalent bonds between the organic and inorganic phases [4].

Injectable biocomposite pastes based on bioactive glass (BG) particles dispersed within a biocompatible (and ideally bioresorbable) organic matrix have emerged recently as an important family of filler materials for bone and tooth treatments [5]. In order to achieve an appropriate injectability, the biocomposites should exhibit tailored viscoelastic properties and ideally undergo a rheological transition from a visco-elastic fluid to a elasto-plastic solid behaviour within a certain time. Thus, appropriate visco-elastic properties allow pastes to be easily injected; whereas, their post solidification is of crucial importance to provide mechanical stability in the implanted area. It is anticipated that the composition of the pastes, and the nature of the interactions between their organic and inorganic components might have a significant impact on the rheological properties under shear, and on the structural recovering behaviour under rest conditions.

Interestingly, so far only few investigations have been focused on the effects of the organic-BG interactions on the visco-elastic properties and structural recovery of composites. The influence of the BG particle size on the dynamic rheological changes over time (viscosity, storage and loss moduli) was recently investigated [6–8]. The main efforts aimed at tailoring the compositions and the textural properties of BG-organic carriers in order to improve the biomineralisation kinetics, i.e., the deposition of a surface apatite layer [9–12].

In the present work we report on the preparation of novel injectable biocomposites based on the melt-quenched glass $CaO–MgO–SiO_2–Na_2O–P_2O_5–CaF_2$, which was recently used in clinical studies concerning healing of bone defects [13,14]. The specific aim of this study is to

investigate how the interactions between the organic phase, i.e. glycerol (Gly) or polyethylene glycol (PEG), and the surface of the BG particles affect the rheological properties and the structural recover under small oscillatory deformations.

2. Materials and methods

2.1. Preparation of the biocomposites

A bioactive glass (BG) with the nominal composition (mol%) 4.33Na_2O–30.30CaO–12.99MgO–45.45 SiO_2–2.60P_2O_5–4.33CaF_2 was produced from powders of technical grade of silicon oxide (purity 99.5%) and calcium carbonate (99.5%) and of reagent grade 4$MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, Na_2CO_3, CaF_2, and $NH_4H_2PO_4$. Thus, glass-frits were prepared by quenching the melt into cold water as described elsewhere [13–15]. The frits were dried and then milled in a high speed porcelain mill to obtain BG powders with mean particle sizes within the range of 11–14 μm, as determined by light scattering technique, Coulter LS 230, UK, Fraunhofer optical model. Polyethylene glycol 400 (Fluka) or polyol Glycerol (Fluka) were used as organic carriers for the BG particles. The components were premixed in small plastic boxes using a metallic spatula before feeding the mixtures in a laboratory mixer (IKA RW 47 Digital Pilot-Process Mixer, Cole Parmer) at room temperature and 30 rpm. Table 1 summarizes the composition of the prepared pastes.

2.2. Materials characterization

Scanning electron microscopy (SEM) analysis was performed on a Philips XL30 FEG, Netherlands with an acceleration voltage of 10–15 kV. FTIR spectra were collected with a VARIAN 670IR spectrophotometer using attenuated total reflection (ATR) mode.

All solid-state NMR spectra were recorded using a Bruker Avance spectrometer operating at 400 MHz proton Larmor frequency. Magic-angle spinning (MAS) of 11 kHz was pursued using 4 mm rotors. Acquisition times amounted to 15 ms upon use of 76 kHz SPINAL-64 decoupling. Recycle delays amounted to 2.5 s and 15 s for 13C and 29Si spectra, respectively. 1H, 13C, and 29Si hard pulses were applied at 76 kHz (3.3 μs), 42 kHz (6 μs), and 50 kHz (5 μs). CP conditions included a 90–100% ramp on 13C at a B_1 field of 37 kHz and 53 kHz on 1H for a duration of 1 ms. 1H hard pulses were applied at 76 kHz B_1. Temperature was maintained to approximately 10 °C.

The spectra were recorded using total acquisition times of 2 and 8 h for single-pulse (HPDEC) 29Si experiments (without and with PEG, respectively), 24 and 36 h for carbon CP spectra (without and with PEG, respectively), and 8 and 24 h for carbon HPDEC spectra (without and with PEG, respectively).

The rheological properties of the composites were conducted in oscillatory mode, i.e. frequency sweep at a constant strain amplitude of 0.1 [−] (TA Instruments AR-G2 rheometer, plate-plate geometry with diameter 25 mm and gap of 200 μm). The as-prepared pastes were soft enough to be molded and extruded with a syringe.

3. Results and discussion

The morphological features of the as-obtained CaO–MgO–SiO_2–B_2O_3–Na_2O–CaF_2 glass particles are shown in Fig. 1. The micrographs show that the main fraction consists of particles with sizes around 11–14 μm with conchoidal and subconchoidal fracture surfaces. These features are commonly observed in comminuted glassy materials.
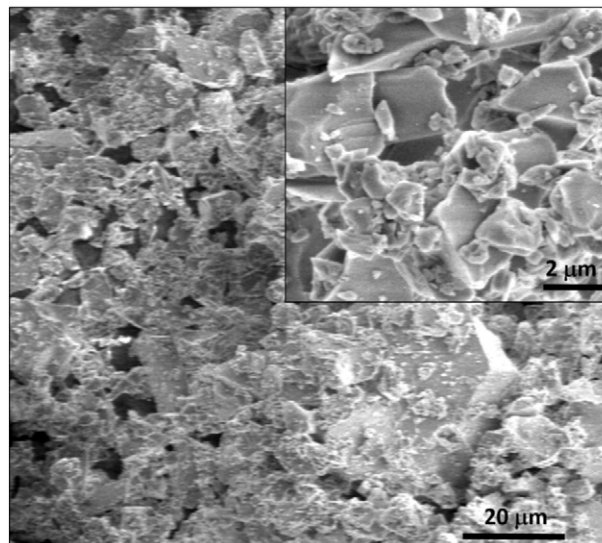

Fig. 1. SEM micrograph of the as-synthesized BG particles.

The structural silicate network features of the as-synthesized BG particles and of the organic-BG composites assessed by Raman and MAS-NMR spectroscopy are displayed in Fig. 2. The 29Si MAS-NMR spectra of the BG particles and the PEG-BG paste are shown in Fig. 2a, red and blue lines, respectively. Both spectra are identical, revealing the dominance of the Q [2] structural units giving a signal with a chemical shift of −84 ppm. It was not possible to analyze the paste containing glycerol MAS-NMR spectroscopy, as its high liquid content did not allow for spinning the sample. Consequently, this sample was studied only by Raman spectroscopy. The Raman spectrum of the as-synthesized BG particles (Fig. 2b, BG) is in good agreement with the NMR results. It shows that the network is mostly dominated by Q [2] units, which exhibit a strong band at 950 cm^{-1}. The presence of the absorption bands corresponding to Q [3] (at 1040 cm^{-1}) and Q [1] (882 cm^{-1}) were also evident, although with low intensity [16]. Interestingly, the Q [2] band at 950 cm^{-1} disappeared upon mixing the BG powder with glycerol in the Gly-BG biocomposite (Fig. 2b, Gly-BG) and the intensity of the band at 1050 cm^{-1} assigned to Q [3] species was significantly enhanced in comparison to that observed for the as-prepared BG.

The interactions between the organic carriers and the BG particles in the as-prepared pastes were also assessed by FTIR spectroscopy (Fig. 3). The spectrum of PEG-BG (Fig. 3b) reveals the same spectral features of pure BG and PEG [17].

Pure glycerol exhibits two characteristic peaks at 1112 and 1038 cm^{-1} (Fig. 3a), which are characteristic of the C—OH stretching vibrations (secondary and primary alcohols, respectively) [18]. However, for the as-prepared Gly-BG paste, these absorptions bands were shifted towards lower wavenumbers (i.e., 1104 and 1027 cm^{-1}, respectively, Fig. 3a) and were assigned to C–O–R stretching [19], indicating that glycerol is chemically bonded to the surface of the BG particles. The obtained results are in agreement with the Raman spectroscopy data, confirming that glycerol chemically interacts with the surface of BG particles through C—O—Si bounds. This fact consequently reduces the fraction of the Q [2] units in the BG and is also likely to alter its demonstrated bioactivity.

Additionally, 13C MAS-NMR spectroscopy using cross-polarization (CP) from 1H (Fig. 4a) and using single-pulse excitation (Fig. 4b) was performed for BG and PEG-BG samples. CP addresses only the rigid components of the sample. Apart from a minimal, unspecific background signal, no rigid carbon spins are expected in either sample. In the presence of PEG, however, some additional contribution from a carbon- and proton-containing subset of temporarily adhered molecules is observed,

Table 1
Formulation of the investigated pastes (wt.%).

Paste	BG	PEG 400	Glycerol
Gly-BG	72.5	–	27.5
PEG-BG	77.0	23.0	–