



# Silica phase formed by sol–gel reaction in the nano- and micro-pores of a polymer hydrogel



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## ABSTRACT

Hybrid composites consisting in a hydrogel matrix with silica micro- and nano-particle reinforcement were produced and characterized. The strategy proposed here to obtain them consisted in a two-step synthesis being the polymer network formation the first step. Porous poly(hydroxyethyl acrylate) hydrogel network was produced by radical polymerization of the monomer diluted in different amounts of ethanol. Polymeric microstructure drives the absorption of a silica precursor solution and the further distribution of the inorganic phase that is formed *in situ*. A fraction of the resulting silica phase occupies the pores and the other part is in the form of nanoparticles dispersed in the polymer phase. Composites with silica content up to ~60% by weight were obtained. Silica phase is continuous and samples maintain their integrity after eliminating the organic phase by pyrolysis. Dependence of hybrid microstructure in compliance, water sorption capacity, bioactivity and the effect of silica content in polymer segmental mobility were assessed.

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## 1. Introduction

Bioactive glasses have shown the ability to bond to bone and other host tissues due to their solubility in physiological conditions, delivering silicon, calcium and phosphorous ions that induce the nucleation of natural hydroxyapatite, the mineral component of bone. Bioactive glasses used in clinics are produced in molten state at high temperatures. Varying compositions of SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, CaO and Na<sub>2</sub>O have been explored by *in vitro* and *in vivo* experiments. When high temperature treatments are used during SiO<sub>2</sub> glass production, a harder solubilization occurs because of the presence of stable covalent bonds in the SiO<sub>4</sub> tetrahedral structure. The presence of CaO disrupting the regular silica structure by means of ionic bonds produces a fraction of oxygen atoms not bonded covalently. It is recognized that glasses with more than 50% SiO<sub>2</sub> are not bioactive [1,2]. Nevertheless, when the bioactive glass is produced by sol–gel reaction at low temperatures, the irregular structure of the formed network expands the composition interval and it has been found that glasses with up to 80% SiO<sub>2</sub> are soluble in physiological fluids and are bioactive [1]. Additionally, pure silica sol–gel

glasses have been found to be bioactive when were tested by *in vitro* assays in simulated body fluids [3–5].

Due to the mechanical properties required, polymer-bioactive glass hybrids have been extensively investigated for bone tissue engineering applications. Obviously the presence of the polymer prevents subjecting the glasses to high temperature of sintering and sol–gel techniques have been developed. Methods for obtaining polymer/silica nanocomposites include: (a) mixing silica nanoparticles and the polymer [6–10], (b) sol–gel processes in the presence of a solution of the organic polymer [6,9,11–14], and (c) *in situ* sol–gel process and simultaneous polymerization [8,10,15]. Furthermore introduction of functional groups along the backbone of the polymer allows the formation of covalent bonds between organic and inorganic phases during sol–gel reaction [13,16,17]. Polymer–silica hybrids have been obtained by using homopolymer and copolymer networks based in hydroxyethyl methacrylate (HEMA) and hydroxyethyl acrylate (HEA) through simultaneous polymerization and silica network sol–gel synthesis [8–10,15,18,19]. Normally, polymerization of HEMA or HEA is slower than sol–gel reaction and thus, silica network formation takes place in the presence of the monomers which act as a template determining nano-porous structure of silica [20]. Nanocomposites with silica contents up to 30% by weight were produced by simultaneous polymerization of both phases. When the contents of the inorganic phase were higher than 15%, percolation of this phase produced hybrids with co-continuous organic–inorganic phases [20,21].

In this work, we analyze a different approach for the formation of the hybrid. Sol–gel reaction is performed with silica precursor absorbed

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in an already formed polymer network. We explore the occurrence of silica inside the macropores, which were produced in the polymer matrix using solid-liquid phase separation during polymerization [22–24]. We will show that silica produced in this way is soluble in SBF and induce formation of a biomimetic hydroxyapatite layer.

## 2. Materials and methods

### 2.1. Hydrogels and hybrid synthesis films

To obtain bulk PHEA films, 2-hydroxyethylacrylate (HEA) 96%, from Aldrich, was polymerized at room temperature under UV radiation for 6 h using as photo initiator, 0.5 wt.% of benzoin 98%, from Scharlau; and as cross-linker, 1% of ethyleneglycol dimethylacrylate (EGDMA) 98%, from Aldrich. In order to have porous PHEA films, solutions of HEA with 20%, 30%, 40% and 50% weight fractions of ethanol synthesis grade, from Scharlau, were prepared. The hydrogel sheets were produced by introducing polymeric solutions in glass molds. Assembled molds were exposed to a post-curing treatment at 90 °C for 24 h. After polymerization, samples were washed with purified water for 24 h at 60–70 °C (changing water every 8 h), dried at room temperature for 24 h and then in a vacuum desiccator for 24 additional hours. Samples were named as PHEAXX, being “XX” the weight fraction of ethanol in the monomer solution.

Hybrids were prepared by means of sol-gel reaction using TEOS 98%, from Aldrich, as silica precursor and hydrochloric acid (HCl) 10%, as catalyzer. Solution consisted in TEOS/water/ethanol/HCl mixture with molar ratio 1/15/1/0.0185. First, TEOS was mixed with water and ethanol under continuous stirring for 5 min, then the diluted HCl was added and the solution was stirred 60 min more. Then, porous or bulk PHEA were immersed in this solution and allowed to swell in an oven at 40 °C, the time to assure constant weight, (~24 h). Simultaneously, during this period the hydrolysis of silica precursor takes place. At the end of that time, hybrid samples were washed with water/ethanol mixtures (15:1) and dried in vacuum at 40 °C to constant weight. Finally, the composites were washed by immersion in purified water until there was no change in the pH of water used. The hybrid samples were named as PHEAXXSI, where “XX” has the same meaning as in pure PHEA samples and “SI” specifies the presence of silica in the material.

### 2.2. Characterization

Most of the assays were done in five replicas, except DSC scans that were made in two replicas and mechanical and bioactivity tests that were made in triplicate.

#### 2.2.1. Hybrid composition

Silica content of the hybrid composites was determined by weighing the dry samples before and after sol-gel reaction. Pyrolysis residue was determined in an electrical tubular oven (Gallur, Spain) subjecting the samples to 850 °C for 2 h in oxygen atmosphere. Thermogravimetric analyses (TGA) were performed in nitrogen atmosphere, during a heating scan at 10 °C/min up to 850 °C in a SDT Q600 analyzer (TA Instruments, United States).

#### 2.2.2. Water sorption

Equilibrium water sorption was measured by immersing the dry samples in purified water at 37 °C. The effect of silica hydrolysis taking place during water sorption experiments was considered negligible due to the previous sol-gel reaction conditions at low water/TEOS ratio and long hydrolysis and condensation periods. Sorption kinetics was measured by weighing samples at 1, 2, 8, 16 and 24 h (time at which all samples of the diverse compositions of PHEA attained an equilibrium plateau). Computed equilibrium water content, EWC, was calculated as the weight of water (g) absorbed at 24 h per 100 g of dry sample.

#### 2.2.3. Scanning electronic microscopy (SEM)

A Scanning Electron Microscope Jeol JSM-5410 equipped with a cryounit Oxford CT 1500 using the low-temperature freeze drying technique (cryoSEM), was used to examine surface and cross-section of samples which were previously swollen in water by 24 h in order to open the pores of hydrogels and composites. Water was sublimated at –90 °C for 90 min. Samples were cryo-fractured inside the microscope and sputtered with a gold layer. Micrographs were taken at an accelerating voltage of 20 kV. Homogeneity of silica phase distribution was assessed both at the surface and cross-section of the samples by Energy Dispersive X-ray Spectroscopy, EDS (from Oxford Instruments). Samples were previously sputter-coated with carbon using an acceleration voltage of 10 kV and a distance of 15 mm. Silica was used as standard.

#### 2.2.4. Atomic force microscopy (AFM)

AFM was performed in a NanoScope IIIa from Digital Instruments, operating in tapping mode in air. Si-cantilevers from Nanoworld were used with a constant force of 2.8 N/m and a nominal resonance frequency of 92–95 kHz. The phase signal was set to zero at the frequency of resonance of the tip. The tapping frequency was 5–10% lower than the frequency of resonance. Drive amplitude was 3.0–4.0 V and the amplitude set point 2.7–3.8 V.

#### 2.2.5. Fourier transformed infrared spectroscopy (FTIR)

FTIR spectra were scanned between 600 and 4000  $\text{cm}^{-1}$  with a Nexus Spectrometer (Nicolet Instruments LTD, Warwick, UK) at room temperature using Attenuated Total Reflectance technique, ATR (for soft PHEA films) or Smart Diffuse Reflectance technique, SDR (for hybrids). The recorded spectra of each sample are the average of 64 scans. Silica gel 0.06–0.2 mm, from Scharlau was used as a reference standard.

#### 2.2.6. Differential scanning calorimetry (DSC)

DSC heating and cooling scans were performed using sample weights ranged between 5 and 10 mg under dry nitrogen atmosphere in a Mettler Toledo 823e DSC, at a scan rate of 10 °C/min. Experiments were carried out for dry and swollen samples. The glass transition temperature,  $T_g$ , and the specific heat capacity increment at the glass transition per gram of polymer,  $\Delta c_p(T_g)/W_{\text{PHEA}}$ , were determined in DSC of dry samples, while the fraction of crystallizable water was calculated in swollen ones. Crystallizable water in the samples was calibrated with the average melting heat found for samples of pure water.

#### 2.2.7. Mechanical testing

**2.2.7.1. Indentation test.** Mechanical tests were performed at room temperature using dry samples (~5 mm × 6 mm × 1 mm) in a Seiko Extar TMA 7s6000 (Seiko Instruments) in indentation mode. Ramp forces at a rate of 0.005–0.05 N/min for PHEA films and 0.5–2.0 N/min for hybrids, with a 0.785 mm<sup>2</sup> flat ended circular indenter, were applied to reach a penetration of at least 45  $\mu\text{m}$  in each sample. Poisson coefficient,  $\nu$ , as determined from the shape of prismatic samples during a tensile experiment. By using a finite element simulation and assuming isotropic deformation of the cross section of the samples, an average value of  $\nu = 0.4$  was found. This value was used in the calculation of the compliance from indentation force-penetration curves.

**2.2.7.2. Dynamic mechanical analysis (DMA).** DMA was performed in a DMS210 Seiko Analyzer in tension mode, at 1 Hz, using dry prismatic samples of ~16 mm × 6 mm × 1.3 mm of PHEA0SI. The thermal history of the experiment included heating at 1 °C/min between 25 and 120 °C, followed by an isotherm of 20 min, and a cooling scan at 1 °C/min to 25 °C.

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