

MULTISCALE VISCOELASTIC INVESTIGATION OF SILICA-CALCIUM-PHOSPHATE SOL-GEL MATERIALS

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Received: 13.5.2015, Final version: 3.8.2015

ABSTRACT:

The sol-gel transition of homogeneous biocomposites synthesized using tetraethyl-orthosilicate alkoxide, calcium nitrate tetrahydrate and di-ammonium hydrogen phosphate salts as reagents are investigated at the macroscopic scale by small amplitude oscillatory shear measurements and probed locally by passive microrheology at 37 °C. Structural evolutions during the sol-gel transition are studied by using Fourier Transform Infrared (FT-IR) analysis. The Young's modulus of the aged gels is measured as a function of time, at room temperature. Moreover the materials are dried, thermally treated and characterized by laser scattering analysis and X-ray diffraction to obtain the particle size distribution and crystallite size respectively and to observe the morphology by Scanning Electron Microscopy.

KEY WORDS:

Gels, sol-gel transition, microrheology, compression, FTIR, SEM

1 INTRODUCTION

The discovery of the first artificial bioactive material [1] has given rise to new strategies in clinical bone repair and replacement, providing new and hopeful possibilities for materials science. Bioactive glasses are materials that react chemically with physiological environments being able to form biomimetic apatite similar to the inorganic component of bones [2]. The ability of non-aqueous sol-gel chemistry to manipulate the structure at the molecular level enables an interesting approach for a wide range of practical applications. In particular, the gel strength of the silica matrix have been modulated leading to the development of new materials with special properties such as biosensors, bioreactors [3], encapsulation of biospecies [4, 5], bioactive glass microspheres [6], silica nanotubes functionalized with different drugs [7], coatings to improve the mechanical properties and to protect the material surfaces [8], hybrid organic-inorganic materials [9]. The control of product purity, improvement of chemical homogeneity, reduction of synthesis temperature and

easy introduction of doping elements are some of the advantages of a sol-gel-derived process over a classic melting-derived route [10]. Tetraethyl orthosilicate alkoxide (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$) is one of the common sol-gel precursors for silicon oxide, being immiscible in water so that a common solvent, usually the parent alcohol ethanol, is often used. The oxo-metallic network progressively grows leading to the formation of oligomers, oxopolymers, colloids (sols) and a solid phase (gel). These reactions can be described as SN_2 nucleophilic substitutions and the chemical reactivity of metal alkoxides toward hydrolysis and condensation depends on the electro negativity of the metal ion and the ability to increase its coordination number [11]. Also it is well known that the silica particles in aqueous medium possess surface charge, where the particles are stabilized predominantly by electrostatic repulsion since the thickness of steric barrier is much smaller than the range of the electrostatic repulsion [12].

Alternatively procedure of increasing the surface area of glasses can be induced by increasing the silica content in matrix, also considered to enhance the bio-

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4 CONCLUSION

Structural evolution of silica-calcium-phosphate sol-gel materials were investigated using macroscopic shear rheology, passive microrheology, uniaxial compression test, laser scattering analysis, Fourier Transform Infrared Spectroscopy and X-ray diffraction. The kinetics and mechanism of gelation was analyzed for two initial sol compositions. The formation of weakly branched structures in high acid conditions and gelation was probed by small amplitude shear oscillatory measurements and confirmed by decrease in intensity of the asymmetric stretching vibration bands of Si-O-Si species with increasing the aging time on FT-IR spectra. It was found that viscoelastic moduli are higher for the gel with the highest content of initial precursor TEOS corresponding to the formation of porous network of aggregated silica particles. The complex structures of pores containing the added salts (calcium and phosphorous) and therefore heterogeneity were probed by passive microrheology. Moreover the presence of these salts was detected on FT-IR spectra.

The time evolution of the rigidity modulus computed from the Young's modulus measured by uniaxial compression with the hypothesis of an incompressible material is similar to time evolution of shear viscoelastic moduli. The equilibrium values of rigidity modulus and elastic modulus are in a good agreement taking into account the difference of volume in both experiments. From XRD diffraction patterns, nature and size of crystalline phases for the heat treated gels were determined. It was shown that the lowest silica content sample had the best influence in obtaining the crystalline phase corresponding to the calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$), the desired component for the bone recovery. The crystallite sizes of the particles are estimated to be in the range of 14–17 nm. From SEM analysis, it was found that frozen gels are composed of hexagonal plates and spheres with a quantity that decreases by increasing the concentration of silica.

ACKNOWLEDGEMENTS

This research was accomplished in the framework PNII IDEI - PCCE 101/2008 PROJECT granted by the Romanian National University Research Council-CNCSIS. F. Taloş author wishes to thank for the financial support provided from programs co-financed by the Sectoral Operational Programme Human Resources Development POSDRU/88/1.5/S/60185-Innovative Doctoral Studies in a Knowledge Based Society.

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