SIZEMAT2 – September 19 – 21, 2010, Nessebar, Bulgaria
Topic D. Biology-Related Materials. Biomaterials for Bone Implants

Calcium Phosphate Formation in Poly(methacrylic acid)-Polysulfobetaine Double Networks

M. Golyakova[1], E.Vassileva[1], D. Rabadjieva[2], S. Tepavitcharova[2]

[1] Laboratory on Structure and Properties of Polymers, Faculty of Chemistry, University of Sofia, Bulgaria. *E-mail:* maria_st_g@abv.bg
[2] Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

Double networks (DN) are a specific type of interpenetrating polymer networks that consists in a polyelectrolyte network with high crosslinking density (high density single network, HDSN) which is interlaced with a loose crosslinked network of a neutral polymer (low density single network, LDSN) [1]. This structure defines a very good mechanical performance of DN hydrogels – property which is a serious shortcoming in relation to hydrogels applications. Recently, we have observed a grain-like phase-separated morphology of DN made by polyacrylamide and polysulfobetaine (PSB) with grain size in the nanometer range which exact value strongly depended on DN composition [2]. In the present study we aim to explore this specific DN morphology in order to induce crystallization of calcium phosphates in the nanosized grains and to control this process via DN composition. The components of the new DN were chosen because poly(methacrylic acid) (PMAA), in the role of HDSN, is a polyelectrolyte that has many pending carboxylic groups (known to be nucleating sites for calcium phosphate crystallization) while polysulfobetaine, in the role of LDSN, is a neutral polymer with the very specific property to swell better in salty solutions than in pure water (that is the so called antipolyelectrolyte effect).

Three PMAA films have been synthesized differing in their crosslinking densities and these were further swelled into either 0.5 M or 1 M sulfobetaine solutions containing also small quantities of crosslinking agent and initiator (for both networks N,N'-methylene-bis-acrylamide was used as a crosslinking agent). Then the PSB network was obtained *in situ* after heating the samples at 60^{o}C for few hours. The microhardness of thus obtained films was measured and their swelling kinetics in both pure water and 0.15 M NaCl was determined. The elastic modulus of the obtained hydrogels was obtained by using the Hertz's theory. The DN samples were used for in situ formation of calcium phosphates by using two alternative ways, namely, by swelling into simulated body fluids and by the sequential diffusion of HPO_4^- and Ca^{2+} ions. In both cases calcium phosphates were obtained as evidenced by scanning electron microscopy and X-ray diffraction.

References:

[1] Jian Ping Gong, Yoshinori Katsuyama, Takayuki Kurokawa, Yoshihito Osada, "Double-Network Hydrogels with Extremely High Mechanical Strength", *Advanced Materials* **15**(14), 1155-1158 (2003).

[2] George Georgiev, Konstantina Dyankova, Elena Vassileva, Klaus Friedrich "Synthesis and some Mechanical Properties of Polysulfobetaine–Polyacrylamide Double Networks", *e-polymers* **054,** 2006

Acknowledgements: This work is financially supported by the Bulgarian Ministry of Education Youth and Science under Projects **DTK 02-70/2009** and **DO-02-82/2008**.