Structure and Mechanical Properties of Hydroxyapatite Nanoparticle Compacts

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Statement of Purpose: The vast majority of hydroxyapatite (HA) based bioceramic materials is prepared at high sintering temperatures to attain suitable mechanical properties. The sintering process usually results in a material which is compositionally and morphologically different from nonstoichiometric nanocrystalline HA phase of hard tissue. At the same time, HA particulates used as precursors for ceramic manufacturing are often very similar to the natural HA nanocrystals. It has been shown that synthetic nanoparticle HA (nanoHA) based materials improve the biological response in vitro and in vivo, but the information on mechanical properties and stability of those materials is scarce. The present study was focused on the analysis of the microstructure evolution and mechanical properties of the solution precipitated porous nanoHA compacts subjected to mild thermal treatment.

Methods: HA nanoparticles were synthesized by chemical precipitation using $Ca(OH)_2$ and H_3PO_4 in presence of NH_4OH and the temperature of the solution in the range of 20 – 100 ^oC. $Mg(NO_3)_2$ served as the source of Mg for Ca substitution in some experiments. The amounts of the chemicals were chosen to obtain the (Ca+Mg)/P ratio of 1.67 in the reaction product. The reaction was performed in a dry box with CO_2 supply to control the amount of CO_3^{2-} ions in the product. The precipitated HA nanoparticles were washed in deionized water, placed in cylindrical Teflon forms, and dried at room temperature. The structure and surface morphology of the resulting solid nanoHA compacts were studied before and after the annealing up to 800 ^oC using X-ray diffraction, FT-IR, SEM, and AFM. The nanoparticle size was determined from the XRD data using the Lorentzian fitting of (002), (210) and (211) peaks and Scherrer equation. Home-made load cell with a piezoelectric force sensor was used to measure the compressive strength of the compacts, and Nanoindenter XP (MTS Systems) was used to determine the Young's modulus and hardness. A Berkovich diamond indenter with total included angle of 142.3° was used for all nanoindentation measurements. A 10 seconds hold time at maximum load and 50 second at 10% of maximum load during unloading was used in order to minimize thermal drift. The data set was processed using proprietary software to produce load-displacement curves and the mechanical properties were calculated using the Oliver and Pharr method. To evaluate the effect of simulated body fluids (SBF) on the stability of the mechanical properties, the nanoHA compacts were kept in Hank's balanced salt solution and Dulbecco's phosphate buffered saline without or with acidic buffers (pH~5-6.5) at 37^oC for the periods up to 30 days.

Results / Discussion: The precipitated compacts had apparent density 1.10 – 1.50 g/cm^3 (porosity 50 – 65 %). According to the XRD results, precipitated ceramic nanoparticles represented a single phase hydroxyapatite (Fig.1) with the mean particle size in the range of 10 – 80 nm depending on the reaction temperature and Mg concentration (2 – 10 %at.). The HA structure remained unchanged after annealing up to 600 ^oC for 2 hours, and the particle size increased only slightly. There was no evidence of secondary phases in the material in any experiment. The XRD results were supported by FT-IR spectroscopy data.

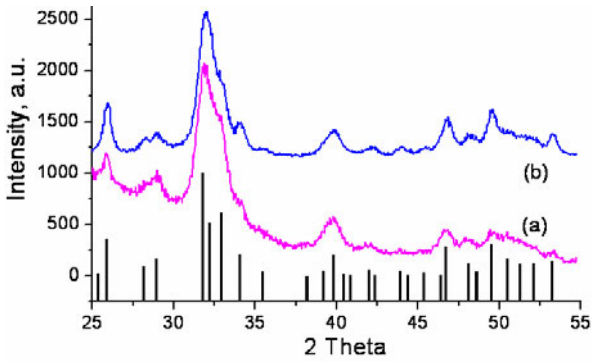

Figure 1. XRD patterns of nanoHA compacts: (a) as prepared, (b) annealed at 600 ^oC. The diffraction data for HA from JSPDC 74-0566 are given as a reference.

Compression strength was measured in the range of 1.4 – 8 MPa, and 30 – 45 MPa for unannealed and 600 ^oC (50% porosity) compacts, respectively. The Young's modulus and hardness of unannealed nanoHA compacts with 50% porosity were 6.8±0.68 GPa and 206±21 MPa, respectively. The compacts annealed at 600 ^oC had Young's modulus of 12.4±1.7 GPa and hardness of 420±0.12 MPa, as well as better stability in SBF (Fig.2). Annealed compacts with 65% porosity had the mechanical properties similar to unannealed compacts with 50% porosity.

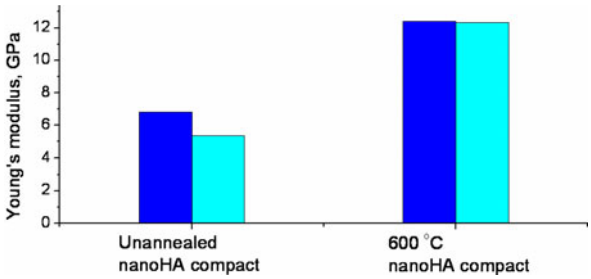

Figure 2. Young's modulus of nanoHA compacts before (dark columns) and after SBF exposure (light columns).

Conclusions: Carbonated and Mg-substituted low-density low-temperature HA nanoparticle compacts exhibit the mechanical properties similar to porous high-temperature ceramics. The compacts show good stability in SBF at 37 ^oC in static conditions for at least 1 month.

References: 1. Tadic et al, Biomat. 2003, 24:4565;
2. Donadel et al, J Am Ceram Soc. 2005, 88:2230;
3. Rodriguez-Lorenzo et al, J Biomed Mater Res. 2002, 60:159.