The Relationship between the Ceramic Nanoparticle Loading and Mechanical Properties of Collagen/Hydroxyapatite Nanoparticle Composites

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Statement of Purpose: The growing need for resorbable bone substitutes and scaffolds require the development of materials that are both resorbable and bioactive, while structurally and mechanically similar to bone and stable for certain periods of time. Bone consists from up to 70% of mostly nanocrystalline hydroxyapatite (HA), and the rest is mostly collagen, and one can suggest that synthetic nanoHA/collagen composites could potentially be chemically and structurally the closest materials to resemble a low level of the bone microarchitecture. A number of researchers have prepared different HA/collagen composites [1]. However, the data on the mechanical properties and property/structure relationships of HA/collagen composites are still scarce. In this study, we report the results of an investigation of the structure, surface morphology, and elastic properties of HA/collagen composites with 0 to 100 % HA nanoparticle loading.

Methods: HA nanoparticles were prepared by wet precipitation at pH ~10 using $Ca(OH)_2$ and H_3PO_4. The HA nanoparticles were washed in deionized water and methanol, and finally redispersed in Hexafluoropropanol (HFP). The HA dispersions were mixed with collagen solution in HFP in different ratios. The HA/collagen composite sheets with the thickness in the range of 50 – 150 μm were prepared by placing a few drops of the mixture onto a glass slide. The composites were characterized using X-ray diffraction, FT-IR, SEM, TEM, and AFM. The nanoparticle size was determined from the XRD data and TEM images. Nanoindenter XP (MTS Systems) with a Berkovich diamond indenter was used to determine the Young's modulus and hardness. The measured data sets were processed to produce load-displacement curves and the mechanical properties were calculated using the Oliver and Pharr method.

Results / Discussion: The HA/collagen layers develop specific surface morphology that strongly depends on the amount of the HA phase. Collagen fibrils are seen in AFM images of pure collagen layers, whereas the material with 80/20 HA/collagen ratio exhibits a uniform nodular texture. The size of nodules is 200 – 500 nm that is much larger than the mean size of HA nanoparticles. The samples with 20 % – 60 % HA content display intermediate surface morphologies as demonstrated in Fig.1a for the material with 20/80 ratio. Some areas in this image show the nodules as well as the surface features with the parallel alignment that can be related to the competing self-organization processes of HA particles and collagen during the evaporation of the solvent as seen in the TEM image (Fig.1b). The Young's modulus of the composite samples below 60/40 HA/collagen ratio resemble the data obtained by Tai et al [2] in a model study of cortical bone with different mineral content. The maximum values of 10.3 ± 2.5 GPa and 290 ± 70 MPa for the Young's modulus and hardness, respectively, were obtained for uncross-linked 45/55 HA/collagen bulk sample (Fig.2). A reduction in the values of Young's modulus at higher HA content can be related to the increased effect of the HA particle/particle interaction in the composite with a low polymer content.

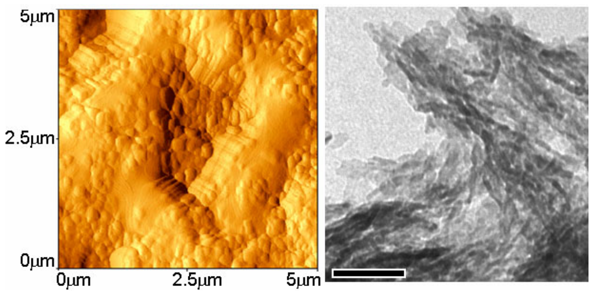

Figure 1. AFM (a) and TEM (b) images of 20/80 HA/ /Collagen composite. Scale bar in TEM image is 50 nm.

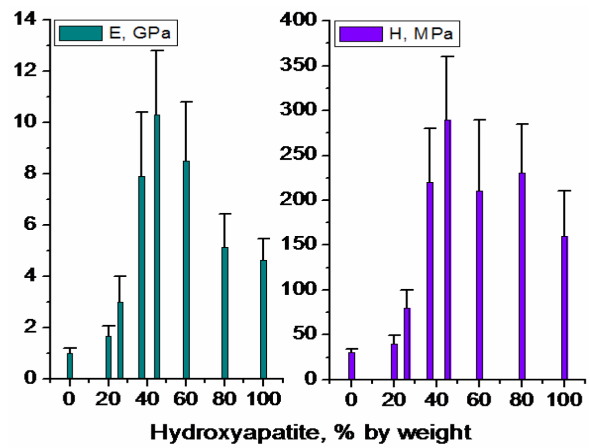

Figure 2. Young's moduli (E) and hardness (H) of HA/collagen composites.

Conclusions: Composite materials with various HA/collagen ratios can be easily prepared from the dispersions of HA nanoparticles and collagen in HFP. The surface morphology and mechanical properties of such composites are determined by the HA/collagen ratio. The Young's modulus and hardness of these composite materials seem to achieve maximum values for 40% - 55% HA content by weight.

References: 1. Itoh S, Kikuchi M, Koyama Y, Takakuda K, Shinomiya K, Tanaka J. Biomat 2002;23:3919; 2. Tai K, Qi HJ, Ortiz C, J Mater Sci Mater Med 2005;16:947.