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COMPUTATIONAL MODELING OF MECHANICAL PROPERTIES OF CARBON NANOTUBE-REINFORCED HYDROXYAPATITE NANOCOMPOSITE BY MEANS OF MECHANICAL NANOMETROLOGY

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Abstract – In this study, a classical molecular dynamics (MD) simulation of the stress–strain properties of the nanocomposite made from HAP and a single-walled carbon nanotube and a double-walled carbon nanotube is presented to validate the experimentally measured mechanical properties of hydroxyapatite (HAP) -based composites via computational modeling techniques. The Young modulus and the yield points of both pure and nanotube-reinforced HAP are determined and the results are exploited in HAP-based bioceramics for use of medical nanotechnology as bone-replacing tissue engineering.

Keywords: Mechanical Nanometrology, Hydroxyapatite, Nanotubes, MD Simulation, Yield Point.

1. INTRODUCTION

Nanometrology is related to measurement techniques determining the properties of materials in the nanoscale level. The improvement of traceable and multifunctional instrumentation, standardization methods and computational modeling tools are emerging issues for nanometrology [1]. Mechanical nanometrology is one of the most advanced disciplines of nanometrology and is associated with the determination of the mechanical properties (strength, toughness, surface adhesion, creep) of nanostructures and biological materials. The most widely used methods include nanoindentation, nanoscretch, atomic force microscopy (AFM) and scanning probe microscopy (SPM). The evaluation of nanomechanical properties and the determination of stress-strain, time-dependent behavior and viscous response of materials (metals, polymers, ceramics, composites and biological materials), through computational modeling, contribute to the estimation of manufacturing processes resulting in standardization and optimization [2]. Modeling and simulation are intrinsic elements of measurement techniques and are expected to play a significant role in process and nanotechnology-based product design. Computational simulation tools are needed to describe the connection between mechanical measurements and related material properties [27]. Computational modeling methods assist in designing new modes of measurements by giving an insight into background physical processes. Simulation and modeling efforts include largescale finite element methods, classical atomistic simulations (Monte Carlo Methods, Molecular Dynamics), ab initio quantum mechanical calculations and density functional theory, to mention the most frequently used techniques for predicting nanoparticle properties.

Hydroxyapatite (HAP) molecule, $Ca_{10}(PO4)_6(OH)_2$, is one of the most important and stable calcium phosphate bioceramic minerals and forms the primary structural component of the bone, and materials for bone implant [3]. Research into the mechanical properties of bioceramics forms an active area as most bioceramics are employed for the repair and reconstruction of degenerated or damaged segments of human bones. Despite these excellent properties, HAP is mechanically quite weak and brittle, having a rather low tensile, compressive and flexural strength, which severely limits its use in applications in which load bearing is important [4, 5]. Several methodologies have been proposed to offset these mechanical weaknesses. Among these, the suggestion to reinforce HAP with carbon nanotubes is particularly attractive since it has also been shown experimentally that tissue engineering scaffolds made of carbon nanotubes that are chemically functionalized can promote the proliferation of the bone-forming cells, namely the osteoblasts [6]. Furthermore, recently a combination of HAP and multi-walled carbon nanotubes, produced via plasma spaying of the nanotubes into the HAP matrix without the use of any functionalizing material has been synthesised to be used for coating the orthopedic bioimplant material [7-9].

Several researcher have attempted to synthesize pure HAP and CNT/HAP composites and to measure their mechanical properties experimentally [10-23]. To validate the experimentally measured mechanical properties of HAP via computational modeling techniques, we introduce a classical molecular dynamics (MD) simulation of the stress–strain properties of the nanocomposite made from hydroxyapatite (HAP) and a single-walled carbon nanotube and a double-walled carbon nanotube. The successful use of this nanocomposite in biomedical applications requires a good understanding of its response characteristics, at nano-scales, to applied stresses and its stress–strain behaviour under different loading conditions. In this work, we determine the Young modulus and the yield points of both pure and nanotube-reinforced HAP. Our results are in agreement with several experimental observations. It is seen that while there is no enhancement of the magnitude of the Young modulus of the reinforced HAP, vis-a-vis the pure HAP, there is, however, a significant change in the yield strain of the reinforced nanocomposite. This increase in ductility can be usefully exploited in HAP-based bioceramics employed in such areas of medical nanotechnology as bone-replacing tissue engineering.

2. STRUCTURE OF SYNTHETIC HAP AS BONE REPLACEMENT MATERIAL

Synthetically prepared HAP ceramics has the same chemical composition as this major mineral constituent of bone. HAP crystallizes in either monoclinic or hexagonal symmetry. The space group of the unit cell of monoclinic HAP is P21/b and consists of 88 atoms as represented in the Fig 1. Its lattice parameters are a = 9.4214 Å, b = 2a, c = 6.8814 Å, α=90º, β= 90º, γ = 120º and Z = 4 [28], where Z is the symmetry number. The HAP molecule consists of Ca+2 ions surrounded by PO3-4 and OH- ions. In the HAP crystal, the OH ions are located into arrays whose direction is parallel to the c-axis. The two positions of OH ions are alternately occupied. The periodicity along the b-axis is twice as along the a-axis. Nano structured HAP single crystals were grown by the molten salt synthesis method [29]. B. Viswanath et al. determined mechanical properties of the HAP single crystal by micro- and nanoindentation studies, which reveals that these crystals are mechanically anisotropic. Other methods for synthesizing dense HAP have been employed over the past few decade [30]. Kokubo and co-workers produced HAP layers on various organic or inorganic substrates in simulated body fluids (SBF) [31]. Nowadays, synthetic HAP is being used as coating material on prosthetic metallic implants. HAP coated implants allow natural bone re-growth and results in excellent fixation of the prosthesis. While HAP has excellent bioactivity and osteoconductivity, its poor mechanical properties compared with bone have hindered its use in clinical applications. Dense HAP has a compressive strength four times that of cortical bone, yet a significantly lower tensile strength and fracture toughness. Therefore, HAP does not match the mechanical behavior of natural bone and thus cannot be used in major load-bearing applications in its present form. Additionally, it is worth noting that the Young's modulus of HAP far exceeds that of cortical bone. This may be a concern, as a phenomenon known as „stress shielding" prevents bone from being loaded properly when it is in contact with an implant material of higher elastic modulus. In this case, the implant takes most of the load and, as a result, the surrounding bone tissue remodels itself with weaker mechanical properties . This can, in turn, cause a breakdown in the implant material-bone interface, resulting in the mechanical failure of the implant-bone system. Reinforcing HAP with a second phase such as CNTs offers a possibility to overcome these limitations.

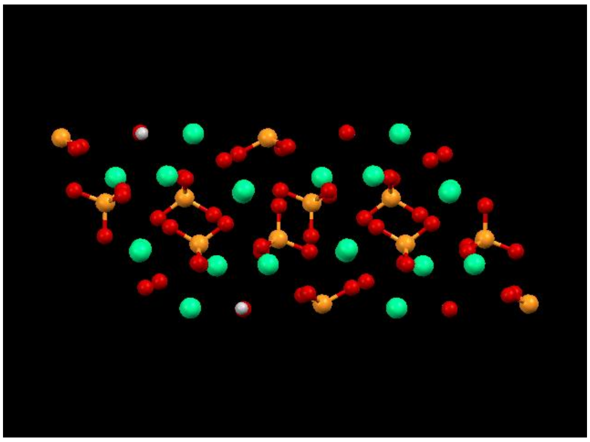


Fig. 1. Unit cell of HAP molecule [28]

3. CARBON NANOTUBES AS SCAFFOLD IN BONE TISSUE ENGINEERING

Bone tissue engineering offers a promising new approach mimicking natural manufacturing methods to generate artificial tissues (scaffolds) those might be used as temporary or permanent replacements of the missing, lost, injured or damaged bones and teeth [32,33]. Over the years, the artificial scaffolds, designed to support cell and tissue regeneration, have traditionally been focused on a macroscopic level. Their aim was to match the properties similar to natural tissues without reconstructing the nano-scale features that were observed in native tissues. All tissues of the human body, however, contain differentiated cells living in an extracellular matrix (ECM), which shows hierarchical organization from nano- to macroscopic length scale interacting with nanometer length-scale elements [34]. Thus to recapitulate proper function and organization of native tissues in tissue engineering approaches, it is important to mimic tissue properties at the nanoscale [35].

One of the most promising nanomaterials, which have a great potential for multiple uses in tissue engineering, are the CNTs. Their Young's modulus is estimated to be of the order of TPa, making them the material with the highest tensile strength known by far, capable of sustaining high strains without fracture. It is now suggested that these nanotubes form the main functional units in molecular scale machines, nano-scale systems and devices, and also as reinforcing fibers in many smart and advanced alloys and composites. The appeal of CNTs arises from the fact that they have a structure that can be tailored to mimic closely the nano-scale of native ECM as represented in the Fig 2. Zhao et al. have shown the potential of nanotubes to mimic the role of collagen to serve as a scaffold for growth of HAP [36].

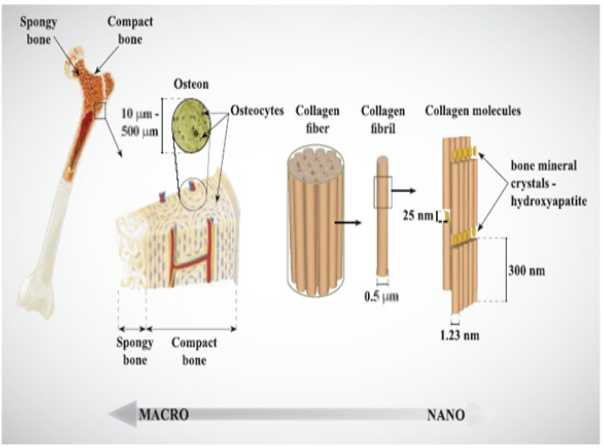
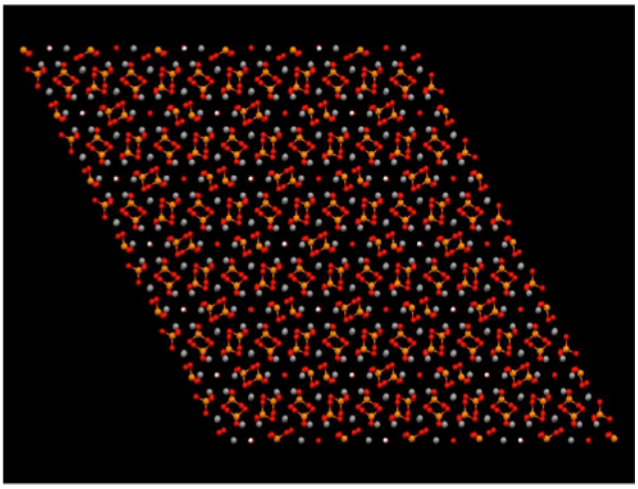


Fig. 2: Complex hierarchical bone structure [35]

4. RESULTS

In this work, we determined the Young's modulus and the yield points of both pure and carbon nanotube-reinforced HAP (*without* functional groups), Fig. 3. Our MD-based simulations employ a set of rather accurate interatomic potentials that provide an adequate description of the energetic and dynamics of the various elements that make up the nanocomposite.



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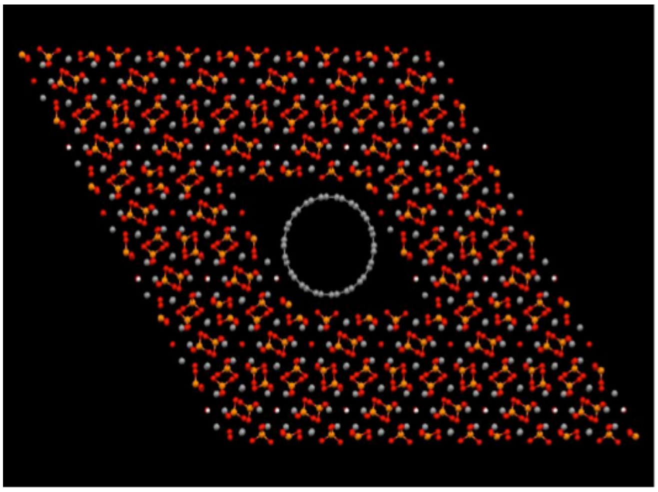

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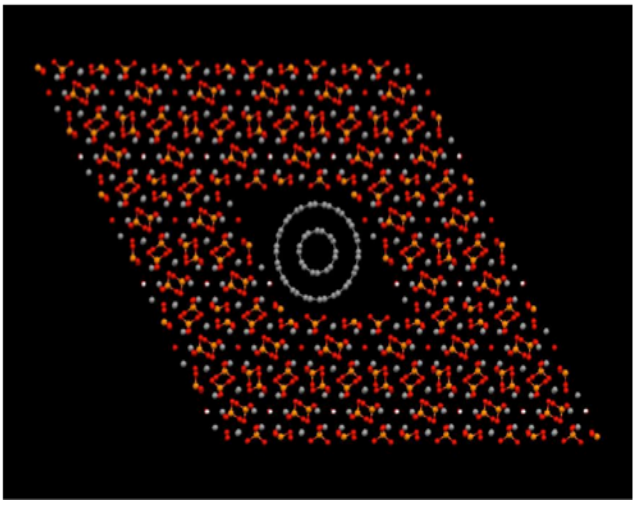

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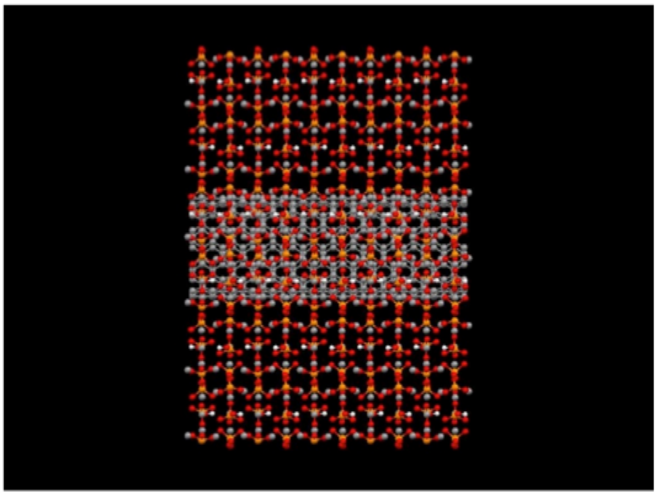

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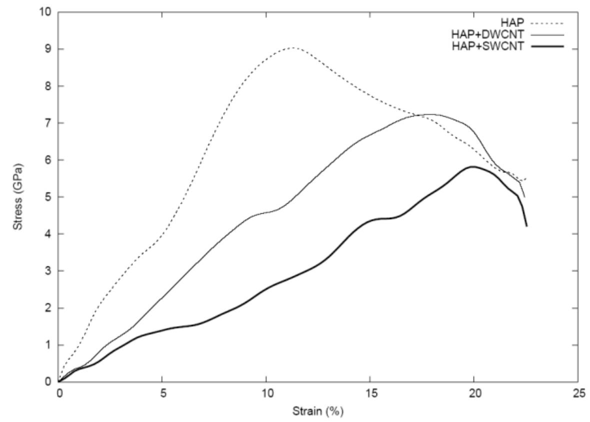
Fig. 3. The snapshot a) of the initial pure HAP monoclinic crystal, b) of the initial HAP+SWCNT composite containing a (9,9) SWCNT, c and d) of the initial HAP+DWCNT composite containing a (4.4)@(9,9) DWCNT.

The interatomic potential that describes the energetics and dynamics of the solid monoclinic HAP is due to Hauptmann [24]. This potential is composed of an inter- and an intra-molecular component. The consistent valence force field (CVFF) has been used to provide a parameterization of the Hauptmann potential for the mineral phase of the HAP [25]. The results of mechanical properties of both pure and carbon nanotube-reinforced HAP under different loading conditions are presented in the Fig. 4. It was shown that while the stiffness of the CNT/HAP composite, as measured by its Young's modulus, is not significantly affected by the inclusion of the nanotubes, the yield points of the composite show a rather significant variation vis-a-vis the pure HAP. The computed stress-strain variations for P-HAP, HAP+SWCNT, and HAP +DWCNT systems under an applied compressive strain in y-direction shows an increase from 10.2% to 20.08%, which shows an increase in ductility about 97% for HAP+SWCNT composite. This value is for tensile strain in y-direction, tensile strain in z-direction and compressive strain in z-direction, 87%, 20% and 22%, respectively. The computed values for HAP+DWCNT are for compressive strain in y-direction, tensile strain in y-direction, tensile strain in z-direction and compressive strain in z-direction, 76%, 70%,65% and 24%, respectively. The results show the onset of a brittle-ductile transition in all of our simulations which are in agreement with experimentally measured data [10-23]. This type of toughness or ductility property change can be exploited in the clinical use of this material. On the basis of the experimental evidence [26] that carbon nanotubes can be embedded successfully within a HAP matrix without the use of a functionalizing group linking the nanotubes to the HAP matrix, we have not considered the functionalization of the nanotubes, although we are aware that in studies concerned with the computation of the force to pull out a nanotube from a HAP matrix, functionalization can play an important role as it can influence the CNT/HAP interface interactions.



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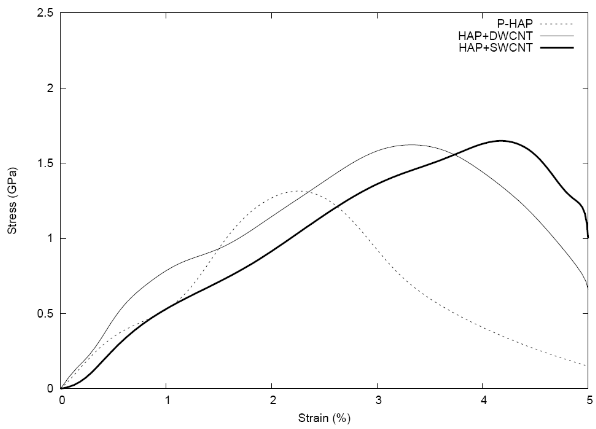

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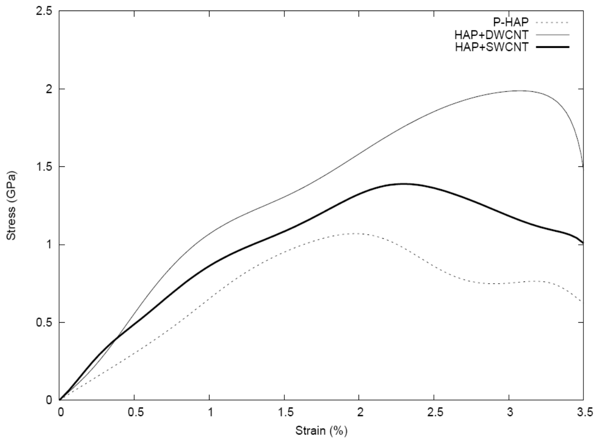

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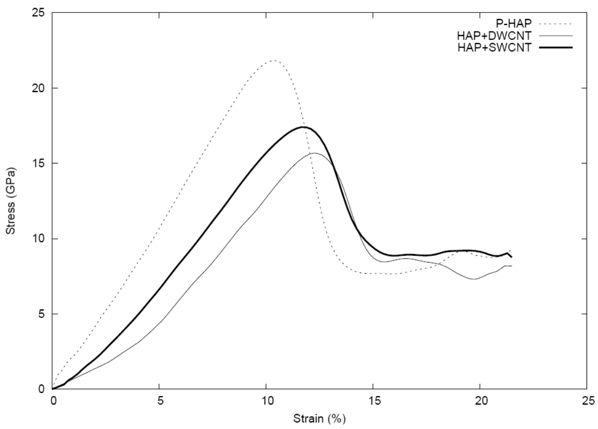

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Fig. 4. The computed stress-strain variations for P-HAP, HAP+SWCNT, and HAP+DWCNT systems under an applied, a) compressive strain in y-direction, b) an applied tensile strain in y-direction c) tensile strain in z-direction d) compressive strain in z-direction

4. CONCLUSIONS

Comparing to the experimentally measured data on yield points, we can state that the insertion of carbon nanotubes into pure HAP improves its ductility under various imposed loading conditions. Furthermore, our results show that, overall, the effect of inclusion of the SWCNT is quite comparable to the effect of a DWCNT. Enhancing the ductility by insertion of nanotubes, while at the same time not increasing the stiffness of this composite, as characterized by its Young's modulus, can be beneficially exploited when using this reinforced material in such areas as bone repair. This property allows the nanocomposite to last longer before plastic deformation sets in leading to the degeneration of its elastic properties.

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