

LATTICE DYNAMICS OF CARBON NANOTUBE INTERACTING WITH HYDROXYAPATITE

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Abstract:

One of the characteristics to be achieved by biomaterials is to have similarity to the host material. In cases of bone substitution, hydroxyapatite (HA) shows considerable similarities to human bone. However, it shows itself with low mechanical resistance, which in many cases makes it difficult to apply in areas subject to high mechanical stress. Carbon nanotubes (CNTs) have low density and strong covalent bonding between their atoms, which gives high mechanical resistance to the material. For this reason, the influence with the HA structure of single wall, pristine CNTs and functionalized with organic hydroxyl (-OH) and carboxyl (-COOH) clusters with functionalization concentrations of 5, 10, 15, 20 and 25% were studied by means of computational simulation. The software used to perform the calculations was GULP and the applied force field was DREIDING. The lattice dynamics revealed that pristine CNTs have a lower interaction with HA because of their high chemical stability. In contrast, the CNTs functionalized with -OH and -COOH interacted better with the HA matrix, indicating that the functionalization may be a factor that optimizes the interaction between these materials. The results of the Root Mean Square Deviation (RMSD), for all systems with functionalized CNTs, reach a stability around a point of equilibrium around 15ps, proving that the interactions are stable. The calculation of the Bulk modulus indicated that we can control the ability of this material to resist volume changes for a given applied pressure, modifying the amount of functionalization present in the CNTs. The functionalities of 20% of -OH and -COOH present greater difficulty in undergoing deformations (greater value of the Bulk module). On the other hand, the functionalizations of 15% of -OH and 5% of -COOH were the most vulnerable to deformation (lower value of the Bulk module). Finally, the Poisson ratio indicates that the theoretical model applied to the systems is reasonable since these coefficients were within the proposed theoretical range.

Keywords: hydroxyapatite, Carbon nanotubes, lattice dynamics

Introduction: The hydroxyapatite (HA), has similar physical and chemical properties with the mineral phase of the bones and human teeth. The characteristics of its structure allow its use in implants and bone grafts, presenting high compatibility with the living tissues of the hosts [1].

However, HA has a small mechanical resistance which may influence bone regeneration in the applications of some types of bone grafts, especially in areas subject to high mechanical stress [2,3]. One possible solution would be the introduction of carbon nanotubes (CNTs) to this material, perhaps the incorporation of this material improves the mechanical properties of hydroxyapatite.

Discovered by Iijima in 1991, the CNTs have several properties of interest such as large surface area, nanocapillary, and environmentally susceptible electronic properties that are exposed [4]. Even with all these properties, there is a discussion about a low reactivity of CNTs, due to its high chemical stability. However, many of the applications take into account a prior treatment, making oxidation that promotes better dispersion or introducing hydrophilic groups such as hydroxyl (-OH) and carboxylic (-COOH) which leads to the functionalization of the material, so we have a probable increase in the reactivity of the CNTs [5].

We use computational simulation based on lattice dynamics, to investigate HA interactions with single wall CNTs pristine and functionalized with the organic hydroxyl groups (CNT-OH) and carboxyl (CNT-COOH).

Materials and Methods: It departed from the cif data-26204-ICSD which contains all the information concerning the crystalline structure, to build the input files [6]. The unit cell of hydroxyapatite is mainly found in the spatial group P63/m with axes $a=b=9,424 \text{ \AA}$ $c=6,879 \text{ \AA}$, this was repeated generating a supercell of $1 \times a$, $4 \times b$, and $6 \times c$ that would provide some flexibility of movement for CNTs. Periodic conditions were employed in the y and z

directions. A vacuum of 20 \AA was added in the x direction.

A CNT was introduced with a separation of approximately 3 \AA in relation to the HA surface. The CNTs have chirality $n=10$ e $m=0$, repeated in three units and passivated with hydrogen. Because pure CNTs exhibit high chemical stability, in practice, this material generally requires a treatment of its surface, making them more reactive. Due to that, we suggest the functionalization of CNTs with oxygenated organic radicals (-OH and -COOH). These groups act as mediators in the interaction between CNTs and other substances. The CNTs were used both as pristine and functionalized with -OH or -COOH, and the percentages of functionalization of CNTs were (5,10,15,20,25) %.

All calculations were performed using the software GULP. The force field used was the DREIDING. This field uses general force constants and the parameters are defined for all possible combinations of atoms [7]. The Canonical Ensemble (NVT) was used, which typically describes a system in contact with a thermal reservoir through a fixed and impermeable diathermic wall, the contacting systems will change their coordinates until they reach a common equilibrium state. The production time was 30 ps, specifying the simulation time to be spent collecting production data for further analysis.

Results and Discussion: In figure 1 is indicated the Root Mean Square Deviation (RMSD). For the HA system we have few changes and after 4 ps the structure remains in an equilibrium position. Already the Hydroxyapatite system plus pristine carbon nanotubes (HACNT) does not reach this stability, probably due to the pristine CNT being little reactive, indicating a high movement on the surface of the HA and not reaching a point of equilibrium. For all other HA systems plus CNT functionalized with -OH or -COOH a stability around a break-even point was reached from approximately 15 ps.

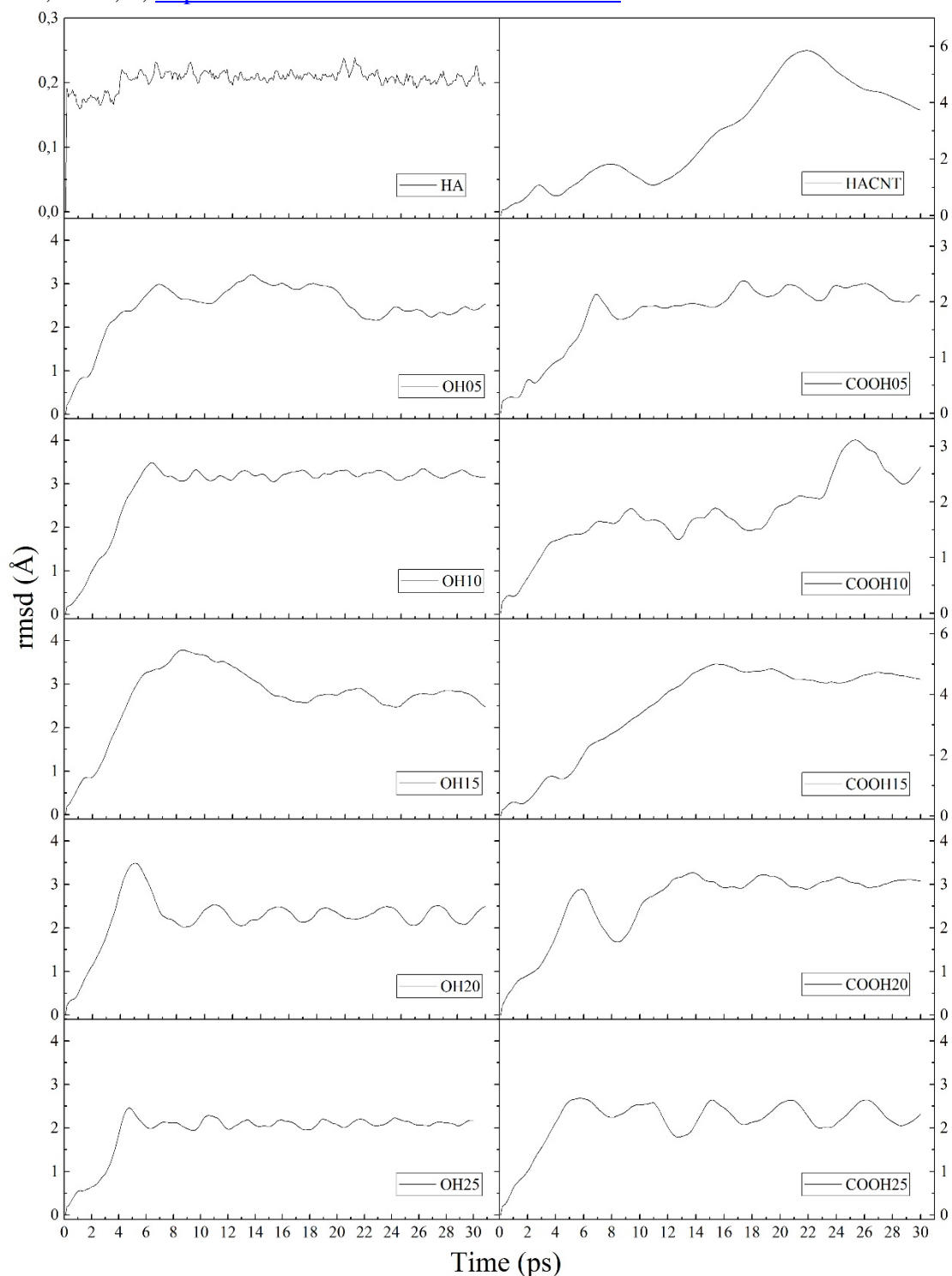


Figure 1- RMSD calculated for the HA and HA structures plus pristine CNT and functionalized with -OH(5,10,15,20,25) % and -COOH(5,10,15,20,25) %.

The measure of the ability of a material to withstand the volume change for a given applied pressure (Bulk module) is indicated in figure 2. The points -5 e 0 in the following graphs indicate the HA and HACNT systems respectively and the other points the percentages of functionalization of -OH or -COOH to which the CNTs were subjected. In the figure 1(a) we have the calculated Bulk module for the -OH systems. For these systems, we observe alternating

variations and the extremes occurring for the functionalization of 15 and 20 % in -OH, being that of 15 % the easiest to undergo volume changes (lower Bulk module), already for the system with CNT functionalized with 20% of -OH we have the greatest difficulty of deformation (highest value Bulk module).

The result for the carboxylated system is shown in figure 1(b). As the percentage of functionalization increases, we have an increase in the Bulk module, achieving a partial stability to a percentage above 15 % in -COOH, being that for 5 % in -COOH the easiest to undergo deformation (lower value of Bulk module) and the 20% that is more difficult to deform (greater

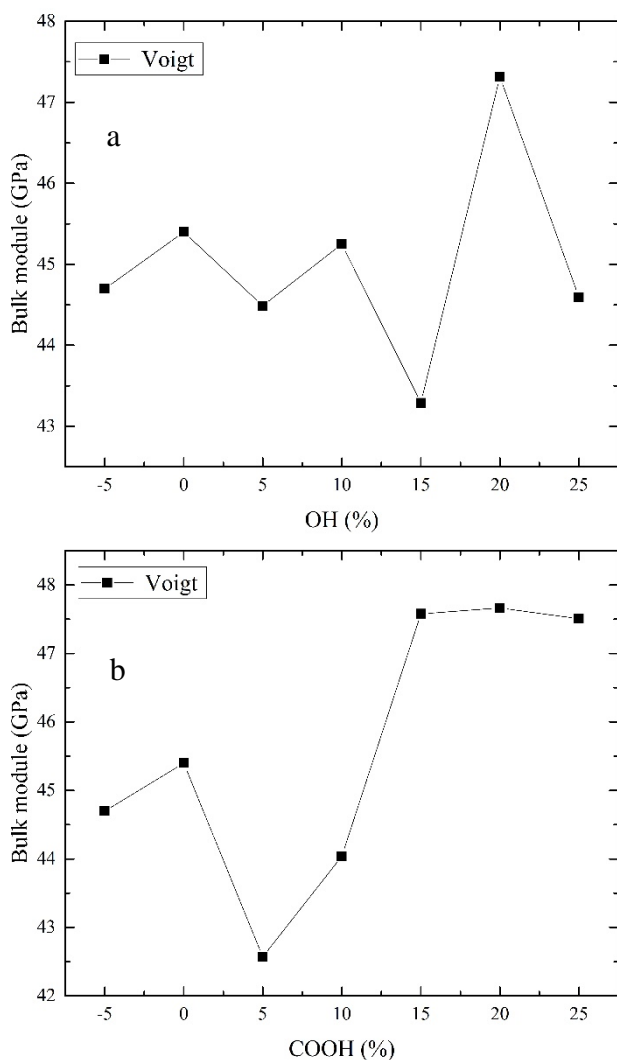


Figure 2- Bulk module versus functionalization percentage. value of the Bulk module).

The Poisson ratio measures the deformation that is established between orthogonal deformations [8]. And through algebraic calculations, this interval for the Poisson coefficient is between $0 < \sigma < 1/2$; $-1 < \sigma < 0$ [9].

If we apply a force in the direction of x, we have that the relation between the lateral deformation and the longitudinal deformation of the force application does not present values typical of the

Poisson ratio, these non-significant results were observed for both systems, -OH and -COOH. Probably the event is related to the fact that this was the direction where we created the vacuum for the introduction of CNTs.

As for the forces applied in the y-direction, the relation between the lateral deformation x and the longitudinal deformation of the force, we observe Poisson coefficients close to zero, indicating that the system suffers high deformations in the direction of x. For both systems when the force is applied in the direction of y and z, the highest coefficients were observed for the 20% of functionalization indicating that, for these directions, we obtained little deformation.

Conclusions: The calculation of RMSD showed that the pristine CNT does not establish strong enough bonds to attach to the HA structure, while the functionalized ones bind to the structure, reaching a position of equilibrium from 15 ps.

The Bulk modulus indicated the functionalization with the highest resistance to deformation and the Poisson ratio indicates that the theoretical model used is reasonable for the description of the systems since these coefficients were within the proposed theoretical range of (0-0.5), except when analyzing the direction of x because it presents the region of vacuum where it was introducing the CNTs generating a greater flexibility of movement of the atoms.

The results obtained from the theoretical calculations indicate that it is possible to change the mechanical properties of HA with the introduction of the CNTs and, for certain percentages of functionalization, we had significant changes in the properties related to the elastic constant of this material.

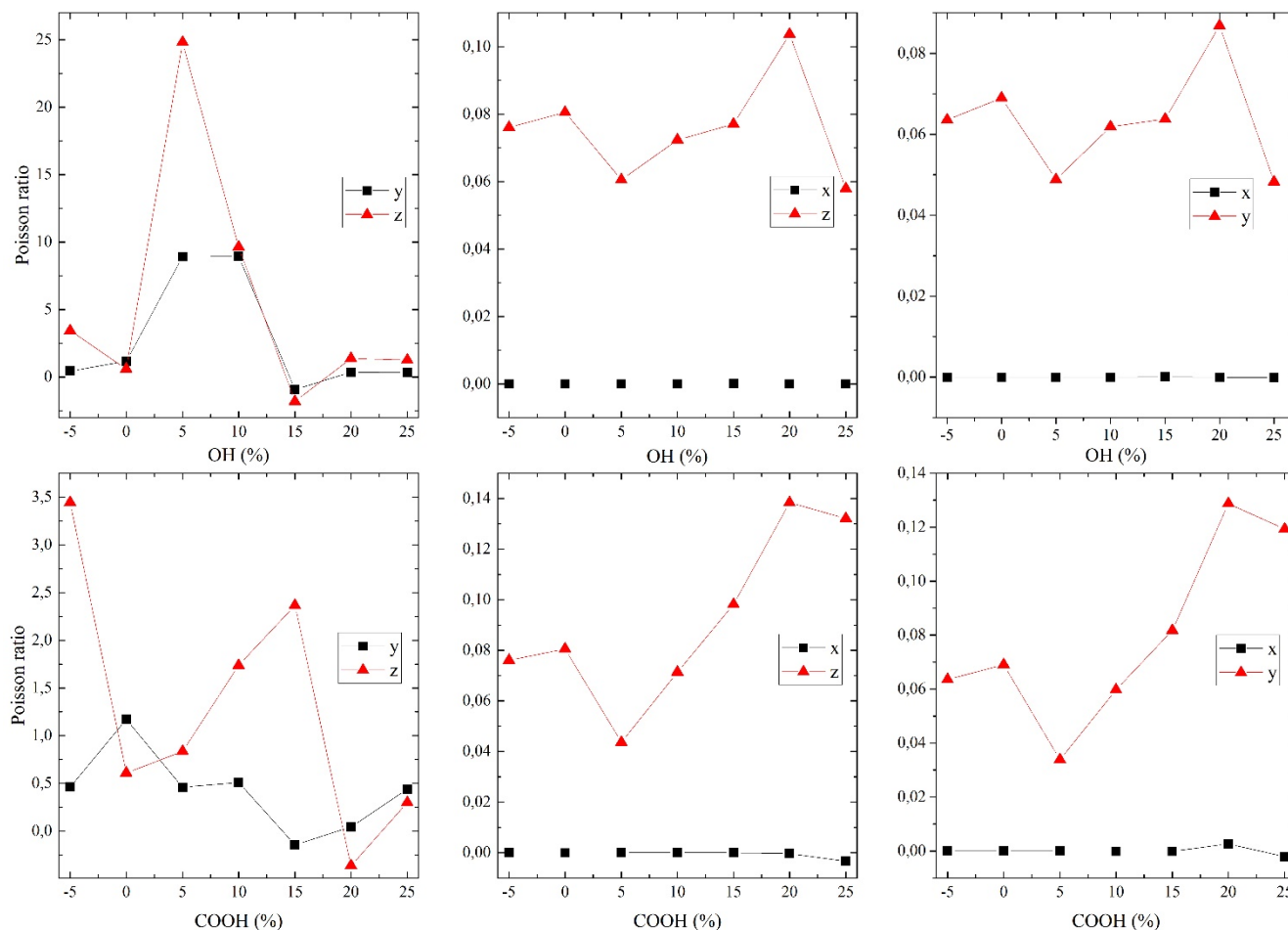


Figure 3- Poisson ratio for the HA point -5 systems, HACNT point zero, and HA with CNT(-OH ou COOH)(5,10,15,20,25) %.

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