



Fabrication and Characterization of Hydroxyapatite-Carbon Nano Tubes Composites

Esmail Salahi^{1,*}, Armin Rajabi²

¹Materials and Energy Research Center (MERC), Karaj, Iran

²Department of Mechanical and Material Engineering, Faculty of Engineering & Built Environment Universiti Kebangsaan Malaysia, Bangi, UKM, Malaysia

Email address:

e-salahi@merc.ac.ir (E. Salahi)

*Corresponding author

To cite this article:

Esmail Salahi, Armin Rajabi. Fabrication and Characterization of Hydroxyapatite-Carbon Nano Tubes Composites. *American Journal of Nanosciences*. Vol. 2, No. 4, 2016, pp. 41-45. doi: 10.11648/j.ajn.20160204.11

Received: September 2, 2016; **Accepted:** November 2, 2016; **Published:** November 30, 2016

Abstract: In this research is proposed a relatively popular approach for fabrication of Hydroxyapatite- carbon nanotubes (HAp-CNT) composite, through suspension and hot press methods. The principle raw materials, namely suspensions of CNT and HAp were mixed with together to produce the composites with different wt% CNT. The sonicated suspension is dried at 110°C and subsequent was hot pressed at 500°C under 500 MPa uniaxial pressures. Microstructure and fracture surface of the composites were studied by scanning electron microscope (SEM). The results revealed that addition of 3 wt% CNT to HAp matrix resulted in an about 70% increase in bending strength of the composite.

Keywords: Microstructure, Nanocomposites, Hydroxyapatite, Carbon Nanotubes, Bending Strength

1. Introduction

The idea of using one-dimensional fillers for the mechanical reinforcement is not something new. In the recent years, fibers made of materials such as alumina, glass, boron nitride, silicon carbide, and especially carbon fibers have been used as the reinforcing agents in different composites [1-3]. These common fibers are usually several ten-micrometers in diameter and several ten-millimeters in length, and their mechanical properties are good. Carbon fibers have stiffness and strength of respectively 230-725 GPa and 1.5-4.8 GPa for instance, but the best mechanical properties should be for the carbon nanotubes [4]. CNTs can have diameters of 1-100 nanometer and lengths of several millimeters [5]. Density of the carbon nanotubes is about 1.3 g/cm³, and their Young's modulus is about 1 TPa, which is much higher than every other carbon fibers [6, 7]. However, it is the exceptional strength of the CNTs that has made them unique and different from every other material in terms of mechanical strength [8, 9]. The highest strength of the CNTs has examined to be about 63 GPa [4]. This is more than 10 times higher than the strength of carbon fibers. Even the weakest types of CNTs have strengths up to several GPa [10].

Although the excellent biocompatibility of the hydroxyapatite bioceramics has been long acknowledged by the scientists, the poor mechanical properties of this material have remained an obstacle to its application as a bulk material in the body skeleton and limited its use under intense mechanical stresses [11]. So far, various solutions have been suggested for the improvement of the mechanical properties of this material which recommend using bioactive glasses, high density polyethylene polymers, carbon fibers and ceramic particles like alumina and zirconia as the secondary reinforcing or toughening agents in the HAp matrix [12]. Among all these materials, carbon has a very good biocompatibility and its different kinds such as pyrolytic carbon or carbon-carbon composites have wide applications as biomaterials. Also, it has been for a while that the biocompatibility of the CNTs is being studied and their desired compatibility with the body tissue, which has been better than some commonly known bioceramic materials, has been noticed [13].

There has been very little research on the application of CNTs as the reinforcing agent in the HAp matrix. In the

present study, bending strength of the HAp-CNT composites as a representative for their mechanical properties has been studied and the possibility of using CNTs as reinforcing agents in HAp matrix has been investigated.

2. Experimental Procedure

The procedure used in this work to obtain nanocrystalline Hydroxyapatite nanoparticles has been described in greater detail elsewhere [14].

Carbon nanotubes were bought from the Research Institute of Petroleum Industry (RIPI, Iran) and were allegedly of less than 40 nm diameters and of higher than 90% purity. CNTs were washed at several stages by nitric acid and a combination of the nitric and hydrogen chloride acids.

In the next step, CNT and HAp suspensions were separately made by the mixing of certain amount of each (proportional to the amount of CNTs in the final composites, 0.5, 1, 3, and 5 wt%) in distilled water using the ultrasonic process. Sodium dodecyl sulfate (SDS) was used as dispersant to stabilize the suspensions, and pH of the suspensions was adjusted to be around 10. After the ultrasonic process on the HAp+SDS and CNT+SDS suspensions, they were mixed with each other and the resulted suspension was also sonicated and put on a hot plate at 110°C for its water to be evaporated. The remained sediment was put in the dryer for 24 hours and then was gently powdered. The final composite powders were hot pressed at 500°C under 500 MPa uniaxial pressures. Morphology of the HAp-CNT composite powders, and also the fracture surface of the composite were investigated by scanning electron microscope (SEM Philips XL30). Bending strength of the samples was tested by a 3-point bending strength testing equipment (Instron, model: 1196) according to the ASTM D970 standard. Surface of all the samples was polished prior to the bending test. Displacement rate of the loading equipment was fixed throughout the test and was equal to 0.5 mm/min. At least 5 samples of each composite composition were used for the bending strength test and the average of the test results was calculated.

3. Results and Discussion

Figure 1 shows the SEM image of the synthesized and heat treated HAp powder and CNTs. It is observed that the accumulation of CNTs into bundles because of the attraction forces existing as a result of the very high surface energy of the CNTs (Fig. 1b). One of the key problems in achieving a desired reinforcement using CNTs is their even dispersion in the composite matrix.

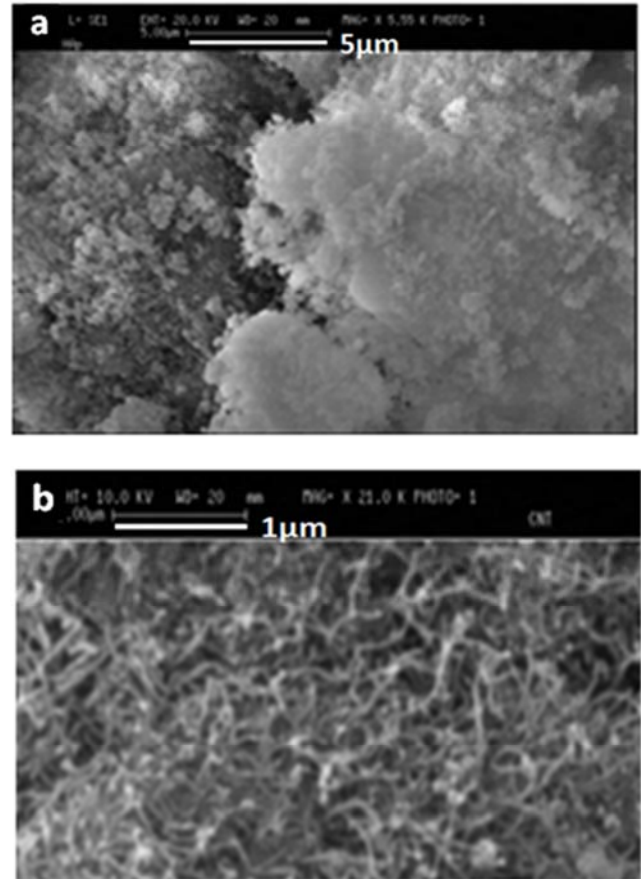


Fig. 1. (a) SEM images of (a) synthesized HAp powder, (b) the carbon nanotubes.

Colloidal processes, among different existing processes for the mixing of CNTs and the matrix material, have had better and more desired results. In this process, despite of the mixing process through milling, CNTs are not damaged and because of the higher mobility of particles in a colloidal environment, it would be possible to get a more even dispersion of the CNTs in the final composite matrix. However, the key factor to achieve that is making stable suspensions of each component, and finally achieving a stable suspension of the mixture of HAp and CNTs. According to literature, sodium dodecyl sulfate (SDS) was used as a dispersant for stabilization of both HAp and CNTs suspensions and its dispersing mechanism, which is based on the electrosteric repulsion, is discussed elsewhere [15, 16].

Figure 2 shows the passage of a laser beam through CNTs suspension without SDS, while it is blocked by the same suspension with SDS. This is because of the scattering of the laser beam by the high amount of suspending CNTs in the SDS included suspension, whereas the other suspension was not stable enough and the CNTs were sedimented after a while, which is the reason for the easy passage of the laser beam through this suspension. Both suspensions were made with the same amount of CNTs, and the photos were taken after 3 days.



Fig. 2. Comparison of the stability of the SDS stabilized CNTs suspension (the right one) with the unstable CNTs suspension without SDS (the left one). The photos were taken after 3 days pH of both suspensions was kept 10.

SEM images of the composite powders including 3 and 5 wt% CNTs are illustrated in Fig. 3. Comparison of the morphology of these powders with the pure HA powder shows that the HA particles in the composite powders are finer, and CNTs are well dispersed among the HA particles in these composites.

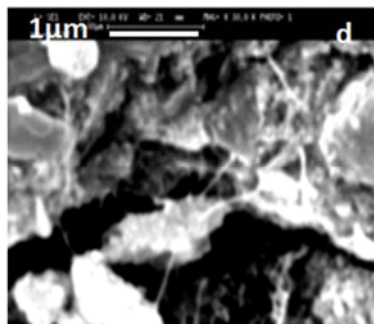
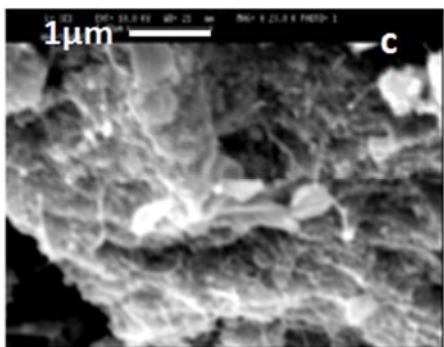
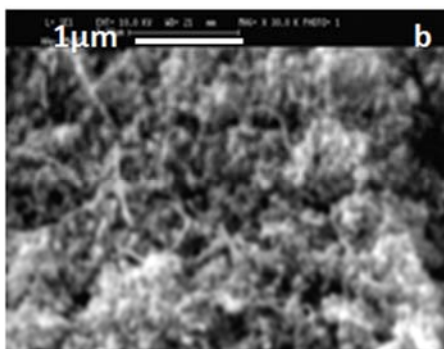
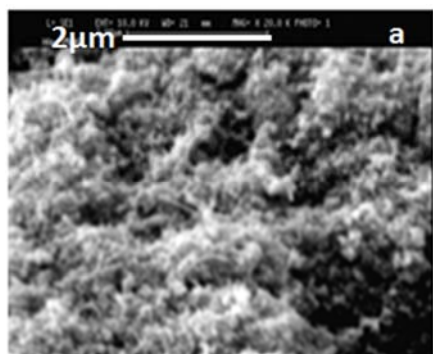


Fig. 3. SEM images of (a) and (b) 3 wt%, and (c) and (d) 5 wt% CNT containing composite powders.

It seems that the ultrasonic process, on both HAP and HAP-CNTs suspensions, has resulted in removing most of the agglomerates and has even broken the coarser HAP particles into finer ones in the composite powder. It also seems that the dispersion of CNTs on the HAP particles has prevented the attachment of HAP particles and formation of coarse agglomerates.

The variation of bending strength of HAP-CNT composites with different CNTs additions is illustrated in Fig. 4. It can be seen that the bending strength has increased from about 30 MPa in pure HAP to about 50 MPa in the 3 wt% CNTs containing composite, which is about a 70% increase. In the composites with lower amount of CNTs, i.e. 0.5 and 1 wt%, the bending strength of the composites is approximately close to that of pure HAP. But after an increase in the bending strength of the composites in 3 wt% CNTs, it has decreased to about 15 MPa in the 5 wt% CNTs composite. Seemingly, a web like network of CNTs that could hold the particles of the matrix together and resist their easy separation and so the crack growth, is not yet formed in the composites containing a low amount of CNTs. And with the excessive increase of the CNTs, on the other hand, their dispersion in the matrix becomes poorer, and more bundles and agglomerates made out of them help the formation of flaws and crack origins in the microstructure, which again result in a decrease in the bending strength after its maximum. Existence of an optimum amount of CNTs for a proper reinforcement of the matrix is also mentioned in the literature [17, 18].

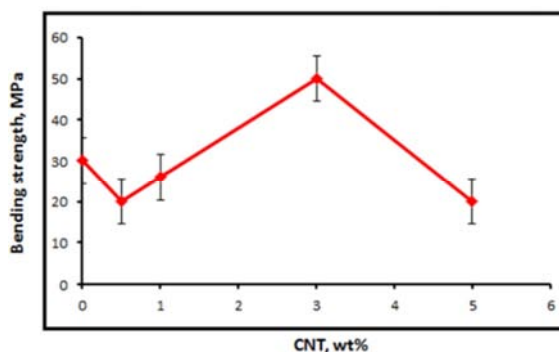


Fig. 4. Bending strength versus CNT wt% in the HAP-CNT composites. The WS (without SDS) point represents the bending strength of the HAP-3 wt% CNT composite made in the absence of SDS.

Figure 5 shows SEM images of the fractured surfaces of the HAp-5 wt% CNT. The web-like network of the CNTs on the matrix particles attaching them together and the bridging of the CNTs between the crack surfaces can be seen in these pictures. It may be induced by bridging mechanism which has slightly improved the bending strength of the CNTs reinforced composites.

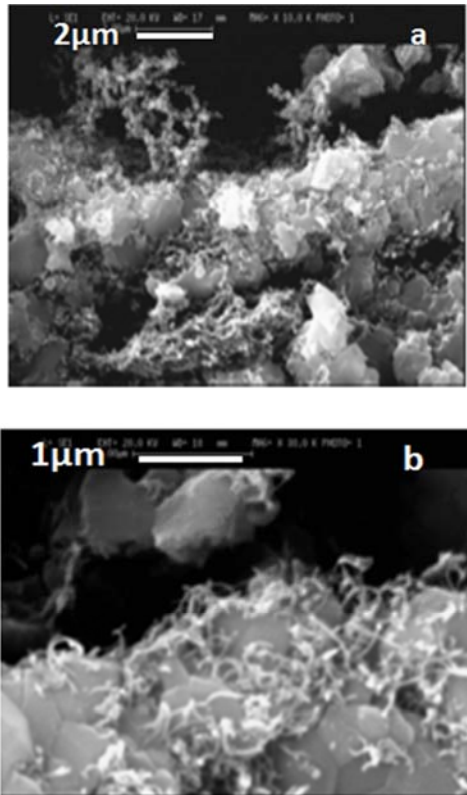


Fig. 5. SEM images of fractured surfaces of (a) 3 wt%, and (b) 5 wt% CNT containing HAp composites.

4. Summary and Conclusion

Upon the addition of different amounts of CNTs into the HAp matrix, the bending strength of the composites decreased a bit or did not have a considerable change at first. It then increased and became more than that of pure HAp as the amount of CNTs increased, and finally decreased again with the further addition of CNTs. Addition of 3 wt% CNTs in the HAp and its even dispersion in the matrix using SDS as a dispersant through the colloidal mixing process, and then hot pressing of the composite powders under 500 MPa pressure and 500°C temperature, and finally sintering the resulted composite at 1100°C under nitrogen atmosphere resulted in a 70% increase in its bending strength compared to that of pure HAp. Regarding the biocompatibility of the CNTs and HAp, it is expected that this kind of composites with a higher mechanical strength than pure HAp, becomes a proper replacement for body implants as bulk materials instead of pure HAp. Of course, this depends on the use of highly pure CNTs in a way that the amount of transition metals (left in the carbon nanotubes as a result of their

synthesis process) in this kind of CNTs reinforced composites, which are harmful for body, does not exceed the allowed and non-harmful amount.

Acknowledgements

This project was accomplished under the funding of Materials and Energy Research Center (MERC). Authors are very thankful to Mr. Babak Alinezhad without whose generous help the project would not be accomplished.

References

- [1] Momprou, F., and Legros, M., 2012, "Plasticity Mechanisms in Sub-Micron Al Fiber Investigated by In Situ TEM," *Advanced Engineering Materials*, 14 (11), pp. 955-959.
- [2] Abdulmajeed, A. A., Walboomers, X., Massera, J., Kokkari, A. K., Vallittu, P. K., and Närhi, T. O., 2013, "Blood and fibroblast responses to thermoset BisGMA-TEGDMA/glass fiber-reinforced composite implants in vitro," *Clinical oral implants research*.
- [3] Li, D., Zhang, C., Li, B., Cao, F., and Wang, S., 2012, "Effects of heat treatment on properties of boron nitride fiber," *Science China Technological Sciences*, 55 (5), pp. 1376-1380.
- [4] Mathur, R., Singh, B., Dhama, T., Kalra, Y., Lal, N., Rao, R., and Rao, A., 2010, "Influence of carbon nanotube dispersion on the mechanical properties of phenolic resin composites," *Polymer Composites*, 31(2), pp. 321-327.
- [5] Zanganeh, N., Rajabi, A., Torabi, M., Allahkarami, M., Moghaddas, A., and Sadmezhaad, S., 2014, "Growth and microstructural investigation of multiwall carbon nanotubes fabricated using electrodeposited nickel nanodeposits and chemical vapor deposition method," *Journal of Molecular Structure*, 1074, pp. 250-254.
- [6] Li, P., You, Z., and Cui, T., 2014, "Adhesion energy of few layer graphene characterized by atomic force microscope," *Sensors and Actuators A: Physical*, 217, pp. 56-61.
- [7] Laborde-Lahoz, P., Maser, W., Martinez, T., Benito, A., Seeger, T., Cano, P., Villoria, R. G. d., and Miravete, A., 2005, "Mechanical characterization of carbon nanotube composite materials," *Mechanics of advanced materials and structures*, 12 (1), pp. 13-19.
- [8] Tan, D., Cheng, H., Nguyen, S., and Duong, H., 2014, "Controlled synthesis of MnO₂/CNT nanocomposites for supercapacitor applications," *Materials Technology: Advanced Performance Materials*.
- [9] Li, G., Huang, Z., Zuo, Z., Zhang, Z., and Zhou, H., 2014, "Progress of electrode materials for high energy lithium secondary batteries," *Materials Technology: Advanced Performance Materials*.
- [10] Xie, S., Li, W., Pan, Z., Chang, B., and Sun, L., 2000, "Mechanical and physical properties on carbon nanotube," *Journal of Physics and Chemistry of solids*, 61 (7), pp. 1153-1158.
- [11] Li, A., Sun, K., Dong, W., and Zhao, D., 2007, "Mechanical properties, microstructure and histocompatibility of MWCNTs/HAp biocomposites," *Materials Letters*, 61 (8), pp. 1839-1844.

- [12] An, S.-H., Matsumoto, T., Miyajima, H., Nakahira, A., Kim, K.-H., and Imazato, S., 2012, "Porous zirconia/hydroxyapatite scaffolds for bone reconstruction," *Dental Materials*, 28 (12), pp. 1221-1231.
- [13] Baradaran, S., Moghaddam, E., Basirun, W., Mehrali, M., Sookhakian, M., Hamdi, M., Moghaddam, M., and Alias, Y., 2014, "Mechanical properties and biomedical applications of a nanotube hydroxyapatite-reduced graphene oxide composite," *Carbon*, 69, pp. 32-45.
- [14] Ruban Kumar, A., and Kalainathan, S., 2010, "Sol-gel synthesis of nanostructured hydroxyapatite powder in presence of polyethylene glycol," *Physica B: Condensed Matter*, 405 (13), pp. 2799-2802.
- [15] Xu, Z., Yang, X., and Yang, Z., 2010, "A molecular simulation probing of structure and interaction for supramolecular sodium dodecyl sulfate/single-wall carbon nanotube assemblies," *Nano letters*, 10 (3), pp. 985-991.
- [16] Dutta, A., and Tekalur, S. A., 2013, "Synthetic staggered architecture composites," *Materials & Design*, 46, pp. 802-808.
- [17] Jiang, L., Gao, L., and Sun, J., 2003, "Production of aqueous colloidal dispersions of carbon nanotubes," *Journal of Colloid and Interface Science*, 260 (1), pp. 89-94.
- [18] Zhao, L., and Gao, L., 2004, "Novel in situ synthesis of MWNTs-hydroxyapatite composites," *Carbon*, 42 (2), pp. 423-426.