Rev.Adv.Mater.Sci. 27(2011) 58-63

EVALUATION OF THE MECHANICAL PROPERTIES AND MICROSTRUCTURE OF HYDROXYAPATITE REINFORCED WITH CARBON NANOTUBES

A. G. Osorio, L.A. dos Santos and C. P. Bergmann

Department of Materials, Federal University of Rio Grande do Sul
Avenida Osvaldo Aranha, 99 Sala 705C, Centro, Porto Alegre (RS), Brazil

Received: June 07, 2010

Abstract. Synthesized hydroxyapatite was reinforced with functionalized carbon nanotubes, and tensile strength, rupture tension, as well as fracture toughness values were calculated from the indirect method of diametric compression test using the Brazilian disc specimen. Five formulations were evaluated covering the range of 0 to 2 wt.% of nanotubes. Results showed that the addition of carbon nanotubes increases the mechanical properties of the ceramic composite until an optimum value, followed by a decrease. Composites evaluated showed an increase of approximately 58% on their fracture toughness property when 0.1wt.% of nanotubes were mixed to hydroxyapatite. Scanning Electron Microscopy analysis shows that percentages higher than 1 wt.% of reinforce material may cause agglomeration and precipitation of a second phase governed by the reinforcement. This phenomenon instigates a reduction on the mechanical properties of the composite since these agglomerates act as a stress concentrator leading the composite to an early failure.

1. INTRODUCTION

Synthetic hydroxyapatite (HA) is an important biomaterial as it is chemically similar to the mineral component of human bone. It is one of the few materials that are bioactive, forming strong chemical bonds with surrounding bones, unlike other materials such as alumina and zirconia, which are identified as foreign materials and become encapsulated by fibrous tissue [1]. Mechanical tests performed in HA, however, show very low values of fracture toughness, turning this material not suitable for heavy load-bearing applications especially in wet environments.

Carbon nanotubes (CNTs) have attracted several researchers' interest because of their remarkable structural, mechanical, electrical, and thermal properties [2-4]. The incorporation of nanotubes into ceramic matrices has been a vast area of study and research lately and has showed outstanding results [4-7]. Recently, different methodologies have been studied in order to manufacture composites of HA reinforced with CNTs [8-11]. The addition of CNTs into an HA matrix could possibly enhance its mechanical properties, specifically its fracture toughness.

HA can be used in powder form as well as bulk material. Its usage as bulk material in biomedical applications would bring the advantage of inserting a material completely bioactive into a human body, which could eventually be absorbed by the organism. Nonetheless, in order to be used as bulk material, fracture toughness of HA must be improved to be able to bear heavy load applications.

Typically, mechanical properties of ceramic materials are evaluated by the fracture toughness property (K_{IC}). This property was investigated in several

Corresponding author: A. G. Osorio, e-mail: osorio.alice@gmail.com

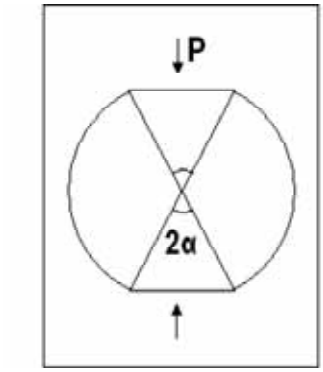

Fig. 1. Illustration of Brazilian disc specimens.

ways in the past due to its great importance to analyze the resistance of ceramic materials in the presence of a crack. This parameter is especially useful for the study of bulk materials for engineering applications. Usually, such parameter is evaluated thoughout the bending test.

Its s well known that when one aims to produce a product that involves nanotechnology, the size of the samples is of crucial importance and the possibility of using smaller specimens is very attractive. Hence, there is a need to develop or adapt a mechanical test that would demand less amount of material for specimens when compared to the commonly used bending test. An indirect method of diametric compression test is successfully used on brittle rocks [12,13]. This experiment presents the flexibility to use smaller samples for the test, requiring little quantities of material.

This paper aims the development of a bulk HA product reinforced with CNTs to be used in biomedical applications. Moreover, the role of CNTs as a reinforcement to HA on mechanical behavior was investigated and mechanical properties as well as microscopic analyses were evaluated. The alternative technique of diametric compression test is, therefore, proposed to evaluate fracture toughness, aiming the utilization of smaller amounts of material for the preparation of the compression samples.

2. EXPERIMENTAL

2.1. Materials

HA was synthesized in the laboratory by precipitation method. Materials used during the reaction were phosphoric acid and calcium hydroxide, resulting in HA and water. The powder produced was calcinated at 900 °C for 1 h.

Table 1. Identification of specimens of HA+CNTs.

Code	% HA	% CNTs
H0	100.0	0.0
H01	99.9	0.1
H05	99.5	0.5
H1	99.0	1.0
H2	98.0	2.0

Pristine CNTs were also synthesized in the laboratory by catalytic vapor deposition (CVD) using Mo/Fe as catalyst (also manufactured in the laboratory). Then, they were purified with chloridric acid (purchased from Synth Laboratory) in order to remove remained metal particles previously used as catalyst. The purification was carried out at room temperature by stirring a solution of chloridric acid with CNTs for 1h. Thereafter, CNTs were functionalized with sulfuric and nitric acids (3:1) [14].

2.2. Composite

The powder of pure HA was mixed with functionalized CNTs in an aqueous media according to Table 1. Each solution of HA and CNTs (HA/CNTs) was firstly sonicated for approximately 30 min to avoid agglomerates. This procedure was followed by the heating of the solution at 90 °C in a plate heater, and 1 wt.% of pressing additive (Polyvinyl Alcohol – PVA - Disperlan LA, Lambra Ltda) was added to this suspension when it reached 90 °C. Hence, the suspension was stirred on a magnetic plate for 10 min and, finally, rapidly frozen by immersing the suspension into liquid nitrogen. The process of freeze-drying was then applied to remove the water from the solution, resulting in a fine powder. This process was undertaken to ensure that a homogeneous powder of HA/CNTs was obtained. The equipment used was a Freeze-dry Edward Modulyo 4k.

Approximately 1 g of powder of HA/CNTs was compacted under a load of 15 kgf in cylindrical-shaped specimens with a gauge volume of approximately 450 mm^2 (12 mm of diameter x 4 mm of thickness). Six specimens were pressed and sintered for each formulation evaluated. Formulations tested are described in Table 1.

The oven utilized to sinter the samples was a Flyever, model FE50RP, at a ramp rate of 10 K/min and a dwell time of 1 h at 1200 °C. Sintering was carried out in stanch atmosphere of argon.

The density of cylindrical specimens was measured according to its geometrical volume: mass in

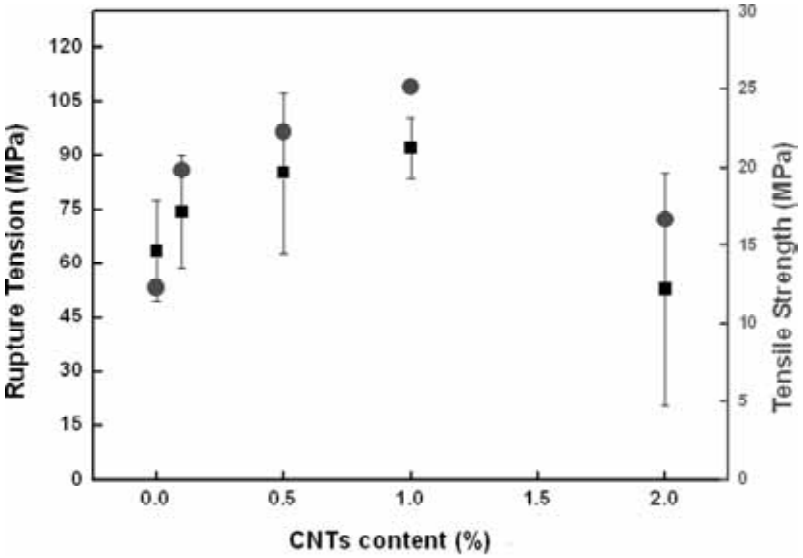

Fig. 2. Graph showing the values obtained for rupture tension and tensile strength for composites reinforced with different contents of CNTs.

grams over the volume of the sample was then calculated. The porosity was measured considering the theoretical density of HA, and the following formula was applied Eq. (1):

$$P(\%) = \frac{D_{calc} \times 100}{D_{theory}}, \quad (1)$$

where, P(%) is the porosity calculated in percentage, D_{calc} is the calculated density and D_{theory} is the theoretical density of HA (3.16 g/cm^3).

2.3. Mechanical characterization of composites

In order to characterize HA/CNTs composites, the indirect method of diametric compression test was carried out. The sample geometry applied was the flattened Brazilian disc specimen [13].

The diametric compression test was carried out in a Shimadzu universal machine of mechanical tests, model AG50KNX. Indirect tensile strength, rupture tension, and fracture toughness values were calculated from this experiment according to Wang and Xing [13] and Wang and Wu [12]. The ramp rate performed was 0.2 mm/min. The crack growth was naked-eye analyzed during and after loading.

Values of tensile strength were calculated from the average value of rupture tension using Eq. (2) therefore the standard deviation was not presented on this case.

$$\sigma_1 = 0.92 \frac{2P_{max}}{\pi D t}, \quad (2)$$

where P_{max} is the maximum load applied, D, and t are the diameter and the thickness of the specimens, respectively.

Fracture toughness values were calculated according to the method proposed by Wang and Wu [12], using 2a = 30° as angle.

Table 2. Results obtained and calculated from the mechanical test of diametric compression.

Formulation	Rupture tension (MPa)	Tensile strength (MPa)	K_{IC} (MPa$\sqrt{m}$)
H0	71.56 ± 14.06	13.81	1.48 ± 0.33
H01	74.19 ± 15.73	19.82	2.34 ± 0.39
H05	82.34 ± 22.29	22.26	2.59 ± 0.45
H1	93.98 ± 8.42	25.15	2.47 ± 0.29
H2	62.72 ± 32.36	16.66	1.72 ± 1.11

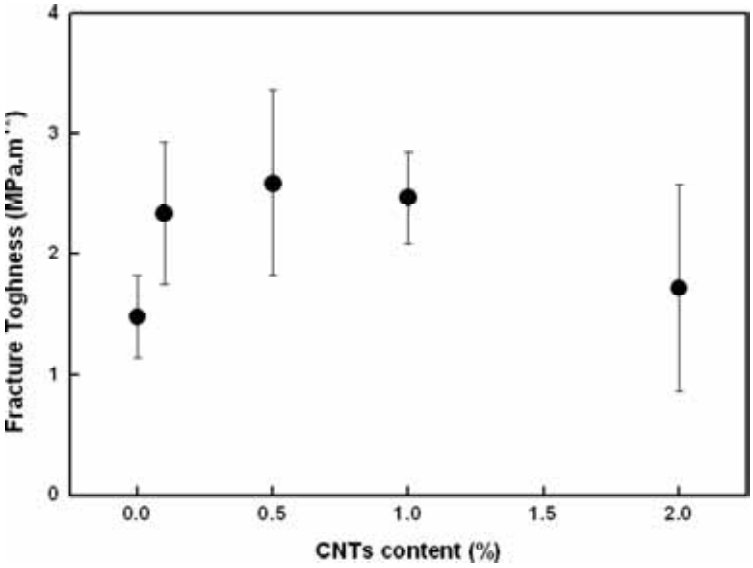

Fig. 3. Graph showing the values obtained for fracture toughness for composites reinforced with different contents of CNTs.

The morphology of the composite fracture was analyzed using a SEM Jeol JSM-5800.

3. RESULTS AND DISCUSSIONS

3.1. Mechanical properties

Values obtained for tensile strength, rupture tension, and fracture toughness are shown in Table 2. The values hereby indicated, discarded non-valid curves. The methodology used to discard non-valid curves was the one proposed by Wang and Wu [12].

The analysis of crack propagation during and after loading indicates that the behavior of the crack growth agrees with the theoretical behavior expected by Wang and Wu [12]. Crack started in the center of the specimen followed by its propagation vertically along the diameter. The density and porosity of specimens registered were 2.6 g/cm^3 and 16%, respectively.

Fig. 2 shows the behavior of the rupture tension and tensile strength of composites of HA reinforced with CNTs. Although standard deviation values interpolate, one can observe that the addition of CNTs tend to increase the mechanical properties of the composite until the percentage of 1 wt.%. A reduction in these properties can be interpreted when 2% of CNTs is added to the ceramic matrix. A large standard deviation is, however, observed for the values obtained for H2 which may induce to a mistaken interpretation. The microstructure of these composites were, therefore, evaluated as an attempt to better understand the mechanical behavior of such composites.

Analyzing the mechanical behavior of composites (mechanical strength versus amount of dispersed phase), a characteristic curve is usually obtained, where mechanical strength increases until an optimum point, followed by a diminution of its value. Theoretically, strength decreases due to a

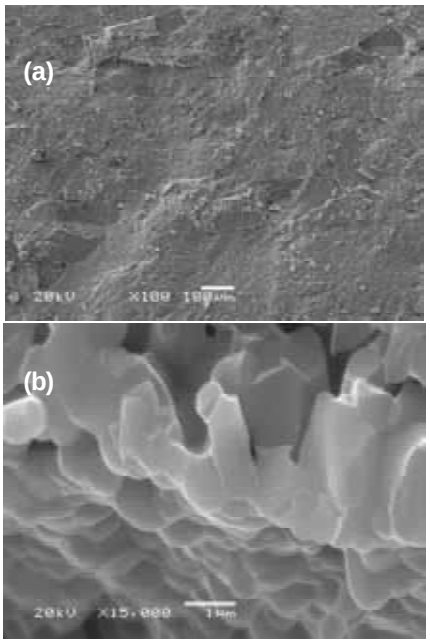

Fig. 4. SEM photographs of the face of a fracture for pure HA sample.

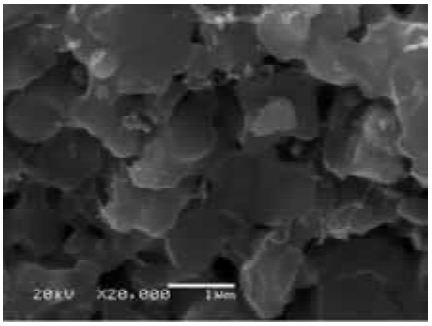

Fig. 5. SEM photograph of the fracture face of H05.

lack on the matrix continuity: the matrix is interrupted by the high quantity of reinforcement present in the microstructure. This reinforcement plays now a different role in the material and the previous reinforce effect may not exist anymore. This phenomenon can be seen as a saturation of dispersed phase in the matrix with consequent precipitation of a second phase that will be controlled by the reinforcement material. This second phase may act as a stress concentrator and as a result, mechanical properties drop down.

Fig. 3 shows a graph plotted for the values of the fracture toughness of composites investigated in function of the CNT content. If a curve is plotted along the values obtained, the behavior of this curve would follow the same behavior identified at the mechanical strength (Fig. 2). The increase of the reinforcement content enhances the fracture toughness of the composite until the amount of 1 wt.% of nanotubes. Subsequently, the values of fracture toughness decrease. It is relevant to mention that the addition of only 0.1 wt.% of CNTs propitiates a gain of 58% in the fracture toughness values. The standard deviation, however, is also observed.

In literature, up to date only few publications have evaluated the fracture toughness of HA/CNTs composites. Li *et al.* [10] analyzed it using the bending test and observed that the fracture toughness increased from 0.32 to 2.40 MPa $\sqrt{m}$ when 3 wt.% of CNTs was added to a matrix of HA. Balani *et al* [11] also inserted CNTs as reinforcement of HA to biomedical applications. The fracture toughness of such composites increased 56% when 4 wt.% of CNTs was added to a coating of HA. Their method of manufacture and analysis were, therefore, different from each other and also from the method here described. Given that, one can conclude that it is not possible to compare such results.

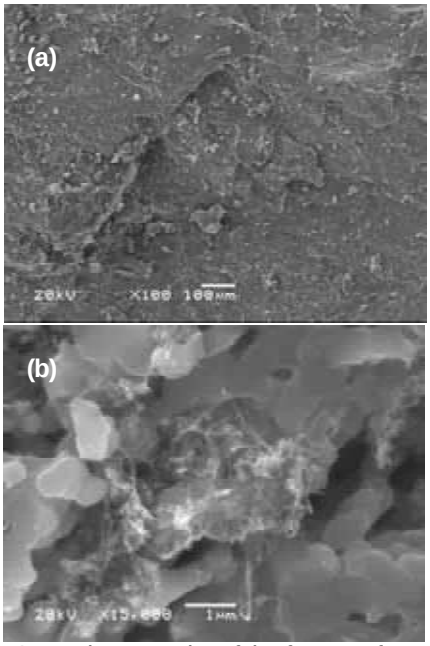

Fig. 6. SEM photographs of the fracture face of H2.

3.2. Scanning electron microscopy

The analysis of fractures of all the specimens carried out by Scanning Electron Microscopy (SEM) revealed a good matrix densification. Figs. 4a and 4b show micrographys of pure HA specimens.

Figs. 4a and 4b show a crack present in the material. Fig. 4b indicates the intra and intergranular fracture of the material. Photos showed on Fig 4 also indicate a high homogeneity of the material.

Fig. 5 shows a detailed photo of the fracture face of the composite HA reinforced with 0.5 wt.% of CNTs (H5). The presence of CNTs is evidenced, and nanotubes are well dispersed along the matrix. The image suggests that CNTs act as reinforcement

Table 3. Concentration of chemical elements obtained by chemical analysis performed on precipitates of composite H2.

Element	Concentration (%)
C	48.30
O	2.76
Si	0.90
P	8.43
Ca	21.78
Fe	9.96
Mo	0.75
Pt	7.13
Total	100.0

through the toughness mechanisms of bridging and pullout. A third mechanism, nevertheless, can be pointed from this image: the fracture of the reinforcement that is indicated by the arrows on the picture.

Micrographs taken from the fracture face of all composites presented a high amount of microcracks (not shown). It is possible that when the disk specimen is under load, compressive tension is concentrated at the vertical direction (between load sites) and tensile tension along the horizontal direction forming this way, such microcracks. These cracks indicate another toughness mechanism of the material. When microcracks are initiated, they consume part of the energy that would be used to propagate the main crack.

The microstructure of composites reinforced with 1 wt.% of CNTs (H1) start to indicate the presence of small agglomerates (not shown). Hence, the mechanical behavior of composites from the formulation H1 does not seem to be affected by these agglomerates. Possibly at this stage, the agglomerates are not significant along the matrix to have any relevant influence on the mechanical behavior of the composite.

Analyzing the fracture face of the composite HA reinforced with 2 wt.% of CNTs (H2), high amount of precipitates can be observed in the matrix, as seen in Fig. 6a (light spots).

Fig. 6b shows a precipitate present in the H2 composite in high magnificaton. These precipitates were hence, evaluated by performing chemical analysis to confirm the chemical composition of them. Chemical analysis pointed the presence of calcium phosphate (material of the matrix) and carbon (Table 3). Small quantities of iron and molybdenum identified during the chemical analysis are remnants from the catalyst used for the synthesis of CNTs. The small percentage of silicon is attributed to impurities during the fabrication of the composites. Nevertheless, these results confirm that these precipitates are CNTs.

Normally, when the reinforcement material agglomerates, it acts like a stress concentrator and the material becomes more fragile at the sites where the agglomerates take place. These precipitates tend to decrease mechanical properties and, consequently, failures are likely to initiate at these sites. This fact agrees with results obtained from the diametric compression test performed, where it is evidenced that the values of mechanical properties decrease for H2 composites. The agglomeration of CNTs, nevertheless, may be due to a saturation of CNTs in the matrix or their insufficient dispersion during the fabrication of the composites.

4. CONCLUSIONS

Mechanical properties were investigated by the diametric compression test using Brazilian disc geometry, and indirect tensile strength, rupture tension, as well as fracture toughness values were calculated.

Results obtained indicated that the mechanical properties of HA increased with the insertion of CNTs until an optimum point (1 wt.%) when CNTs start to perform as a stress concentrator, hastening the failure of the composite.

Dispersion of CNTs as well as toughness mechanisms were observed by TEM analysis. This analysis suggests the presence of bridging, pullout, and fracture of the reinforcement in addition to the microcrack initiation as toughness mechanisms.

REFERENCES

[1] C. Chai and B. Ben-Nissan // *International Ceramic Monoghaphs* **1** (1994) 79.
[2] M. Meyyappan, *Carbon Nanotubes: Science and Applications* (NASA AR Center: Moffett Field, CA. CRC Press LLC, 2005).
[3] Y. Gogotsi, *Carbon Nanomaterials* (Drexel University, Philadelphia, Pennsylvania, USA: Taylor and Francis Group, LLC, 2006).
[4] E.T. Thostenson, Z. Ren and T.-W. Chou // *Comp. Sci. Technol*. **61** (2001) 1899.
[5] S. Pegel, P. Potschke, G. Petzold, I. Alig, S.M. Dudkin and D. Lellinger // *Polymer* **49** (2008) 974.
[6] T. Wei, Z. Fan, G. Luo and F. Wei // *Mat. Lett.* **62** (2008) 641.
[7] G. Yamamoto, M. Omori, K. Yokomizo, T. Hashida and K. Adachi // *Mat. Sci. Eng. B* **148** (2008) 265.
[8] Y. Chen, Y.Q. Zhang, T.H. Zhang, C.H. Gan, C.Y. Zheng and G. Yu // *Carbon* **44** (2006) 37.
[9] A. A. White and S. M. Best **//** *Int. J. Appl. Ceram. Technol.* **4** [1] (2007) 1.
[10] A. Li, K. Sun, W. Dong and D. Zhao // *Mat. Lett.* **61** (2007) 1839.
[11] K. Balani, Y. Chen, S.P. Harimkar, N.B. Dahotre and A. Agarwa **//** *Acta Biomaterialia* **3** (2007) 944.
[12] Q. Z. Wang and L. Z. Wu // *Int. J. of Rock Mech. and Min. Sci.* **41** (2004) 245.
[13] Q.-Z. Wang and L. Xing // *Eng. Fract. Mech*. **64** (1999) 193.
[14] A.G. Osorio, I.C.L. Silveira, V.L. Bueno and C.P. Bergmann // *Appl. Surf. Sci.* **255** [5] (2008) 2485.