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Low temperature consolidation of hydroxyapatite-reduced graphene oxide nano-structured powders

Hassan Nosrati1, Rasoul Sarraf-Mamoory1*, Reza Zolfaghari Emameh2, Dang Quang Svend Le3, Maria Canillas Perez4, Cody Eric Bünger3

1Department of Materials Engineering, Tarbiat Modares University, Tehran, Iran
2Department of Energy and Environmental Biotechnology, National Institute of Genetic Engineering and Biotechnology (NIGEB), 14965/161, Tehran, Iran
3Department of Clinical Medicine, Aarhus University, Denmark
4Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain
*Corresponding Author, rsarrafm@modares.ac.ir

Abstract

In this study, hydroxyapatite-reduced graphene oxide (HA-rGO) powders were first synthesized in situ by a hydrothermal method. These powders were then consolidated using a cold sintering method. The solvent used in this method was water + dimethylformamide + Brushite which was added to the powders at different ratios. The sintered samples were then evaluated using X-ray diffraction, Fourier transforms infrared spectroscopy, Raman spectroscopy, High-resolution transmission electron microscopy, and Vickers microindentation techniques. The results of this study showed that the best conditions for the sintering of rGO-HA nanopowders were the temperature of 200 °C, the holding time of >30 min, and the pressure of 500 MPa. The highest mechanical properties were obtained when the solvent content was considered to be 20 wt%. The crack deflection and graphene bridging were among the mechanisms that increase the fracture toughness of these nanocomposites. By adding 1.5% rGO,
the fracture toughness of this nanocomposite (by the Cold Sintering method) was approximately equivalent to the fracture toughness of the spark plasma sintered HA.

**Keywords:** Hydroxyapatite, Graphene, Cold sintering, Nanocomposites

1-Introduction

Graphene-hydroxyapatite (HA) nanocomposites have received much attention in recent years. These types of nanocomposites have many uses as a biomaterial, either as coatings on other materials or as a bulk sample. The results of this researches show that these two phases have strengthened each other's properties well [1-4]. In graphene-HA nanocomposites, HA is the matrix phase. HA as a member of the calcium phosphate family has a hexagonal structure with a calcium to phosphate ratio of 1.67 and is very similar to the chemical composition of the bone. The biomaterial properties of HA, such as highly compatible with living bone tissues, scaffolding properties, biocompatibility, osteoconductivity, and bioactivity have made it widely used in biomedical fields [5-10]. Therefore, various methods have been used to synthesize this material such as combustion method [11], synthesis by solid-state reactions [12], electrochemical deposition [13], sol-gel process [14, 15], hydrolysis method [16], precipitation technique [17, 18], synthesis via sputtering [19], multiple emulsion system [20], biomimetic deposition of HA on GO [21], solvothermal and hydrothermal process [22, 23]. These methods have led to the synthesis of HA with different morphologies [24-29]. But despite all these properties, HA has poor mechanical properties, including the low fracture toughness, poor tensile strength, and weak wear resistance have led to restrictions on the use of HA as a bone replacement implant [30-33].

It is necessary to improve the mechanical properties of HA with a reinforcing material. Among the various materials used for this purpose, graphene has a high potential due to its good reinforcing properties. Graphene sheets with a carbon atom thickness, honeycomb structure, high
specific surface area (2630 m² g⁻¹), and their unique mechanical properties play a reinforcing role in these nanocomposites [34-39]. Apart from the excellent mechanical properties of graphene such as elastic modulus of 1 TPa and high fracture strength of 130 GPa, good biocompatibility of this material has led to consideration in biomedicine applications such as drug delivery, orthopedics, and bioimaging [40-43]. Published reports show that the addition of graphene and its derivatives (reduced graphene oxide and graphene nanoribbons) to HA, which is performed in various methods such as hydrothermal process, has always improved the mechanical properties of HA [44-46].

In some applications, such as implants, synthesized powders need to be made into bulk shape. Different methods such as hot pressing and spark plasma sintering have been used to consolidate these types of powders [47, 48]. But in most techniques, it is used at high temperatures. That high temperature also increases the cost of production, as well as the risk of material destruction. Recently, consolidation techniques at low temperatures have been very much considered. In this method, which is called cold sintering; it is used at temperatures below 300 °C, with a pressure of 100 to 500 MPa. In the first instance, a liquid phase as a solvent and very little is added to the interface between particles [49-51]. A portion of the particle surface is dissolved in the liquid phase. The powders are then compressed under external pressure and compression is facilitated by the presence of a liquid phase as a lubricant. Dissolution occurs in the interface between particles and sharp edges of particles. It precipitates between particles and hollows. Finally, after applying the heat and pressure and removing the liquid phase, the particles are connected to each other. Important factors of cold sintering process are powder materials, solvents, and physical parameters, but the solvent selection is more important. In some cases, additional heat treatment
for annealing is used [52- 58]. So far, very few reports have been published on cold sintering of hydroxyapatite containing powders [59- 61].

In this study, the hybrid nanostructured powders were synthesized using a high-pressure hydrothermal method utilizing the hydrogen gas injection to increase the reduction rate of GO. To investigate the final composite properties, a cold sintering method has been used. Sintered samples were subjected to a Vickers indentation technique for mechanical evaluation, X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR) analysis, and high-resolution transmission electron microscopy (HRTEM).

2-Experimental

The primary chemicals used in this study, along with their specifications, are listed in Table 1. The initial solution (S1) was first prepared (DMF + DI water with a volume ratio of 20:80). DMF was considered for better dispersion of GO in solvent [35, 45].

| Chemical                                               | Company & Purity               |
|--------------------------------------------------------|-------------------------------|
| Graphene oxide (GO) (CO₃Hᵧ)                           | Abalonyx, 25 g/L DMF          |
| Calcium nitrate tetrahydrate (Ca(NO₃)₂.4H₂O)           | Merck, > 99%                  |
| diammonium hydrogenphosphate ((NH₄)₂HPO₄)              | Merck, > 99%                  |
| ammonium solution (NH₄OH)                              | Merck, 25%                    |
| dimethyl formamide (DMF) ((CH₃)₂NC(O)H)                | Sigma Aldrich, > 99.8%        |

2-1-Synthesis of powders

Schematic 1 shows the rGO-HA powders synthesis process. The amount of rGO in this study is considered to be 1.5% by weight, because according to previous studies [4], this amount has had the greatest effect on increasing fracture toughness of rGO-HA nanocomposites (The
approximate amount of rGO was estimated by trial and error. Given the schematic 1, the following steps were performed in order.

i. The solution containing Ca\textsuperscript{2+} (4.7 grams of calcium nitrate tetrahydrate in 120 mL of S1) was added dropwise to a 20 mL stirred suspension of GO (HA/1.5% rGO) with stirring continued for 1 h (Schematic 1a, b).

ii. The solution containing phosphate ions (1.56 grams of diammonium hydrogenphosphate in 80 mL of S1) was dropwise added to the solution (Schematic 1c).

iii. The pH of the solutions was adjusted to >10 with ammonium solution.

iv. The resulting solution was poured into the Teflon (PTFE) vessel and transferred to the autoclave. The hydrothermal process was carried out for 5 h at 180 °C by injection of hydrogen gas at 10 bar (The volume of the PTFE container was 340 mL).

v. The powders were dried at oven for 12 h at 60 °C.

vi. The resulting powders were consolidated after drying and ball milling (250 rpm, 12 h).

**Schematic 1:** rGO-HA powders synthesis process

### 2-2-Consolidation of powders

Chart 1 shows the steps of consolidation. Figure 1 shows the system used for sintering, and Vickers indentation evaluation of the samples. At cold sintering stage, the mixture (M1) used consists of GO, brushite, and DMF. The mixture of brushite and GO was prepared just like the powders synthesis step (Schematic 1c, at this stage of powder synthesis, a mixture of brushite and GO was synthesized). The use of brushite was due to the fact that this calcium phosphate is converted to HA under high pressure and temperature conditions [23]. The amounts of GO-brushite powders were 5% by weight (DMF). The ratio of calcium to phosphate in this mixture was considered to be 1.67. A cold sintering method was chosen for sintering these powders.
(Chart 1). To form the ceramic pellets, 10 (I), 15 (II), and 20 (III) wt% of M1 mixed with 3 grams of rGO-HA powders using a pestle and mortar. The mixture was then placed in a die (30mm in diameter) and subject to uniaxial pressures of 500 MPa (Figure 1a). The die was held at room temperature (approximately 25 °C) for 10 min and then heated to 200 °C at a rate of 5 °C/min. The holding time of the samples at 200 °C was 60 min. The as-prepared ceramic samples (approximately 30 mm in diameter and ~2 mm in thickness) were dried at 200 °C overnight to remove possible residual solvent in an argon atmosphere. For comparison, a sample of pure HA (0% of rGO) was prepared under similar conditions with 20% of M1.

Before performing the above steps, considering the study sources, the temperature, time and pressure applied were first evaluated and the best conditions were considered for cold sintering with respect to the relative density obtained for each sample (described later).

**Chart 1: Consolidation steps**

The Archimedes method was used to calculate the relative density of sintered samples (ASTM C373-88) [47]. Micrometrics AutoPore III 9410 porosimeter (Mercury porosimetry recorded in the 5x10⁻³ -3x10² μm range) was used to evaluate the distribution of porosity.

**2-3-Vickers indentation**

Instrumented microindentation experiments were conducted on the polished surfaces of samples using Grindosonic tester with a Vickers tip at a maximum load of 1 N (ramp dwell time of 10 s). Nine tests (Figure 1b) were performed at different locations of each sample. Elastic modulus and hardness were calculated from the load-displacement curves (Figure 1c) using Olive-Pharr method [62]. The modified Antis method was used to evaluate the fracture toughness (KIC) of the samples (Eq. 2-1) [63]:

\[
K_{IC} = \lambda \left( \frac{W_i}{W_c} \right)^{0.5} \left( \frac{P}{C_{13}} \right)
\] (2-1)
W is the area below the load-displacement curve and W, the area below the unloading curve which corresponds to the elastic deformation. The energy W is the total of elastic and plastic deformation (W, and Wp respectively). λ is a dimensionless constant is close to 0.0498 for Vickers tip. C is the average crack length and P is the applied force. The use of experimental parameters is the major advantage of this method; it is easy to calculate when using instrumented indentation.

Figure 1: (a) schematic image of the cold sintering system, (b) Vickers indentation evaluation of the cold sintered samples

2.4-Characterization techniques

XRD (X’ Pert Pro, Panalytical Co.) was used to determine the phase constituents of the samples, contained a detector Cu Kα radiation (λ=1.5406 Å, 40 kV, 40 mA) and 2theta scanning range from 10° up to 80° in steps of 0.02°.

FESEM (Hitachi S4700 equipped with energy dispersive X-ray spectroscopy) and a Portable Scanning Electron Microscope (SEM, TM-1000) were used to observe the morphology of samples (mounted in an adhesive carbon film and Au coated by sputtering for its observation).

FTIR (VERTEX 70, Bruker Corp.) was used to identify the functional groups of the samples (resolution of 4 cm⁻¹, scan number of 8, spectral region from 400 to 4000 cm⁻¹ using 2 cm⁻¹ steps). The samples were prepared and mixed with potassium bromide (KBr) in a concentration of 1 mg powdered samples and 300 mg KBr. The mixture was pressed into discs having 1 mm thickness by applying 200 MPa pressure. The spectra were collected at room temperature (25 °C) and 60% relative humidity.

Raman spectroscopy (Renishaw inVia spectrometer) was used in the range of 300–3500 cm⁻¹, recording 5 times for 10 seconds of each accumulation, with a wavelength of 532 nm, green laser
line in a backscattering configuration using a microscope with a 100× objective, 100% power, and an acquisition time of 10 s, which had been excited from an argon ion laser.

HRTEM (TALOS F200A with a twin lens system, X-FEG electron source, Ceta 16M camera and a super-X EDS detector) was used to observe atomic structure of the samples and spatially resolved elemental analysis, with a spatial resolution higher than 2 nm. To study the atomic structure, fast fourier transform (FFT) and inverse fast fourier transform (IFFT) analysis were used. Imagej 1.52d and Diamond 3.2 softwares were used in this study.

3-Results and discussion

Figure 2 shows the FESEM image of the rGO-HA nanopowders and the TEM images of the rGO-HA nanopowders and HA nanorods synthesized via the hydrothermal method. As shown in the FESEM image (Figure 2a), the HA particles are attached to the rGO surfaces, edges and between the graphene sheets while the rGO sheets are folded and wrinkled. In some areas, HA particles have been agglomerated. The TEM image (Figure 2b) also shows the presence of rGO and HA. It is clear that morphology of the HA particles is nanorod shaped (Figure 2c). These nanorods are less than 50 nanometers in diameter while have longitudinal variations. The growth direction of the nanorods is in the C-axis [64-66].

**Figure 2:** (a) FESEM image of rGO-HA nanopowders (1.5% rGO) synthesized by the hydrothermal method, (b, c) TEM images of rGO-HA nanopowders (1.5% rGO) and HA nanorods

Figure 3 shows the EDS analysis of rGO-HA nanopowders (1.5% rGO) synthesized by the hydrothermal method, high-angle annular dark-field (HAADF) image of rGO-HA nanopowders, and elemental analysis of rGO-HA nanopowders. These findings showed that trace elements are present in the final synthesized powder and are distributed homogeneously. Previous researches
have included complementary analyzes that confirm the calcium to phosphate ratio of 1.67 [64-66].

**Figure 3:** (a) EDS analysis of rGO-HA nanopowders (1.5% rGO) synthesized by the hydrothermal method, (b) HAADF image of rGO-HA nanopowders, (c-f) elemental analysis of rGO-HA nanopowders

Figure 4 shows the results of designed experiments to find the best cold sintering conditions. As can be seen from the graphs, the best temperature was 200 °C (Figure 4c), the best holding time was 30 minutes (Figure 4b), and the best applied pressure was 500 MPa (Figure 4a) to reach the highest relative density. It should be noted that the solvent content in these samples was considered to be 20% by weight.

**Figure 4:** Results of designed experiments to find the best (a) uniaxial pressure, (b) holding time, and (c) cold sintering temperature

Figure 5 shows the XRD patterns of consolidated HA and rGO-HA nanocomposites for 10 (I), 15 (II), and 20 (III) wt% solvent along with the crystal structure of HA. According to the XRD pattern of the samples (Figure 5a), full conformity is achieved between the peaks obtained and the reference standard of pure HA (JCPDS 09-0432). Accordingly, the XRD pattern of the rGO-HA nanocomposites are quite similar to pure HA with high purity and hexagonal structure. According to studies, the famous GO peak is located at 2theta≈10. After reduction of GO to rGO, this peak is removed and a new one appears at 2theta≈26. Because of the amorphous structure of rGO, this peak is much weaker and wider than the HA (002) peak. Therefore, the rGO peak is covered by the HA (002) peak which is highly intensified due to its high crystallinity. Table 2 shows the specification of the main HA scatter planes obtained. According to the XRD pattern (002), (211), and (300) planes are the main growth planes in HA crystals.
where, (002) and (300) planes are perpendicular (Figure 5b). Increasing the amount of solvent has increased the intensity of the peaks in some directions and decreased in some directions. In the direction of the (002) plane, increasing the amount of solvent has reduced the peak intensity, but in case (211) and (300) planes the peak intensity has increased. Also, the peaks have been transmitted slightly to the left, which is probably due to increased pressure from the solvent steam. Comparing the peaks obtained, it is clear that the presence of rGO did not have much effect on the peaks movement [65, 66, 45, 47].

**Table 2**: Specification of the main HA scatter planes in rGO-HA nanocomposites

| (hkl)   | (002) | (211) | (300) |
|---------|-------|-------|-------|
| d-spacing (nm) | 0.343 | 0.281 | 0.271 |
| 2theta (deg)  | 26    | 32    | 33    |

**Figure 5**: (a) XRD patterns of consolidated rGO-HA nanocomposites for 10 (I), 15 (II), 20 (III) wt% solvent, and pure HA (b) crystal structure of HA

Figure 6 shows Raman spectroscopy and FTIR analysis for consolidated samples. The Raman spectroscopy has been done to confirm the presence of rGO (Figure 6a). The peaks obtained for nanocomposite samples are almost identical and confirm the presence of graphene sheets. In all spectrums, the peaks located at 962 cm$^{-1}$ are related to P-O symmetric stretching ($\nu_1$ PO$_4^{3-}$) in HA. The peaks located at 1350, 1600, and 2700 cm$^{-1}$ are related to D bond (symmetric oscillations of the A1g of carbon atoms with the sp$^3$ hybrid), G bond (shaking of the E2g of carbon atoms phonon with the sp$^2$ hybrid), and 2D peak (related to the number of layers of the graphene sheets) in rGO. The rGO-related Raman signals in this spectrums are much clearer than the HA signals, although its weight percent in the powders is much lower. The D and G peaks in
the rGO have not had any displacement at the Raman spectra, indicating that the rGO-HA nanocomposites have been successfully synthesized [65, 66]. The FTIR analysis reveals that the nanocomposites contain rGO and HA (Figure 6b). The peaks located at 565 cm\(^{-1}\) (P-O Bending), 925, 1035, and 1095 cm\(^{-1}\) (P-O(H) Stretching vibration), are related to HA. The peaks located at 1055 cm\(^{-1}\) (C-O Stretching vibration), 1230 cm\(^{-1}\) (C-OH Stretching vibration), 1395 cm\(^{-1}\) (C-O-H Deformation vibration), 1620 cm\(^{-1}\) (C=C Stretching vibration), and 1730 cm\(^{-1}\) (C=O Stretching vibration) are related to GO. The peaks located at 3400-3500 cm\(^{-1}\) (O-H Stretching vibration) are related to GO and HA. By comparing the FTIR patterns, it can be seen that the peaks obtained for the nanocomposites correspond to the pure HA peaks. These findings suggest that GO peaks have been moved upwards. The most significant changed peaks are the oxygen-containing functional groups on the GO surface (C-O, C-O-H, C=O) that have been moved upwards due to reduction of GO. However, there may still be oxide groups whose peaks are covered with HA peaks [44, 45]. By juxtaposing the finding of Raman spectroscopy and FTIR analyzes, it is clear that graphene sheets (in the form of rGO) are present in all nanocomposites.

**Figure 6:** (a) Raman spectroscopy and (b) FTIR analysis for consolidated samples for 10 (I), 15 (II), 20 (III) wt% solvent, and pure HA

Figure 7 shows the FESEM images of the samples fracture surface after cold sintering mechanism and the mechanism of cold sintering and post-drying, based on the experimental results. FESEM images show the presence of graphene in three dimensions. The graphene layers are assembled together (Figure 7a) so that the HA particles are placed between them (Figures 7b, 7c). As it is known, the presence of this three-dimensional structure causes incomplete compression during sintering and, in any case, increases porosity and it is expected that by increasing the amount of rGO the porosity will increase equally as previously this issue was
characterized by relative density. The presence of these porosities may in part reduce mechanical properties because they are localized to crack nucleation and to focus stresses, but according to previous studies, the presence of these porosities can increase osteoconductivity for these materials. According to Figure 7(d-f), the powders were first uniformly wetted by the solvent and mixed with brushite and GO (Figure 7d). Under uniaxial pressure, the hydrothermal reaction brushite and GO were redistributed and filled into the interspaces among the rGO-HA particles, thereby aiding the rearrangement of the particles. When the temperature increased up to 200 °C (Figure 7e), the brushite dissolved in water and DMF to form amorphous complexes. Because the temperature is higher than the boiling point of solvent, the water and DMF in the samples continuously evaporated until it was exhausted. The amorphous phase filled into the interspaces of the particles, and dense crystal/amorphous coexist ceramic were obtained. The amorphous phase transformed into the crystalline phase during the annealing process (Figure 7f). The grains grew gradually, and the interspaces were filled further.

**Figure 7:** (a-c) FESEM images of the samples fracture surface after cold sintering mechanism for III sample, (d-f) the mechanism of cold sintering and post-drying, based on the experimental results

Figure 8 shows the FESEM images of the pores in HA and rGO-HA samples (20% solvent), pore size distribution, and relative density of the samples. The FESEM images show that the presence of rGO has caused larger pores (Figures 8a, 8b). The pore size distribution diagram drawn using the Washburn equation [67] (Figure 8c) shows that the size of the porosity in the rGO-HA sample has increased. The total porosities were 3.5% for HA and 5% for rGO-HA nanocomposite. Also, densitometry results (Figure 8d) showed that the highest relative density was related to the III sample with 20% solution.
Figure 8: (a) FESEM images of the pores in HA sample (20% solvent), (b) FESEM images of the pores in rGO-HA sample (20% solvent), (c) pore size distribution, (d) relative density of the samples

Figure 9 shows the force-displacement diagrams of the sintered samples. To compare the effect of solvent percentage during the cold sintering process on the final properties of the nanocomposites, all samples were subjected to a Vickers test. As the curves show (Figure 9a) the contact depth for (I) is greater than that for (II) and (III) samples. In other words, more force is needed to achieve a constant contact depth in (II) and (III). This conclusion is also valid for (III) compared to (II). Considering the same conditions for the preparation of samples, it is likely that another mechanism including a higher degree of GO reduction or higher crystallinity, and a stoichiometric most likely is responsible for this phenomenon. Also, according to these diagrams, the elastic work in (I) is greater than the other samples. Also, the plastics work is slightly higher in (I), but with a smaller ratio, which is obtained from the surface below the curves. In these diagrams, the transition to the left means the improvement of mechanical properties. In Figure 9b, the force-displacement curve shows that the Vickers indenter has hit a hole in its path. The part shown with the arrow shows the contact depth where the cavity is located. These changes are more evident in samples with more porosity. In some curves, these changes appear several times in a curve. These cases involve some errors in the calculations. The indentation analysis results (Table 3) show that the hardness, the Young's modulus of (II) and (III) samples are higher than that of (I). Also, (III) showed better mechanical properties than the (II). The reason for this increase in mechanical properties should be examined from two perspectives. First, increasing the hydrothermal pressure increases the crystallinity of the primary powder and improves the properties of the HA, and secondly, the presence of more hydrogen gas.
increases the reduction degree of GO and increases the mechanical properties of the graphene sheets [45, 47]. The fracture toughness of this nanocomposite (III, by the Cold Sintering method) was approximately equivalent to the fracture toughness of the spark plasma sintered HA [68].

**Table 3:** Mechanical properties of the samples extracted from load-displacement diagrams

| Sample | Hardness (GPa) | Elastic modulus (GPa) | Fracture toughness (MPa.m\(^{0.5}\)) |
|--------|----------------|-----------------------|--------------------------------------|
| HA     | 2.5±0.5        | 58±6.4                | 0.41±0.13                            |
| (I)    | 3.1±0.4        | 79.5±5.7              | 0.85±0.11                            |
| (II)   | 3.7±0.2        | 87.2±4.6              | 0.97±0.09                            |
| (III)  | 4.3±0.3        | 95.7±5.2              | 1.12±0.03                            |

**Figure 9:** (a) force-displacement diagrams of the sintered samples, (b) indentation affected zone

Figure 10 shows the FESEM images of cracks formed during mechanical analysis on sintered samples. In these images, crack bridging and the crack deflection are shown. Graphene sheets have increased the samples fracture toughness with these mechanisms. The graphene's pull out energy is much higher than the energy needed to pull out of HA from each other because graphene sheets have a higher specific surface [45].

**Figure 10:** FESEM images of cracks formed during mechanical analysis on sintered samples (III) with 20% solvent

Figure 11 shows the interface analysis between the two phases after consolidation. In this figure, HA, graphene sheets, and three areas identified for analysis. Figure 11a shows the HA and rGO phases together. In Figure 11b, the d-spacing of graphene sheets is 0.34 nm, which shows that GO is well reduced. In Figure 11c, the d-spacing confirms the growth of (211) planes in HA. Figure 11d shows that the two phases are well connected. Previous researches have confirmed that there is a coherent interface between the two phases of HA and rGO [4, 69, 70].
**Figure 11:** Interface analysis between the two phases after consolidation for III sample, (a) HRTEM image of the consolidated sample, (b) FFT and IFFT analysis of the A area, (c) FFT and IFFT analysis of the B area, (d) FFT and IFFT analysis of the C area

**4-Conclusions**

The results of this study showed that the best conditions for sintering of rGO-HA nanopowders were the temperature of 200 °C, the holding time of >30 min, and the pressure of 500 MPa. The highest mechanical properties were obtained when the solvent content was considered to be 20 wt%. By increasing the amount of solvent up to 20 wt%, hardness, elastic modulus and fracture toughness of rGO-HA nanocomposite reached values of 4.3±0.3 GPa, 95.7±5.2 GPa, and 1.12±0.03 MPa.m^{0.5}, respectively. By adding 1.5% rGO, the fracture toughness of this nanocomposite (by the Cold Sintering method) was approximately equivalent to the fracture toughness of the spark plasma sintered HA. The interface between the two phases in this nanocomposite was coherent. The crack deflection and graphene bridging were among the mechanisms that increase the fracture toughness of these nanocomposites.

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(a) M1 was mixed with 3 gr of the rGO-HA powders

(b) The mixture was placed into a die (30 mm in diameter) and subjected to uniaxial pressure of 500 MPa

(c) The die was held at room temperature for 10 min and then heated to 200 °C at the rate of 5 °C/min

(d) The holding time of the samples was 60 min

(e) Drying at 200 °C overnight
350x172mm (300 x 300 DPI)
(a) HA
rGO
1 μm
(b) rGO
HA
100 nm
(c) HA
100 nm

397x351mm (300 x 300 DPI)
(a) 

Load (N) vs. Displacement (nm) for samples I, II, III, and HA.

(b) Inset image showing a scale bar of 30 µm.

436x326mm (300 x 300 DPI)
