Enhanced elastic behavior of all-carbon composites reinforced by in-situ synthesized morphed graphene

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ABSTRACT
We present the mechanical properties of all-carbon composites reinforced with in situ incorporated morphed graphene nanostructures by means of high energy ball milling and spark plasma sintering. The composites demonstrate enhanced elasticity for carbon sp³/sp² ratio \( \frac{1}{4} \). High resolution TEM characterization and molecular dynamics simulations show that this bonding type ratio is due mostly to the morphed graphene structures. Specifically, the presence of Rh6, crosslinked graphene-like, nanostructures is attributed to the enhanced elastic properties of these all-carbon composites. The improvements in mechanical properties is approximately 2 orders of magnitude when compared to similar composites produced with graphene.

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1. Introduction

The development of all-carbon composites reinforced with carbon fibers has been investigated for several decades targeting key applications such as: thermal shock, wear, ablation, toughness and friction resistant [1]. The carbon fibers themselves have strengths of up to 4 GPa [2], that is, about four times stronger than modern steels [3]. The discovery of advanced carbon nanostructures has opened a new era in materials science, engineering and technology [4–7]. Pristine CNT have shown strengths [8] two orders of magnitude higher than that of advanced steels, titanium and super alloys [9]. Carbon reinforcements are desirable for their mechanical, electrical and thermal properties [10,11] and have been used in polymeric [12–14], textiles [15], metallic [16–19] and ceramic [17,20–23] matrices. Well documented improvements for a variety of matrices include: hardness [17], toughness [20,24], electrical conductivity [22,24], and piezoelectric characteristics [25]. One of the most effective manufacturing practices involve mechanical milling and spark plasma sintering [22,26]. The improvement of properties of carbon reinforced materials, however, is typically below theoretical predictions by 2–3 orders of magnitude [18,27] mainly due to poor percolation, agglomeration and unwanted chemical reactions.

In the present work we provide evidence that the improved mechanical behavior observed in all-carbon composites is due to carbon allotropes called morphed graphenes. The composites were prepared from fullerene soot using mechanical milling and consolidated by means of spark plasma sintering. A unique characteristic of our composite processing technique is the in situ synthesis of morphed graphenes during milling. The results presented herein are supported by evidence gathered from various characterization methods, including X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and numerical simulations based on molecular dynamics (MD).
Mechanical properties were characterized by means of nanohardness testing and successfully reproduced by MD simulations.

2. Experimental

The starting material was fullerene soot purchased from SERES Company. The milling was conducted on batches of 1 g in a high energy ball mill (SPEX) for 0, 0.5, 2, 5, 10, 20 and 50 h using steel hardened mills and milling media. The sintering was carried at 1500 °C in a spark plasma sintering system (SPS) at a heating rate of 140 °C/s for 1 min. The consolidated samples have dimensions of 12 mm in diameter and 4 mm in thickness. Sintering at lower temperatures was carried; however, the consolidation and densification were not as satisfactory. The sintered products were polished following standard metallographic procedures to a final finishing of 0.05-μm using a vibratory polisher for 3 h for metallography and nanohardness.

X-ray diffraction (XRD) was carried in a D5000 SIEMENS diffractometer equipped with a Cu tube and a characteristic \( K_a = 0.15406 \) nm operated a 40 kV and 30 mA. The SEM work was carried out on a FEI XL-30FEG operated at 15 kV. The transmission electron microscopy was conducted on the TEAM 0.5 microscope operated at 80 keV. Dose rate in use is below 10 cps equivalent to 12 \( e^{-}/Å^{2}s \) per image for a total dose of around 500 \( e^{-}/Å^{2} \). The Raman characterization was done on a confocal micro-Raman microscope XploRA™, Horiba JY. A 638 nm diode laser was used for excitation. The nanohardness testing was carried in a Hysitron TI-900 Tribolindenter™ to obtain quantitative nanomechanical test results and real-time data collection. The loading environment is as follows: 7000 μN and 5 s dwelling time. The transducer used for this evaluation was a SN5-138-189 with a maximum Force: 9.562 mN. The hardness, stiffness and modulus were calculated following the standard procedures proposed in Ref. [28].

3. Experimental results and discussion

Fig. 1a presents the Raman spectrum of carbon soot used for synthesis of the all-carbon composites. It is worth noting that similar spectra are characteristic for a wide range of alternatives carbon with quasi-amorphous characteristics [29]. The spectrum features four main bands located at approximately 1320 cm\(^{-1}\), 1580 cm\(^{-1}\) and 2665 cm\(^{-1}\) corresponding to the “D”, “G”, “2D” bands along with the combinational “D + G” two-phonon scattering [30] at 2900 cm\(^{-1}\). It is expected that the main structure is a graphitic sp\(^2\) type. The XRD results presented in Fig. 1 (b), however, show only one reflection at about 26.5° - 20 degrees that is typical of the benzoic rings of graphitic structures. In graphite it corresponds to (002) XRD reflection. The absence of other reflections in the XRD spectra is a clear indication that there is no long range ordered graphite structure in this material. Instead, the order is short range, similar to that in amorphous carbon [27,31] and it is attributed to staking of sp\(^2\) honeycomb lamellas. The HRTEM results in Fig. 1 (c) demonstrate that the raw material is amorphous with no evidence of graphitic domains. In conclusion, our

![Figure 1](image-url)
characterization confirms that the fullerene soot is mainly composed of short range order graphitic-like carbon.

The mechanically milled powders show a clear ordering in carbon nanostructures as a function of time. The prevalent mechanisms is associated with cold welding [32,33]. The Raman spectra in Fig. 1 (d) show the effects of milling on soot as a function of time and demonstrated that the largest amount in graphene (sp²) bonding is observed at short milling times (<10 h). The intensity and width of the D band indicates that part of the carbon is amorphous and this is further confirmed with the HRTEM images in Fig. 1 (c) and 1(g–k). As far as contaminations are concerned, Fig. 1 (c) shows that hardened steel media introduce less impurities than zirconia and tungsten carbide media. The grain grow was calculated based on the Scherrer method and the results are presented in Fig. 1 (f).

Since the contamination of ceramic milling media (Fig. 1 (e)) was significantly above trace levels, we limited the research to steel media where the contamination was always way below 1 wt% Fe. The evolution of carbon nanostructures in material particles produced by varying milling time is depicted in Fig. 1(g–k). Previously, we have proposed the carbon structure called morphed graphene that has been characterized extensively [31] and modelled numerically. At short milling time one can observe double or triple layer graphenes followed by a multi-layer graphenes and then a mix of multi-layer graphene and morphed graphenes. For longer milling time the dominating graphene-like phase is morphed graphene (e.g., Rh6 and Rh6-II) [31,34] though still embedded in amorphous carbon.

A higher abundance of Rh6 and Rh6-II in carbon nanostructured phases is observed in sintered samples of carbon milled longer than 10 h as demonstrated by HRTEM results shown in Fig. 2. A notable distinction between graphene and the morphed graphene is the d-spacing. The d-spacing in graphene is 0.33 nm [35], in morphed graphene varies from 0.35 to 0.37 nm for the Rh6 and Rh6-II structures, respectively [31,36]. Fig. 2 (a) shows a distribution of the phases identified in the microstructure. One of the very distinctive characteristics between the morphed graphene and graphene is an intermediate plane at approximately 0.175 nm in the former. HRTEM results in Fig. 2 reveal multiphase carbon composites that consist of graphene, Rh6, and Rh6-II embedded in amorphous carbon matrix. After the sintering, the carbon material reveal increased ordering or crystallinity of the phases and the amount of morphed graphene. To get further insight into the carbon structures we measured the sp² and sp³ bonding balance using XPS. SEM images of the sintered composites are presented in Fig. S1 (e–f) in which large graphitic layers are seen as well as the layered structured of the consolidated product.

The XPS results shown in Table 1 reveal that the density of sp³
bonding increases with milling time, reaching a maximum of 18.2% in the milled samples for 20 h, and it is attributed mostly to the Rh6-II phase. The SPS process further promotes the sp³ bonding, all sintered samples have more sp³ phases than in the milled ones. The increase of sp³ bonding reaches its maximum for the sintered plastic deformation under the indenter is basically nonexistent the acronyms N, S, M stand for hardness, stiffness and modulus. [31,38]. The XPS results show that Fe contamination increases strongly after 20 h of milling and to investigate the actual bene-
s(see, e.g., Fig. S2 (b)) but some residual displacement remains. This indicate a relaxation process typical for elastoplastic materials [28] with weak plastic deformation in contrast to that in martensite as shown in Fig. S2 (a). Table 1 presents the nanoindentation results. The higher hardness is achieved in composites milled for less than 10 h. The sample milled for 20 h possess the best elastic properties that is attributed to the presence of sp² carbon, mainly Rh6 structures, as demonstrated in Fig. 1(g–k) and Fig. 2. The elastic behavior deteriorates with increasing of sp³ bonding. Additionally, similar trends are observed for the stiffness and modulus. Therefore, the main elastic contributors herein are the morphed graphene type Rh6 having modulus of up to 1 TPa [39]. The outstanding recovery of the samples after nanoindentation tests results in permanent deformations 13.5%, 8.5% and 14.9% milled for 0.5, 2 and 20 h, respectively. The loading range in our nanoindentation test is two orders of magnitude higher than previously reported for composites manufactured under comparable conditions using pure graphene [28]. Here we can conclude that the presence of morphed graphene in all carbon composites have outstanding benefits.

The mechanical milling process is effective in two ways: at early stages it sponsors the synthesis of graphene and morphed graphene (Rh6) and as the milling time increases (above 10 h) the synthesis of Rh6 and Rh6-II prevails. In a similar work pure graphene platelets (no milling involved), sintered using SPS, show a plastic deformation of ~50% [40]. In this work the loading environment is 120 μN, that is, orders of magnitude lower than the load that applied (7 mN) in our tests and yet the composites behaving purely elastic. The mechanical testing results present a remarkable elastic behavior that has not been reported and is attributed to the in situ synthesis of morphed graphene, particularly the Rh6.

### 3.1. Molecular dynamics simulations of elastic properties

Although the elastic behavior of the material has been enlightened from an experimental mechanics viewpoint, its origin at the atomic level is not completely understood. In order to gain further insight into the enhanced elastic properties of the nanocomposites presented here, we performed molecular dynamics (MD) simulations on cell models with material bulk density in the range of our experimental results, that is, between 2.0 g/cm³ and 2.3 g/cm³. Initial structures are based on a graphite crystal cell with periodic conditions on the three axes. The cell dimension along the x and y axes were fixing to 54.12 Å, whereas the length along the z axis change as function of bulk density. Subsequently, Rh6-II nanoparticles with diameters of 20 Å were incorporated to these cells and the entire model relaxed by a thermally annealing in molecular dynamics (MD) process using the GULP code [41] and the Tersoff force field [42,43]. From these three dimensional bulk models, we created a series of surface models with an empty space in the cells along [001] direction. A full outline of the construction of the

![Fig. 3. Nanoindentation results for SPS consolidated samples milled at different times. The composition and mechanical properties of the samples are given in Table 1.](image-url)
models and a more detailed description is presented in Fig. S3 of the Supplementary Information. From the set of bulk cells generated, we have selected 4 cells with sp³/sp² hybridization ratio that is closest to experimental one reported in Table 1. The cutoff radius to determine the coordination of an atom was selected considering the first minimum of the function of radial distribution of the material, which in this case was 1.9 Å. This criterion is commonly used for the study of amorphous materials which meets the experimental and theoretical values in carbon-based materials. A detailed description of the distribution of the sp¹, sp² and sp³ fractions inside the simulation cells using this geometric criterion is given in Figs. S4–S7 of the Supplementary Material.

The elasticity of the models were determined by emulating the nanoindenter penetration process on the surface. We choose a rigid capped nanotube as a nanoindenter that was introduced in a succession of steps on the surface allowing a surface model relaxation each time the nanoindenter penetration depth was increased. Relaxation of the system was obtained through a thermal MD annealing process at 1000 K during $1 \times 10^4$ simulation steps and using a time step of 1 fs. As a result of this succession of simulations, the energy of the system is mapped as a function of penetration depth. Because simulations at atomistic level that reach micas sizes are computationally nonviable, it is not possible to reach the experimental nanoindentation depths. To overcome this obstacle, we extrapolated the simulated behavior along the first nanometers of penetration to micrometric depths through polynomial fitting; for details see, e.g., Figs. S4–S7. Finally, the deformation force or the load was determined from the energy vs depth curves through the first derivative $F = \frac{dE}{dx}$, where $dx$ is the penetration depth. The comparison between the extrapolated load vs depth curves obtained from simulation data and the experimental nanoindentation results is shown in Fig. 4.

The force field used in the MD simulation was limited in reproducing completely the Rh6 structure. The crosslinking observed in MD simulations between the graphite sheets, however, resemble those found in crystalline structures type Rh6. An example of this similarity is given in Fig. 5, in which the simulated spongy structure in Fig. 5(a and b) concurs with the crosslinked graphene-like layers of the Rh6 structure in Fig. 5(c and d). We believe that the crosslinking that is inherent for the Rh6 and Rh6-II structures plays an important role in enhancement of mechanical properties of all-carbon composites.

4. Conclusions

We have presented the mechanical properties of all carbon nanocomposites prepared with in situ incorporated morphed graphene structures. The presence of Rh6, sp² type, morphed graphene is attributed to the enhanced elastic properties of these all carbon nanocomposites over those prepared only from graphene. The MD modeling shows that the material densities that best reproduce the mechanical properties of the reported all-carbon composites are between 2.1 and 2.3 g/cm³. In this density range it is possible to generate bonds between the graphite sheets, crosslinks, which improve their elastic response with respect to the non-crosslinked graphite sheets. The similarity of the simulated crosslinking
structure of graphene sheets with that of Rh6 and the experimental (HRTEM) observation of Rh6 in the all-carbon composites lend support to the claim that Rh6 morphed graphene is mostly responsible for the enhanced elastic properties of the composites.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbon.2019.07.012.

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