

# Interfacial Nanostructure Dictates Macro-structural Properties of Carbon-carbon Composites

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## ABSTRACT

Carbon-carbon composites, originally developed for aerospace applications, are materials that consist of a carbonaceous matrix with an embedded carbon filler providing the required reinforcement for thermal and mechanical stability. An important aspect of composites is the interdependence of the matrix and additive phases to strengthen one another and the material as a whole with the interfacial stress transfer being key to this reinforcement. The bonding between the matrix and the additive is crucial in understanding its behavior at the macro-scale. Understanding the material's nanostructure to shed light on its interfacial dynamics is an unexplored aspect owing to experimental and probing challenges. This study attempts to probe nanostructure impact on carbon-carbon composites by embedding pre-synthesized nano-carbons with diverse morphology - 1-dimensional nanotubes, and 2-dimensional graphene sheets - in an amorphous carbonaceous matrix of varying chemistry.

**Keywords:** Carbon, composite, graphitization, graphene, templating.

## 1 INTRODUCTION

Carbon-carbon (C-C) composites are a unique class of materials consisting of a carbon filler within a carbon matrix [1,2]. This carbon matrix is typically formed after carbonization and graphitization of a carbon precursor material [3,4]. Fibers made from carbon precursors such as polyacrylonitrile (PAN), rayon or pitch are typically used as the filler weaved in varied directions to get desired properties within a resin or pitch-based matrix formed from a liquid precursor or by impregnation within a matrix formed from a gas precursor [1,5]. These are also referred to as carbon-fiber reinforced carbon composites [6,7]. Carbon-carbon composites have found application in the aerospace industry as aircraft disc brakes and rocket re-entry nose cones, for instance, because of their superior tensile strength, electrical conductivity, and integrity at high temperatures [5,6]. More recently, other nanomaterials such as graphene and carbon nanotubes (CNTs) have been used as fillers in carbon-polymer composites with subsequent tests of its mechanical and electrical properties [8–11]. These composites are different from the aforementioned C-

C composites because they use a polymer as their matrix without undergoing the carbonization-graphitization treatment process. Other works have studied the properties of C-C composites in detail. For instance, preferential alignment of carbon layer planes on carbonization-graphitization heat treatment and its subsequent effect on bulk properties has been talked about in the late 1900s viewing composite properties in light of the differences in the degree of graphitization and subsequent stresses that the filler and matrix are subjected to when heat treated [6,12,13].

When it comes to composites, carbon has also been used as a template [14] or been templated off of other materials like silica [15]. A template is referred to as something that establishes a pattern to guide the formation of a second material around it. This concept is important and largely unexplored in C-C composites. Templating in C-C composites refers to the interfacial interactions between the matrix and the filler to reinforce each other's structure at a molecular level resulting in a 'molecular template' of sorts with either one forming a pattern under the influence of the other material. This interaction and the importance of studying it to further our understanding of its effect on bulk material properties have been addressed at the micro-scale using polarized light microscopy [16] and scanning and transmission electron microscopy [17].

This work aims to address the effect of this filler-matrix interdependence in C-C composites by visually analyzing their interfacial interaction at the nanometer scale using high-resolution transmission electron microscopy (HRTEM). Mechanical hardness, observed as a consequence of this interaction, is inferred using nanoindentation.

## 2 EXPERIMENTAL METHODOLOGY

C-C composites have been synthesized by mixing pre-synthesized nano-carbons with a matrix. These nano-carbons are multi-walled carbon nanotubes (MWCNTs) 10-30  $\mu\text{m}$  in length and graphene nano-platelets with an X-Y dimension of 1-2  $\mu\text{m}$ . These have been embedded in a matrix of novolac, a phenolic resin with a formaldehyde to phenol ratio of less than 1. Here, a 0.8 molar ratio of laboratory grade formaldehyde to phenol was heated on a hot plate under continuous magnetic stirring to which 5 ml hydrochloric acid was added with a pipette to catalyze the

polymerization reaction. Once initiated, a sonicated solution of the nano-carbon in methanol was immediately added to the mix and allowed to set, forming novolac impregnated with the nano-carbon. Nano-carbon doping is approximately 5% by weight of the composite. Once cooled and set, the material was subjected to carbonization under an inert atmosphere at 800°C for 5 hours in a tube furnace. This was followed by high-temperature graphitization heat treatment at 2700°C for one hour in a Centorr Vacuum Industries graphitization furnace, under an inert. The graphitized composites were then analyzed for their nanostructure in a transmission electron microscope (TEM) by depositing a few drops of a sonicated solution of the composite in methanol on lacey C/Cu 300 mesh grids.

Nano-indentation was done using a Hysitron TI-900 equipped with a diamond tip that indents the sample. Samples are prepared by creating a sample mount in epoxy and polishing the cured sample to a flat surface to have minimum tilt ( $< 1^\circ$ ) and surface roughness ( $< 100$  nm).

### 3 RESULTS AND DISCUSSION

Novolac, when subject to carbonization and high-temperature heat treatment by itself forms a non-graphitizing carbon, as shown by the fullerenic structure in Figure 1.

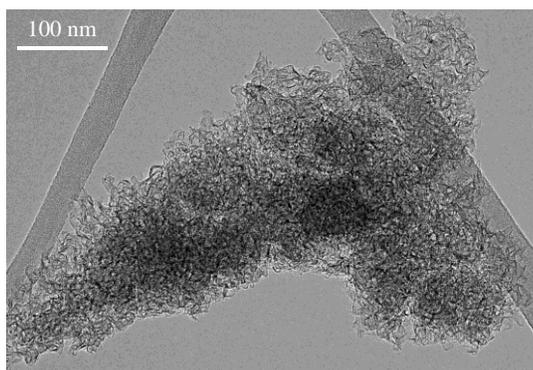


Figure 1: TEM micrograph showing nanostructure of novolac after high-temperature heat treatment.

Figure 2 shows contrasting nanostructure of a novolac-graphene nano-platelet composite when compared to a similar composite but now embedded with MWCNTs instead. This difference in material nanostructure compared to pure novolac and observed by changing only the filler is indicative of interfacial templating where the nanostructure of novolac, as it sets into its polymerized form, is governed by the filler interface that acts as a template – redirecting the nanostructure of the adjacent novolac as it bonds with the filler to form an integral composite material.

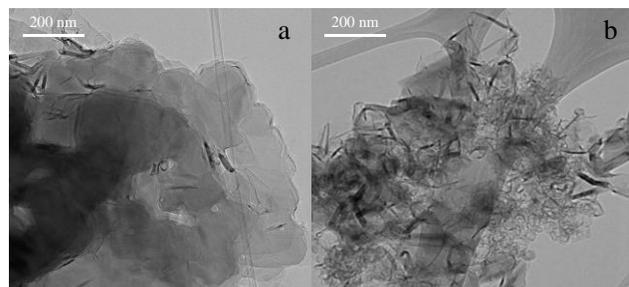


Figure 2: Novolac embedded with (a) graphene nano-platelets and (b) MWCNTs as fillers.

The graphitizing nature of the novolac-graphene nano-platelet composite is best illustrated by the selected area electron diffraction (SAED) pattern shown by in Figure 3. The sharp distinction between the (100) and (101) diffracting beams is characteristic of high crystallinity. The arrow points to fragments of non-graphitized novolac at the periphery of the graphitized composite. This is evidence of the novolac forming around the platelet and resulting in a graphitized composite by templating off of the embedded graphene.

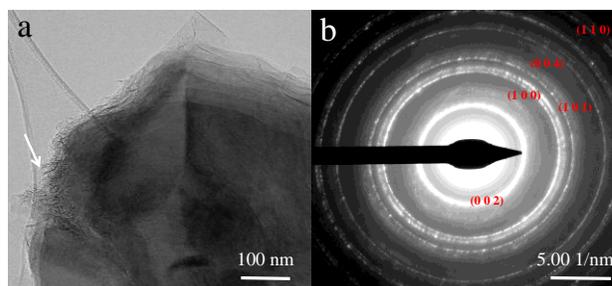


Figure 3: (a) Micrograph showing novolac formation around the graphene platelet and (b) SAED pattern of the resulting graphitized composite.

The two composites' response to nano-indentation is summarized in Table 1. The novolac-graphene nano-platelet composite shows greater hardness, measured by nanoindentation, as compared to the novolac-MWCNT composite. This indicates greater reinforcement in the former composite when compared to the latter. Again, this is contrary to traditional hardness associated with non-graphitizing carbons making the former composite an intriguing material for further study of its hardness and mechanical properties given its graphitic nanostructure.

Filler/Property	Graphene Nano-platelets	MWCNT
Hardness (GPa)	2.70	1.70
Contact Depth (nm)	260	372

Table 1. Material hardness and depth of contacts obtained from nanoindentation measurements.

It is shown that the filler provides a physical boundary that directs the development of the matrix structure during thermal processing, consequently impacting the material's bulk properties such as its mechanical hardness. Other analyses, yet to be completed, include differences based on the material's electrical conductivity and mechanical strength that will be telling of the material's performance at the macro-scale. Increased interfacial structure and stronger matrix-additive interaction can then be correlated to the composite's thermal and mechanical properties.

#### 4 SUMMARY

Novolac, a non-graphitizing carbon, is shown to template around nano-carbon fillers forming composites with variable nanostructure dictated by the filler used. With graphene nano-platelets as a filler, novolac forms around it resulting in a graphitic composite, despite novolac being a non-graphitizing carbon (precursor). Novolac mirrors the graphene layer plane arrangement and likely forms subsequent layers following the interfacial guide as the material is graphitized. Using other fillers such as MWCNTs on the other hand, results in a composite that lacks the organized nano-, micro-structure and interfacial reinforcement, thereby resulting in a reduced hardness as compared to the graphitized composite.

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