

## COMMUNICATION

# Enhanced mechanical properties of epoxy-matrix nanocomposites reinforced with graphene synthesized in atmospheric plasmas

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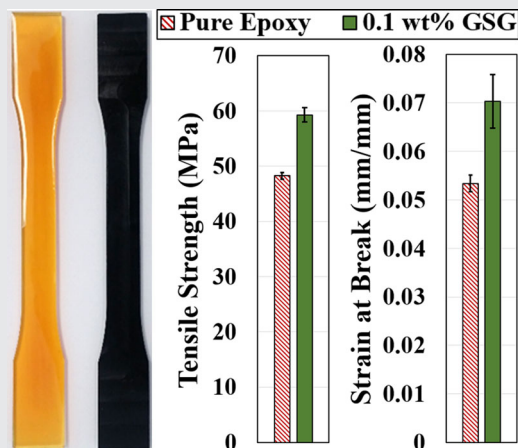
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## Abstract

Graphene can be synthesized in the gas phase using atmospheric plasmas. Gas-phase-synthesized graphene (GSG) possesses features that make it a promising filler material for enhancing the properties of polymers. In this study, epoxy-matrix nanocomposites reinforced with GSG were investigated. Mixing GSG with epoxy showed that the nanomaterial effectively disperses and resists aggregation in polymer resins. Significant increases in both strength and strain at break were revealed through the tensile testing of GSG-filled nanocomposites. In contrast, nanocomposites containing graphene nanoplatelets exhibited enhanced strength but diminished strain at break. Imaging of nanocomposite fracture surfaces by scanning electron microscopy indicated considerable matrix reinforcement by GSG. These results show that unique strengthening mechanisms exist in polymers reinforced with graphene synthesized in atmospheric plasmas.



## KEYWORDS

graphite, microwave discharges, nanocomposites, nanotechnology

## 1 | INTRODUCTION

Graphene, a single layer of carbon atoms densely packed in a honeycomb lattice, has a Young's modulus of 1,000 GPa and an intrinsic strength of 130 GPa.<sup>[1]</sup> The remarkable mechanical properties of graphene have driven countless researchers to incorporate the nanomaterial into numerous polymers to create high-strength

graphene-based nanocomposites (GNCs).<sup>[1–3]</sup> GNCs can enable a diverse range of applications, such as automobiles and aircraft with increased fuel efficiency and performance. Pristine graphene flakes can be created through the repeated peeling of highly oriented pyrolytic graphite (HOPG) with an adhesive tape.<sup>[1]</sup> However, GNCs require much higher quantities of graphene than the peeling of HOPG can produce. Therefore, the vast

majority of published studies on GNCs have used carbon nanomaterials obtained through top-down methods that exfoliate naturally occurring flake graphite into graphene oxide (GO), reduced graphene oxide (RGO), or graphene nanoplatelets (GnPs).<sup>[1–3]</sup>

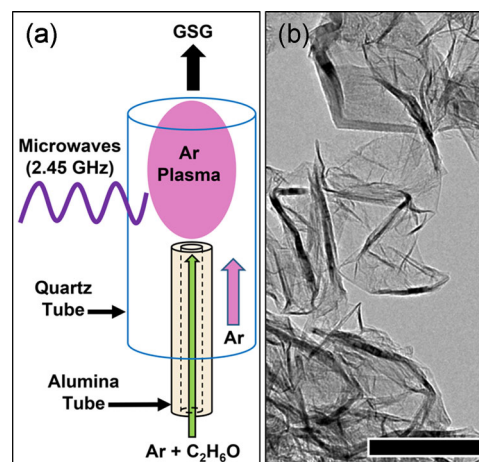
Parameters that affect the mechanical properties of GNCs include the structure, dimensions, preparation method, filler–matrix interactions, dispersion, and orientation of graphene in polymer matrices.<sup>[1–3]</sup> Despite the massive investment in research, GO, RGO, and GnPs have three issues that continue to limit enhancements in the mechanical properties of GNCs: (a) defects, (b) dispersion, and (c) aggregation.<sup>[1–3]</sup> Defects that are intrinsic to the structure of GO, RGO, and GnPs make these materials up to five times weaker than pristine graphene.<sup>[1]</sup> Obtaining homogeneous suspensions of these carbon nanomaterials in polymers is challenging, and numerous dispersion strategies that have been successful in laboratories are impractical for the large-scale manufacturing of GNCs.<sup>[3]</sup> Once dispersed in polymers, GO, RGO, and GnPs also have a propensity to aggregate, especially at higher filler loadings. Aggregated regions reduce the exposure of filler surfaces to polymers and act as stress concentrators, which detrimentally affect the mechanical properties of GNCs.<sup>[1,4]</sup>

Gas-phase-synthesized graphene (GSG) can be produced in a single step through the delivery of a carbon-containing precursor into microwave-generated atmospheric pressure argon plasmas.<sup>[5,6]</sup> The continuous synthesis process does not require substrates or catalysts. Numerous studies have shown that precursors that have a C:H:O ratio of 2:6:1, such as ethanol and dimethyl ether, are conducive to GSG production in atmospheric plasmas.<sup>[6]</sup> However, GSG was not created through the delivery of methanol and isopropanol, which have C:H:O ratios of 1:4:1 and 3:8:1, respectively.<sup>[6]</sup> GSG is highly ordered and does not exhibit contamination, holes, substitutions, or extended topological defects.<sup>[6]</sup> GSG also has a crumpled morphology, and recent studies have shown that crumpled graphene sheets are capable of effectively dispersing and resisting aggregation in liquids.<sup>[7,8]</sup> Due to these features, GSG is a promising filler material for GNCs. However, there are only few reports of nanocomposites containing graphene powder synthesized in plasmas for use in structural applications,<sup>[9–14]</sup> and these studies only focused on nanocomposites with polyethylene<sup>[9,10]</sup> and elastomer<sup>[11–14]</sup> matrices. Thermosetting resins, such as epoxy, have a broad range of applications where enhancements in mechanical properties are desirable, such as wind turbine blades and aircraft components. Here we show that incorporating GSG into epoxy results

in nanocomposites that exhibit significant enhancements in both strength and strain at break.

## 2 | EXPERIMENTAL SECTION

GSG was produced by the substrate-free gas-phase synthesis method.<sup>[5,6]</sup> Pure ethanol (Sigma-Aldrich 200 proof, HPLC/spectrophotometric grade) was delivered directly into an argon plasma that was generated using an atmospheric pressure microwave (2.45 GHz) plasma reactor (MKS/ASTeX AX2518). Pure ethanol was used to ensure that the resulting synthesized powder only consisted of GSG. As shown in Figure 1a, argon gas was passed through a quartz tube (21 mm internal diameter) at a rate of 1.71 L/min, which was chosen because lower flow rates increase precursor residence time in the plasma and result in the formation of graphite.<sup>[6]</sup> An argon plasma was sustained at the intersection of the quartz tube and a microwave guide at an applied microwave forward power of 250 W. A jet nebulizer (Respironics HS860) was used to generate an aerosol consisting of argon gas (2 L/min) and ethanol droplets ( $2 \times 10^{-4}$  L/min). A smaller alumina tube (3 mm internal diameter) that was located within the quartz tube was used to pass the aerosol directly into the plasma. The entire process of precursor delivery, precursor decomposition, and GSG formation took place over a time period on the order of  $10^{-1}$  s. GSG sheets were collected downstream from the plasma on membrane filters (Pall Nylaflo membrane disc filters,  $0.42 \mu\text{m}$  pore size). GSG was procured by gently scraping the powder from filters using a laboratory spatula. A 120-kV Tecnai12



**FIGURE 1** (a) Diagram of the graphene synthesis process in microwave-generated atmospheric plasmas. (b) Transmission electron microscope image of GSG sheets. Scale bar is 100 nm. GSG, gas-phase-synthesized graphene

transmission electron microscope was used to obtain the image of GSG sheets shown in Figure 1b.

Nanocomposites were fabricated by mixing as-synthesized GSG powder with epoxy resin (FibreGlast System 2000) and 120-min pot life hardener (FibreGlast System 2120) using a planetary centrifugal mixer (Mazerustar KK-250S). The mixer was capable of creating homogeneous GSG–epoxy suspensions, which were subsequently degassed in a vacuum chamber for 10 min. ASTM D638 uniaxial tensile test specimens were formed by pouring the GSG–epoxy suspensions into silicone molds (Smooth-On OOMOO 25). The specimens were allowed to gel in the molds at room temperature for 1 hr and were subsequently cured in an oven at a temperature of 363 K for 4 hr at atmospheric pressure. Specimens were smoothed using sandpaper to ensure uniform dimensions and remove any surface imperfections that would have caused premature fracture during tensile testing. Pure epoxy specimens and nanocomposites containing 0.1 wt% GnPs were also fabricated using the same procedure. GnPs, with an average flake thickness of 8 nm, were obtained from Graphene Supermarket. The dispersion and aggregation resistance of 0.1 wt% GSG–epoxy and 0.1 wt% GnPs–epoxy suspensions were observed over time. The suspensions were created using planetary centrifugal mixing, except that no hardener was used in these tests. As shown in Figure 2, the suspensions were deposited in vials and left standing for 1 year.

Pure epoxy and nanocomposite specimens were subjected to uniaxial tensile testing using an MTS 810 Materials Testing System. The elongation of specimens during testing was measured using an axial extensometer (MTS 634.31F-21) and ASTM D638 test procedures were followed. Load and elongation data were obtained for each specimen, which was used to generate the engineering stress versus strain plots shown in Figure 3.

Scanning electron microscope (SEM) images of specimen fracture surfaces were used to understand how GSG and GnPs reinforce epoxy. Pure epoxy and

nanocomposite specimens that were fractured during tensile testing were coated with gold using a sputter coater (Cressington 108 Auto) to prepare them for SEM imaging. A Hitachi SU-70 SEM was used to obtain the images of specimen fracture surfaces shown in Figure 4.

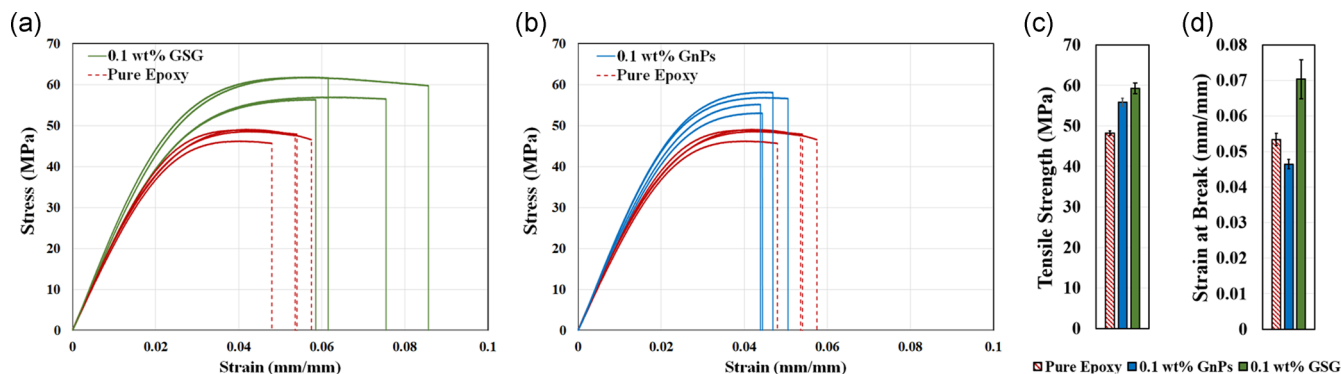
### 3 | RESULTS AND DISCUSSION

Tensile tests revealed differences in mechanical property enhancements between nanocomposites containing GSG and GnPs. Figure 3a shows engineering stress versus strain plots generated from pure epoxy specimens and GSG-reinforced nanocomposites. Figure 3b shows the results for the same pure epoxy specimens and nanocomposites filled with GnPs. The plots show that incorporating a relatively small amount of GSG into epoxy (0.1 wt%) resulted in a 23% increase in average tensile strength (Figure 3c) and a 32% increase in average strain at break (Figure 3d). Nanocomposites containing GnPs had a 15% increase in average tensile strength (Figure 3c) but the average strain at break decreased by 13% (Figure 3d). Therefore, GSG-filled nanocomposites exhibited simultaneous increases in strength and strain at break, which was not achieved in specimens containing similar loadings of GnPs.

The SEM images in Figure 4 reveal the effective reinforcement of epoxy by GSG. Figure 4a shows that the pure epoxy specimen had a featureless and smooth fracture surface, with straight lines characteristic of brittle fracture. This result is typical of a brittle thermosetting polymer with high crosslink density, which causes weak resistance to crack propagation and low absorption of energy during fracture.<sup>[15]</sup> In contrast, an SEM image of a GSG-reinforced nanocomposite reveals a very rough fracture surface (Figure 4b). Figure 4c shows the fracture surface of a nanocomposite filled with GnPs, which appears less rough relative to the GSG-filled specimen. Therefore, SEM images suggest that GSG sheets were more effective than GnPs in



**FIGURE 2** (a) Vials containing 0.1 wt% GSG in epoxy, pure epoxy, and 0.1 wt% GnPs in epoxy immediately after mixing, (b) after 1 week, and (c) after 1 year. The GSG remains dispersed in epoxy, while the GnPs in epoxy aggregate and result in a heterogeneous suspension. GnP, graphene nanoplatelet; GSG, gas-phase-synthesized graphene

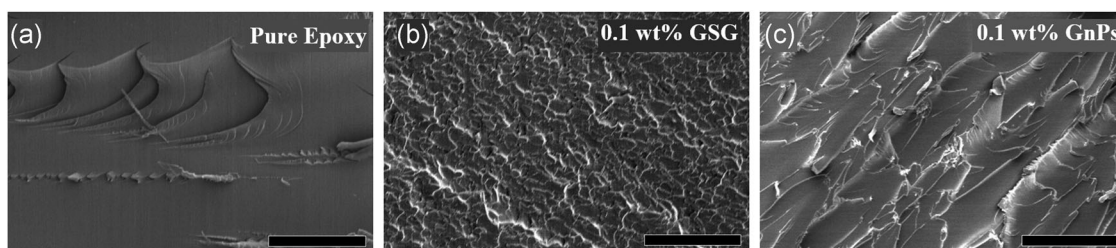


**FIGURE 3** (a) Engineering stress versus strain plots for pure epoxy (red curves) and 0.1 wt% GSG specimens (green curves). (b) Engineering stress versus strain plots for pure epoxy (red curves) and 0.1 wt% GnPs specimens (blue curves). (c,d) Comparisons of the tensile strength and strain at break of pure epoxy, 0.1 wt% GnPs specimens, and 0.1 wt% GSG specimens. Standard error bars are shown. GnP, graphene nanoplatelet; GSG, gas-phase-synthesized graphene

dispersing in epoxy and deflecting propagating cracks,<sup>[15]</sup> which resulted in GSG-filled nanocomposites requiring more energy to fracture than specimens containing GnPs.

The mechanical property enhancements in GSG-epoxy nanocomposites may be the result of a number of unique features in GSG that are not present in graphene fillers produced from graphite. For example, the enhancements in mechanical properties shown in Figure 3a could be the result of the highly ordered structure of GSG.<sup>[6]</sup> The presence of defects on graphene can have a detrimental effect on nanocomposite mechanical properties.<sup>[1-3]</sup> In GO, the defects created during oxidizing and exfoliating processes result in the mechanical properties of GO being lower than pristine graphene.<sup>[1]</sup> RGO, which is produced through the chemical or thermal reduction, of GO also contains contamination, disorder, holes, and other defects.<sup>[16]</sup> GnPs typically have thicknesses  $>2$  nm because monolayer GnPs are a challenge to create.<sup>[1]</sup> Polymers filled with GnPs have shown enhanced mechanical properties,<sup>[4,17]</sup> but the level of reinforcement of GnPs is less than GO flakes<sup>[2]</sup> because of the multilayered structure of GnPs.<sup>[1]</sup> On the basis of the current understanding of GNCs,<sup>[1-3]</sup> the highly ordered structure that is inherent to GSG may contribute to the enhancements in mechanical properties.

Figure 2 shows another unique feature of GSG that may be contributing to the observed property enhancements, which is the ability of GSG to effectively disperse and resist aggregation in epoxy in its as-synthesized state. A significant challenge in GNC fabrication is achieving uniform dispersions of nanomaterials in polymers.<sup>[1-3]</sup> GO, RGO, and GnPs are difficult to disperse in polymers and have a tendency to aggregate due to Van der Waals forces.<sup>[1-3]</sup> Aggregated fillers can act as failure points during the elongation of nanocomposites,<sup>[3]</sup> and aggregation continues to be a problem even in recent reports of GNCs.<sup>[3]</sup> Figure 2a shows that suspensions containing GSG and GnPs were homogeneous immediately after the nanomaterials were dispersed. After 7 days, the GSG sample remained a homogeneous black suspension while the vial containing GnPs became a heterogeneous black-gray suspension, which indicated that some aggregation of GnPs had occurred (Figure 2b). After 1 year, the GSG remained dispersed in epoxy while most of the GnPs aggregated and settled to the bottom of the vial (Figure 2c). The ability of the GSG-epoxy suspension to remain homogeneous over a 1-year period may be a result of the crumpled morphology of GSG. Indeed, researchers have deliberately deformed flat graphene flakes and observed that crumpling enables dispersion and prevents the restacking of individual graphene sheets



**FIGURE 4** Scanning electron microscope images of the fracture surfaces of (a) pure epoxy, (b) 0.1 wt% GSG, and (c) 0.1 wt% GnPs specimens. Scale bars are 100  $\mu\text{m}$ . GnP, graphene nanoplatelet; GSG, gas-phase-synthesized graphene



in liquids.<sup>[7,8]</sup> Therefore, the inherent crumpled structure of GSG could have contributed to the increases in mechanical properties.

In the current knowledge of GNCs,<sup>[1–3]</sup> the effective reinforcement of polymers requires graphene that (a) has a highly ordered structure; (b) effectively disperses and resists aggregation in polymers; (c) does not have wrinkles that are detrimental to interfacing with a polymer matrix; (d) is functionalized to enhance bonding with polymers; (e) is oriented parallel to the direction of applied stress; and (f) has a large lateral size and aspect ratio (sheet length divided by thickness). Recent studies have estimated the critical length of reinforcement of flat graphene flakes to be 3  $\mu\text{m}$ , and flakes  $>8 \mu\text{m}$  in size are needed for efficient reinforcement of nanocomposites.<sup>[3]</sup> GSG exhibits the first two characteristics, but it is randomly oriented in the matrix, not functionalized, and consists of crumpled sheets with lateral dimensions that are typically  $<1 \mu\text{m}$  (Figure 1b), which indicates that other features that are inherent to GSG may also be contributing to property enhancements.

The simultaneous increases in strength and strain at break could be a result of the graphitic nanocrystals in GSG sheets. A recent study showed that graphitic nanocrystals enable GSG to resist being flattened through mechanical manipulation.<sup>[18]</sup> GSG sheets that became unfolded by an applied mechanical force were observed to quickly revert to their original crumpled form upon removal of the force.<sup>[18]</sup> This phenomenon has not been experimentally observed in GO, RGO, and GnP. The nanocrystals in GSG could be contributing to the reinforcement of epoxy in two ways. First, the nanocrystals maintain the crumpled morphology of GSG, which enables it to disperse in epoxy and resist aggregation. Second, for GSG to fracture in epoxy, the applied tensile forces must first overcome the resistance of the nanocrystals as individual GSG sheets in the matrix become uncrumpled. Once the sheets become uncrumpled, additional force is required to break the high-strength carbon–carbon bonds in the highly ordered GSG structure. Therefore, the presence of graphitic nanocrystals in GSG sheets is another unique feature that may improve mechanical properties.

## 4 | CONCLUSION

The results presented here indicate that unique strengthening mechanisms may exist in polymers reinforced with GSG. Therefore, the structure-properties-processing relationships in GSG-filled nanocomposites require further investigation. Future research should focus on the impact of increasing GSG loading on the mechanical properties of nanocomposites. The aggregation resistance of GSG may enable

enhancements in mechanical properties above the optimal filler loadings for GNCs reinforced with GO, RGO, and GnP. The fracture surfaces of GSG nanocomposites can be imaged at higher SEM magnifications to further investigate strengthening mechanisms. Stress relaxation measurements and transmission electron microscopy characterization of GSG in polymers will elucidate GSG–matrix interactions and could reveal additional mechanisms of reinforcement. The results from this study demonstrate that there is much more to be discovered about polymers reinforced with graphene synthesized in atmospheric plasmas.

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