Composites with graphene as reinforcement

A O Surendranathan\textsuperscript{1,2}
\textsuperscript{1}National Institute of Technology Karnataka, India

E-mail: aos_nathan54@au.yahoo.com

Abstract. In this paper, the developments in the area of graphene-reinforced composite have been reviewed. It also depicts the work guided by the author. In the work, WC powder with 6\% cobalt (Co) and graphene (0.2\%) in the form of graphene nanoplatelets (GPLs) was prepared by high energy rate ball milling and ultrasonification. The mixture was sintered using spark plasma sintering at 1250\°C for 10 min. To study the effects of graphene reinforcement, the sample was analyzed for the physical (density), magnetic (coercivity, and magnetic saturation), microstructural (porosity) and mechanical properties (hardness, fracture toughness).

Under Visual Inspection of the Spark Plasma Sintered (SPS) sample, the top surface showed more homogeneous distribution of the constituents than the bottom surface. The results of the surface measurements showed that the top and bottom surfaces have almost the same roughness. It was found that the SPS sample exceeded liquid phase sintered (LPS) specimens with respect to hardness and fracture toughness values. The coercive force was found to be higher for the LPS sample whereas the saturation magnetization value was found to be higher for the SPS sintered specimen. The density value is higher for the LPS sintered specimen. The presence of pores is seen in the back scattered electron (BSE) image. There was certain amount carbon pick up from the graphite die used in SPS. There was uniform distribution of the cobalt binder. The x-ray diffraction pattern for the SPS sintered sample indicates the presence of WC, Co and GNP.

1. Introduction
In the recent past, carbonaceous nanofillers play a promising role [1]. This is because they have better structural and functional properties. Also, they have broad range of applications in each field. Examples for such fillers are graphene and carbon nanotubes (CNTs).

2. Literature review
Garima \textit{et al} [1] has reviewed the synthesis and properties of CNTs. Along with CNTS, the use of graphene as a novel substitution to the nanotubes as fillers was also reviewed. They resolved that CNTs and graphene have the power to alter properties of materials. The alteration can be exploited in the broad spectrum of applications. Xu and Gao [2] reported an efficient method to prepare nylon-6−(PA6−) graphene (NG) composites by \textit{in situ} polymerization of caprolactam in the presence of graphene oxide (GO). During the polycondensation, GO was thermally reduced to graphene simultaneously. By adjusting the feed ratio of caprolactam to GO, various composites with 0.01−10 wt \% content of graphene were obtained. The highly grafting nylon-6 arms on graphene sheets was confirmed by XPS, FTIR, TGA and AFM measurements, showing the grafting content up to 78 wt \% and homogeneous 2D brush-like morphology from AFM observations. The efficient polymer-chain grafting makes the graphene homogeneously dispersed in PA6 matrix and depresses the crystallization of PA6 chains.
Barun et al [3] evaluated the mechanical properties of polyvinyl alcohol (PVA) and poly (methyl methacrylate) (PMMA)-matrix composites reinforced by functionalized a few-layers graphene (FG) using the nano-indentation technique. A significant increase in both the elastic modulus and hardness was observed with the addition of 0.6 wt.% of graphene. The crystallinity of PVA also increased with the addition of FG. This and the good mechanical interaction between the polymer and the FG, which provided better load transfer between the matrix and the fiber, are suggested to be responsible for the observed improvement in mechanical properties of the polymers.

Fan et al [4] dispersed a few-layered graphene sheets, synthesized by direct current arc-discharge method using NH3 as one of the buffer gases, in chitosan/acetic acid solutions. FTIR and X-ray photoelectron spectroscopy showed the presence of oxygen-containing functional groups on the surface of graphene sheets that may assist the good dispersion of graphene in chitosan solution. Graphene/chitosan films were produced by solution casting method. The mechanical properties of composite films were tested by nanoindentation method. With the addition of a small amount of graphene in chitosan (0.1–0.3 wt%), the elastic modulus of chitosan increased over ~200%. The biocompatibility of graphene/chitosan composite films was checked by tetrazolium-based colorimetric assays in vitro. The cell adhesion result showed that the L929 cell can adhere to and develop on the graphene/chitosan composite films as well as on pure chitosan film, indicating that graphene/chitosan composites have good biocompatibility. Because there is no metallic impurity in graphene raw materials, the time-consuming purification process for removing metal nanoparticles entrapped in carbon nanotubes is thus avoided when graphene is used to prepare biomedical materials. Graphene/chitosan composites are potential candidates as scaffold materials in tissue engineering.

Wang et al [5] reinforced aluminum composites with graphene nanosheets (GNSs) through a feasible methodology based on flake powder metallurgy. The tensile strength of 249 MPa was achieved in the Al composite reinforced with only 0.3 wt.% GNSs, which is 62% enhancement over the unreinforced Al matrix.

Chatterjee et al [6] investigated the influence of reinforcements on the mechanical and thermal properties of graphene nanoplatelets/epoxy composites. Amine functionalized expanded graphene nanoplatelets (EGNPs) were dispersed within epoxy resins using high-pressure processor followed by three roll milling. Functionality on the EGNPs was confirmed with FTIR and micro-Raman spectroscopy. Bending and nano-mechanical testing was performed on the composites. Incorporation of EGNPs improved the flexural modulus and hardness of the composite and increased fracture toughness by up to 60%. Marked improvement was observed in thermal conductivity of the composites reaching 36% at 2 wt.% loading. Functionalized EGNPs exhibited significant improvements indicating favorable interaction at EGNPs/polymer interface.

Zhao et al [7] report that nanocomposites based on fully exfoliated graphene nanosheets and poly (vinyl alcohol) (PVA) were prepared via a facial aqueous solution. A significant enhancement of mechanical properties of the graphene/PVA composites was obtained at low graphene loading; that is, a 150% improvement of tensile strength and a nearly 10 times increase of Young’s modulus were achieved at a graphene loading of 1.8 vol%.

Garima et al [8] reviewed the synthesis and properties of CNTs along with the use of graphene as a novel substitution to the nanotubes as fillers. A comparative analysis has been carried out between the importance of graphene and carbon nanotubes as fillers and the substantial changes in mechanical and electrical properties of matrix.

Lenka et al [9] had prepared silicon nitride + 1 wt.% graphene platelet composites using various graphene platelets with the aim to improve the fracture toughness of Si3N4. The fracture toughness was significantly higher for all composites in comparison to the monolithic Si3N4, with the highest value of 9.92 MPam1/2. The main toughening mechanisms originated from the presence of graphene platelets, and the increase in the fracture toughness values was attributable to crack deflection, crack branching and crack bridging.

Li et al [10] grew hybrid fillers composed of carbon nanotubes (CNTs) on graphene nanoplatelets (GNPs). They were dispersed into epoxy matrix to serve as promising reinforcements. And the CNT–
GNP/epoxy composite shows distinctive self-sensing behavior for *in situ* monitoring the onset of irreversibly permanent deformation. Here it has been established that the embedding of CNT–GNP hybrids into pristine epoxy endows optimum dispersion of CNTs and GNPs as well as better interfacial adhesion between the carbon fillers and matrix, which results in a significant improvement in load transfer effectiveness. Remarkably enhanced mechanical properties in the CNT–GNP/epoxy composite were achieved at ultralow hybrid loading (0.5 wt.%). The tensile modulus showed ~40% increase and the tensile strength was enhanced by ~36% with respect to the neat epoxy. The reinforcement efficiency of the CNT–GNP hybrids is found to outperform that of the CNT+GNP mixture predicted using the modified Halpin-Tsai modelling.

Xia *et al* [11] established the electrical behaviour of both uncured and oven cured GNPs/epoxy composites with loadings of up to 10 wt%. Above the critical loading found for oven cured materials (~8.5 wt%) the electrically conducting networks of GNPs formed in the matrix showed the ability to act as integrated nanoheaters when an electric current was passed through them, successfully curing the composites by Joule heating. Composites prepared by this Out-of-Autoclave (OoA) curing method (as an alternative to the traditional oven based one) at 10 wt% loading of GNPs were also prepared and compared to the oven cured ones. They showed more compact composite structures, with less micro voids and a preferred orientation of the GNPs in the matrix relative to the oven cured material at identical loading.

Chu *et al* [12] has shown that approximately 2 wt. % of graphene in the matrix of a unidirectionally-reinforced carbon fiber epoxy composite leads to a significant enhancement in mechanical properties. Particularly, it is found that the axial stiffness of the composites is increased by ~10 GPa accompanied by an increase in axial strength of 200 MPa.

Young *et al* [13] have undertaken a detailed study of the mechanisms of stress transfer in polymeric matrices with different values of Young's modulus, $E_m$, reinforced by graphene nanoplatelets (GNPs). For each material, the Young's modulus of the graphene filler, $E_f$, has been determined using the rule of mixtures and it is found to scale with the value of $E_m$.

Li *et al* [14] prepared epoxy nanocomposites reinforced by graphite nanoplatelet (GNP) and nano-scale X-ray computed tomography was used to visualize the geometry, morphology and defects of the flakes, as well as the three-dimensional agglomerates that are normally difficult to characterise by other techniques. In combination with micromechanical analysis, the taxonomy of the nanoplatelets is shown to be of great importance in controlling the mechanical properties of nanocomposites, and this has been shown to explain the deviations of the predictions of micromechanical models from the measured values.

### 3. Our work [15]

#### 3.1. Experimental

**3.1.1. Characterisation of graphene.** The graphene powder used was characterized using Raman spectroscopy.

**3.1.2. Processing of WC-Co powder.** Wax, which acted as the binder during compaction, was added to the composition of WC-6% Co. This mixture was analyzed for its magnetic properties. It was then subjected to high energy rate ball milling. The jar used was made up of WC. The balls used were having 1 cm diameter and was made from WC. The ball: powder ratio was 10:1 by weight. The speed selected was 200 rpm, and the milling duration was 1 h.

**3.1.3. Ultrasonication.** Different percentages of graphene were added. The mixture was ultrasonicated in N-Methyl Pyrrolidone for 1 h. The compositions of ultrasonicated WC-Co-graphene composite powders are given in table 1.
3.1.4. Vacuum drying. To separate liquid incorporated during ultrasonication, the mixture was dried in an oven at a temperature of 140°C for 12 h.

3.1.5. Spark plasma sintering (SPS). The dried mixture was subjected to SPS. The die used was made of graphite and it was cylindrical in shape with 20 mm dia. The SPS temperature was 1250°C for a time duration of 10 min. Uniaxial pressure of 50 MPa was applied.

3.1.6. Characterisation

- Coercive force ($H_c$)
  The sintered specimen was fully magnetized in an electric field in a coil. Afterwards, it was demagnetized by applying electric field in the opposite direction. The coercive force (force required to reduce residual magnetism to zero) was determined.

- Magnetic saturation ($4\pi\sigma$)
  In order to find the saturation magnetic field, the sintered sample was magnetized fully in permanent magnetic field. Then the sample was removed and the magnetic moment was measured. The obtained magnetic moment was divided by the weight of the sample to get the saturation magnetic field.

- Specific gravity
  The specific gravity of the sintered sample was measured using Archimedes principle.

- Hardness
  In order to check the hardness of the sintered specimen, it was ground with fine diamond grit. Later polishing was effected using diamond paste on rigidly supported laps. Then it was subjected to ultrasonic cleaning. The hardness was measured on the cleaned surface using Vickers indentation method. For the measurement, 30 kgf load was applied with a dwelling period of 10s at three sufficiently distant spots.

- Fracture toughness
  The fracture toughness of the sintered specimen was evaluated by indentation method. For this, the lengths of the cracks emanating from the corners of Vickers hardness indentations were measured using optical microscope at 400X magnification. The obtained values were plotted as $P$ (indentation load) vs. $L$ (sum of the lengths of the four cracks). From the plot, $W$ (slope) was found out. The fracture toughness ($K_{IC}$) was calculated using the formula:

$$K_{IC} = 0.0889(HW)^{1/3}$$

where, $H$ is the Vickers hardness number.

- Porosity
  The unetched specimen was analyzed for the presence, type and distribution of porosity and uncombined carbon using a metallurgical microscope (Olympus make). To observe the pores up to 10 μm, a magnification of 200X was used. To observe the pores in the range of 10 to 25 μm, a magnification of 100X was used. Uncombined carbon / graphite was assessed by comparing 100X micrographs with standard charts.

- Etching
  The polished specimens were subjected to two levels of etching using Murakami’s etchant.
    - γ-Etching
      The surface that was etched with Murakami’s reagent was analyzed for γ-phase. The etching was done at a temperature just below 100°C for 15 min [16]. Care was taken to photograph the same spot on the specimen with this etch. A light and careful retouching on the polishing cloth was necessary to

| Grade Name | Composition                          |
|------------|-------------------------------------|
| G0         | WC + 6 w/o Co + 0 w/o graphene      |
| G1         | WC + 6 w/o Co + 0.2 w/o graphene    |
remove a film formed on the surface of free tungsten carbide. Microscopic examinations and photomicrographs were made with a 4 mm apochromatic objective of numerical aperture 0.95 and with a green light filter. Etching was done in a solution held just below the boiling point.

- **α-Etching**

  For obtaining the percentage of α-phase, the surface of the polished specimen was etched with Murakami’s reagent in the presence of an electric current. Then the surface of the specimen was assessed for grain size and size distribution.

3.1.7. **Grain size measurements.** Two types of parameters were measured under grain size measurements.

  - **α_{max}**

    The first parameter was the maximum grain size of α-phase (α_{max}). For this, the α-etched specimen was scanned at 100X for the identification of the largest α grain. Its approximate size was measured.

  - **Coarse α Patches (CaP)**

    Coarse α patches in the specimen were analyzed for the size range that encapsulated the maximum number of coarse α grains. For this again the α-etched specimen was observed at 100X magnification.

3.1.8. **X-Ray diffraction.** The phases present in the SPS sample were identified using the X-Ray diffractometer (make-JOEL, model-JPX8). Nickel filter was used for the Cu Kα radiation (λ = 1.54 angstroms). Scanning rate of 2°/min was used. The diffraction angle (2θ) range was 20°-90°. The diffraction spectrum was analyzed using Xpert Pro software.

4. **Results and discussion**

4.1. **Characterization of graphene using Raman spectroscopy**

The Raman spectrum obtained is shown in figure 1. High intensity G peak was obtained at 1585.7 cm⁻¹. The moderately intense D peak was seen at 1357.6 cm⁻¹. A fraction of graphene was present with a disordered structure. The lower intensity D peak indicates lower magnitude of defects. 2D peak (figure 2) at 2725 cm⁻¹ indicates the presence of small amount of impurities.

Planar crystallite size was:

\[ L_a = 4.4(I_G/I_D) = 5.9 \text{ nm} \]  

**Figure 1.** Raman spectrogram of graphene showing G and D peaks.  
**Figure 2.** Raman spectrogram of graphene showing 2D peak.

4.2. **Visual inspection of the spark plasma sintered sample**

The top surface showed more homogeneous distribution of the constituents than the bottom surface. No contrast was seen on the side as it is as sintered without etching.

4.3. **Surface roughness measurements**

The results of the surface measurements are given in table 2. It is found that the top and bottom surfaces have almost the same roughness. The side is far smoother than the top and bottom surfaces. This is because the densification takes place along the side. It is the characteristic of uniaxial pressing. The table also gives the roughness values for the liquid phase (LP) sintered specimen. It is almost
having the same values as that of the side of a SP sintered one. This is because the liquid formed during LP sintering spreads and fills all the open pores as well. On cooling after sintering, this results in a continuous solid phase without any pores. Surface roughness of SPS specimen is higher than that of LPS one because hot working gives rougher surface than cold working.

Table 2. Results of surface measurements.

| Location            | Ra (μm) | Rt (μm)  | Rz (μm) |
|---------------------|---------|----------|---------|
| Top Surface         | 2.9-4.2 | 19.8-30.6| 14.7-22.4|
| Bottom Surface      | 2.8-4.3 | 20.7-29.0| 15.9-20.8|
| Side                | 1.0-1.8 | 9.6-18.0 | 5.8-11.3 |
| WC-Co (LPS)         | 0.9-1.0 | 6.0-7.0  | 8.0-9.0  |

LPS-Liquid Phase Sintered.

4.4. Hardness and fracture toughness
The hardness and fracture toughness values of both the SPS and LPS specimens are given in table 3. Both the values exceed that for LPS sample.

Table 3. Hardness and fracture toughness values.

| Location            | Vickers Hardness, \( H_v \) (kgf/sq.mm) | Palmqvist Fracture Toughness, \( K_{IC} \) (MPa√m) |
|---------------------|----------------------------------------|----------------------------------|
| SPS                 | 2000                                   | 11.8                             |
| LPS without graphene| 1595 (kgf/sq.mm)                        | 9.7                              |

4.5. Magnetic properties & density
These properties are given in table 4. The coercive force was found to be higher for the LPS sample whereas the saturation magnetization value was found to be higher for the SPS sintered specimen. This shows that SPS sintering makes the material more ferromagnetic. The density value is higher for the LPS sintered specimen because of the presence of a liquid phase during sintering. The liquid phase fills the pores.

Table 4. Magnetic & physical properties of LPS & SPS samples.

| Sample Type     | Coercive Force, \( H_c \) (Oersted) | Magnetic Saturation, \( 4\pi\sigma \) (μTm²/kg) | Density \( \rho \) (g/cm³) |
|-----------------|-------------------------------------|-----------------------------------------------|--------------------------|
| LPS             | 200                                 | 11.3                                          | 14.89                    |
| SPS             | 284                                 | 5.2                                           | 15.20                    |

4.6. Microstructural characterisation

![Figure 3. Scanning Electron photomicrograph of LPS sample.](image)

The scanning electron photomicrograph of the LPS sample is shown in figure 3. The white areas in the
The 6th Global Conference on Polymer and Composite Materials (PCM 2019)  IOP Publishing
IOP Conf. Series: Materials Science and Engineering 634 (2019) 012001  doi:10.1088/1757-899X/634/1/012001

Figure show the presence of cobalt, whereas the grey areas represent the WC phase. The black areas contain the pores. The carbide particle size ranges from 978 nm to 1.41 μm. Figure 4 compares the secondary and back-scattered electron images of the SPS sample. The presence of pores is clearly seen in the back scattered electron (BSE) image.

Figure 4. Scanning electron photomicrographs under secondary and back-scattered electron modes.

4.7. Carbon pickup & binder distribution

It is found from the photomicrograph of the top surface of the SPS sample (figure 5) that there was certain amount carbon pick up from the graphite die used in SPS. The same figure also shows that there was uniform distribution of the cobalt binder.

Figure 5. Optical photomicrographs of SPS sample showing carbon pickup (top) and binder distribution (side).

Figure 6. X-ray diffractograph of SPS sample.
4.8. X-ray diffraction
The x-ray diffraction pattern for the SPS sintered sample is shown in figure 6. It indicates the presence of WC, Co and GNP.

5. Conclusion
Composites with graphene as reimbursement has become a hot topic of the day as evidenced by the number of papers getting published. Spark plasma sintering of GNP-reinforced WC-Co composite resulted in significant increase in toughness. SPS gave higher hardness (~400 H$_{1}$). SPS makes the grain size distribution narrower. Reaction of graphene is limited in SPS. Graphene acts as a protective coating against oxidation.

References
[1] Garima M, Vivek D, Kyong Y R, Soo-Jin P and Wi R L 2015 A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites Journal of Industrial and Engineering Chemistry 21 11-25
[2] Xu Z and Gao C 2010 Macromolecules 43 6716-23
[3] Barun D, Eswar Prasad K, Ramamurty U and Rao C N R 2009 Nano-indentation studies on polymer matrix composites reinforced by few-layer graphene Nanotechnology 20 12
[4] Fan H L, Wang L L, Zhao K K, Li N, Shi Z J, Ge Z G and Jin Z X 2010 Fabrication, mechanical properties, and biocompatibility of graphene-reinforced chitosan composites Biomacromolecules 11 2345-51
[5] Wang J Y, Li Z Q, Genlian Fan, Huanhuan P, Zhixin C and Di Z 2012 Reinforcement with graphene nanosheets in aluminum matrix composites Scripta Materialia 66 594-7
[6] Chatterjee S, Wang J W, Kuo W S, Tai N H, Salzmann C, Li W L, Hollertz R, Nüesch F A and Chu B T T 2012 Mechanical reinforcement and thermal conductivity in expanded graphene nanoplatelets reinforced epoxy composites Chem. Phy. Letters 531 6-10
[7] Xin Z, Qinghua Z, Dajun C and Ping L 2010 Enhanced mechanical properties of graphene-based poly(vinyl alcohol) composites Macromolecules 43 2357-63
[8] Garima M, Vivek D, Kyong Y R, Soo-Jin P, Wi R L 2015 A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites J. of Industrial and Engineering Chem. 21 11-25
[9] Lenka K, Annamária D, Pavol H, Ján D, Péter K and Csaba B 2012 Fracture toughness and toughening mechanisms in graphene platelet reinforced Si$_3$N$_4$ composites Scripta Materialia 66 793-6
[10] Weikang L, Anthony D and Jinbo B 2013 Carbon nanotube–graphene nanoplatelet hybrids as high-performance multifunctional reinforcements in epoxy composites Composites Science and Tech. 74 221-7
[11] Tian X, Desen Z, Zheling L, Robert J Y, Cristina V and Ian A K 2018 Electrically conductive GNP/epoxy composites for out-of-autoclave thermoset curing through Joule heating Composites Science and Techn. 164 304-12
[12] Jingwen C, Robert J Y, Thomas J A S, Timothy L B, Broderick C, Ludovic C, Aurèle V and Zheling L 2018 Realizing the theoretical stiffness of graphene in composites through confinement between carbon fibers Composites Part A 113 311-7
[13] Robert J Y, Mufeng L, Ian A K, Suhaol L, Xin Z, Cristina V and Dimitrios G P 2018 The mechanics of reinforcement of polymers by graphene nanoplatelets Composites Science and Technology 154 110-6
[14] Zheling Li, Thomas J A S, Xinyu M, Yingjie Y, Robert J Y, and Timothy L B 2019 The taxonomy of graphite nanoplatelets and the influence of nanocomposite processing Carbon 142 99-106
[15] Gorti V K, Golla S, Bhavani S B, Kantubhukta J, Kokkiligadda J, Ramesh S R and Surendranathan A O 2018 Fabrication and characterization of graphene reinforced tungsten
carbide-cobalt composite The Journal of Advances in Mechanical and Materials Engineering 1 12-22

[16] Watertown Arsenal 1945 Report No. 710/412