



Rationally Designed Graphene Oxide-PVA Composite Fillers for Modern Manufacturing Applications

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Authors' contributions

This work was carried out in collaboration between both authors. Authors BMI and SI designed the study, BMI performed the statistical analysis, author SI wrote the protocol and authors BMI and SI wrote the first draft of the manuscript. Authors BMI and SI managed the analyses of the study and performed the literature searches. Both the authors read and approved the final manuscript.

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ABSTRACT

This work aims at developing a rational design of graphene-oxide based filler and addresses modifications to the filler architecture in generating fillers that can adapt to the needs of additive manufacturing and lead to superior performance. Novel graphene-based fillers are synthesized through a facile self-assembly and surface functionalization techniques specifically tailored for additive manufacturing-based composite applications. Taking nylon as a model polymer system, we prepared graphene oxide, self-assembled them into well-ordered layered macroscopic structures that can slide over each other through cooperative interactions to result in superior toughness of the manufactured composites. To improve the matrix filler interaction, we adopted polyvinyl alcohol (PVA) based surface functionalization technique to develop covalent bonding between the GO and nylon. The Raman analysis revealed that an intensity ratio of 0.88 was observed for 1 wt% GO/PVA as compared to a ratio of 0.98 for pure PVA. Similarly, the stress-strain curves reveal a sharp increase in linear characteristic for the 1 wt% GO/PVA and a 40 % increase in the elongation at break due to a strong crystallinity and orientation. Owing to the unique

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architecture of the filler, its combination with superior matrix-filler interaction resulted in a composite with a balance of mechanical properties, which may be adapted to create futuristic composite structures.

Keywords: Graphene oxide-PVA composite fillers; hardness test; modified hummer's method; matrix polymer; Raman analysis.

1. INTRODUCTION

Graphene has emerged as a unique material in the field of nanotechnology because of its rigid planar nanostructure made of a single layer of carbon atoms arranged in a hexagonal crystal lattice. It can be considered as a sort of two-dimensional macromolecule, where benzene is the repeating structural unit [1]. Graphene can be prepared with various methods, among which the most applied methods include exfoliation of graphite, reduction of graphene oxide (GO) and chemical vapor deposition (CVD) [2].

Similarly, Graphene oxide (GO) is an oxidized form of graphene, laced with oxygen-containing groups [3, 4]. The preparation of GO can be modified to produce certain functionalized GO which has lower or higher conductivity properties than pristine graphene [5]. Graphite oxide can be exfoliated using any organic solvent to form GO and produce different form dispersion with different long-term stability and thickness of single layer GO. Elimination/removal of oxygen functional group increases electrical conductivities of GO [6-9]. Graphene oxide is synthesized using four basic methods: Staudenmaier, Hofmann, Brodie, and Hummers. Many variations of these methods exist, with improvements constantly being explored to achieve better results and cheaper processes [10].

Several modifications to graphene such as, graphene-nylon composite, have been reported in the past. The nylon-based composites are manufactured using the anionic ring opening polymerization technique. The nylon fibers are generally processed using electro-spinning [11]. The fibers were incorporated into a matrix of two-component phenolic epoxy resin (Epoplast), forming films with the desired thickness. This matrix has adhesion between the fibers, and the epoxy matrix is high, so maximum benefit from adhesion is achieved owing to the high surface area of the fibers [12]. Modified hummer's method is employed to study asymmetric configuration of pseudocapacitive composite and r-GO electrodes and MnFeO₄/r-GO for enhanced capacitive deionization [13-16].

Several GO-polymer composites were initially used in additive manufacturing to achieve accurate dimensional stability, machinability when compared to conventional injection molding. However, there were few limitations in using GO as a filler. It was because there existed a phase separation between graphene sheets and the polymer to form the composite. Using the polymers acrylonitrile-butadiene-styrene (ABS) and poly (lactic acid) (PLA) and graphene oxide as a filler polymer composites were manufactured by the 3-D printer. The filaments required were extruded with a diameter that best suits the 3-D printer. Composite parts are also made by compression molding (CM) as a comparison. Due to the presence of gaps between deposition lines and poor bonding between polymer and fiber, 3D printed composite samples showed significant void formation [17]. In this paper, we discuss methods to synthesize GO; self-assembled GO through vacuum filtration and the composite manufactured using nylon as a polymer with fiber extruder.

2. EXPERIMENTAL PROCEDURE

2.1 Modified Hummer's Method

The synthesis of graphene oxide was prepared using the modified Hummers method (Fig. 1). This method has mainly two steps involved: Peroxidation of graphite and Oxidation of graphite.

2.1.1 Peroxidation of graphite

Concentrated H₂SO₄ (25 ml) was heated at 90^oC in a beaker, to which 5g of K₂S₂O₈ and 5g of P₂O₅ were added with stirring until the reactants were dissolved completely in H₂SO₄. 6g of graphite powder was added slowly to the previous H₂SO₄ solution when the reaction temperature was decreased from 90^oC to 80^oC. This resulted in bubbling, and the reaction was maintained at 80^oC for 5 hours. After the completion of 5 hours, the heating was stopped, and the mixture was diluted with 2 L of distilled water and left overnight [18]. The mixture was then filtered and washed to remove the traces of

acid if any. The remaining solid was dried overnight.

2.1.2 Oxidation of graphite oxide

The concentrated H_2SO_4 (230 ml) was kept in an ice bath which is maintained at $0^{\circ}C$. The previously prepared peroxidized graphite was added to the acid and stirred. Then 30 g of $KMnO_4$ was added to the solution slowly and allowed to dissolve. The addition of $KMnO_4$ to the above solution was done at a temperature that does not exceed $10^{\circ}C$. The mixture was allowed to react for 2 hours at $35^{\circ}C$ temperature. After 2

hours, 1L distilled water was added in such way that the temperature did not exceed $50^{\circ}C$. This mixture was stirred for another 2 hours and at the end of 2 hours, 3L distilled water and 25 ml of 30% H_2O_2 was added. The mixture was kept undisturbed for a day, and the supernatant was decanted [19]. The remaining solution was centrifuged at 500 rpm and washed with 10% hydrochloric acid solution followed by washing with distilled water. The material obtained after centrifugation was put for dialysis and the graphite oxide obtained was dried using the vacuum dryer.



Fig. 1. Graphene oxide (GO) obtained from Hummer's method



Fig. 2. Vacuum filtration set-up

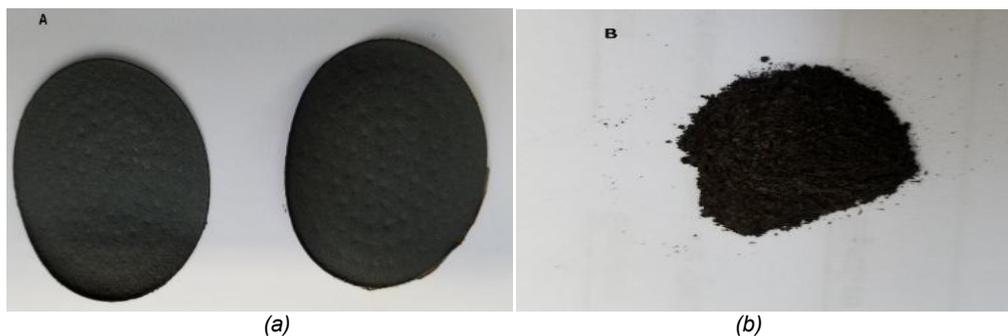


Fig. 3. (a) Self-assembled graphene oxide, (b) Graphene oxide filler

2.1.3 Self-assembly of graphene oxide

The fabrication of thin films using graphene oxide is to obtain the polymer composites using the additive manufacturing (3-D printing) and testing the mechanical properties of the desired parts. Fabrication of these thin films is performed using the vacuum filtration.

The graphene oxide thin films are formed through self-assembly through vacuum filtration as shown in Fig. 2. The graphene oxide synthesized from the Hummer's method is diluted with deionized water and is used for self-assembly. The filtration rate depends on the porosity of the filter paper used. Here, in this experimental setup, for each batch of graphene assembly, 10ml diluted graphene oxide is used which is again reduced to 0.05% weight by adding 200ml deionized water. This solution is sonicated for 15-20 mins and used. The so formed self-assembled film was dried in a vacuum oven and made into a powder similar to that of the graphene oxide, as shown in Fig. 3 (a,b). This is known as filler preparation, and the structure of the same is viewed under the scanning electron microscope (SEM).

2.1.4 Fabrication of functionalized graphene oxide

The functionalization is through esterification reaction between PVA and graphene. The materials used for the functionalization reaction are dimethyl sulfoxide (DMSO), N, N-dicyclohexylcarbodiimide (DCC), 4-(dimethyl amino)-pyridine (DMAP), and N-hydroxybenzotriazole (HOBT). In this reaction, the graphene oxide (166 mg) prepared is dispersed in DMSO (15 ml) via sonication and added to a solution of DCC (400 mg), DMAP (66 mg), and HOBT (130 mg). This solution was sonicated for 1 hour. Then a solution of PVA (166 mg/ml) in DMSO (10 ml) was prepared and added to the previous solution containing graphene and DMSO. The solution was sonicated for additional 24 hours. After the completion of sonication, the mixture was precipitated into acetone to recover the functionalized sample. For purification, the sample was dissolved in hot water and precipitated with acetone. The aqueous solution was put for dialysis for three days and the sample is dried to obtain the functionalized graphene oxide (Fig. 4) [20].

2.2 Composite Preparation

The composite preparation requires nylon as a base polymer which has to be extruded using a

fiber extruder. Since we are aiming at processing graphene filler-based polymer composites, the graphene oxide is thoroughly mixed with powdered nylon and extruded using the extruder.



Fig. 4. Functionalized GO

3. RESULTS AND DISCUSSION

The morphology of graphene oxide that is synthesized through Modified Hummer's method is analyzed through SEM imaging illustrated in Fig. 5. To obtain the image, GO powder was initially deposited on a carbon tape or silicon wafer. The following figures reveal the structure of GO which confirms the covalently bonded carbon atoms together. Also, it depicts that the graphene oxide is a single layer with a minimal thickness.

To analyze the dispersion of graphene oxide in the carboxylic groups, we use the Fourier Transform Infrared Spectroscopy (FTIR). FTIR of the Graphene oxide obtained successful oxidation of the graphite as shown in Fig. 6. The presence of different types of oxygen functionalities in graphene oxide was confirmed at broad and wide peak at 3352 cm^{-1} is attributed to the O-H stretching vibrations of the C-OH groups. Similarly, the sharp, intense peak at 1670 cm^{-1} is attributed to CO carboxylic [21].

3.1 Mechanical Testing

The tensile stress-strain curves of pure PVA and PVA/GO is illustrated in Fig. 7a. The stress-strain curves for both the samples presented an untypical stress yield behavior, and with the incorporation of GO, compared with neat PVA hydrogel, PVA/GO hydrogels presented a sharp increase of the slope of linear portion of the stress-strain curves in the range of 20-60% strain indicating the orientation of GO sheets and PVA crystalline regions. A maximum tensile strength of 80 MPa is observed for 1 wt% GO/PVA as

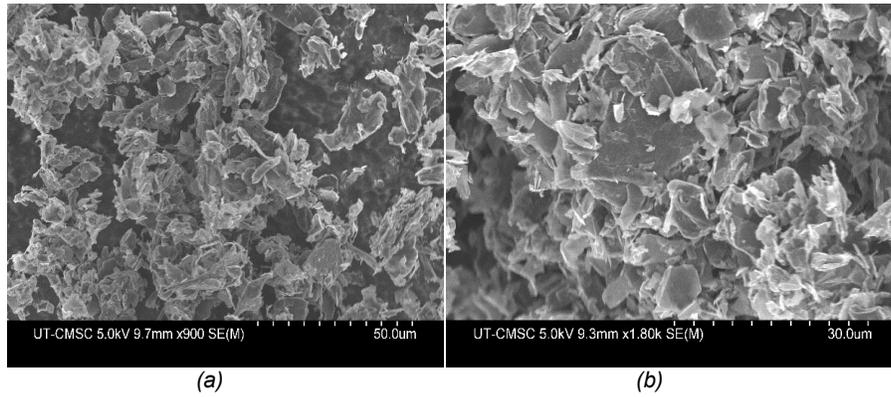


Fig. 5. SEM images of pure GO

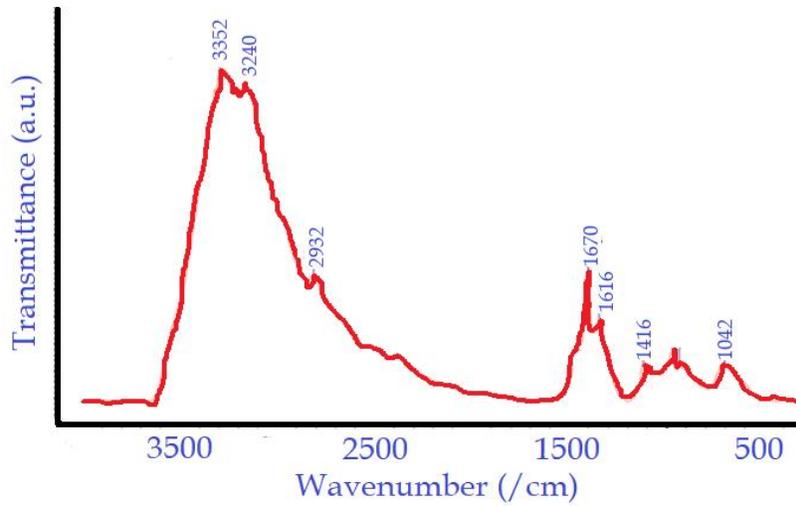


Fig. 6. FTIR spectrum of GO

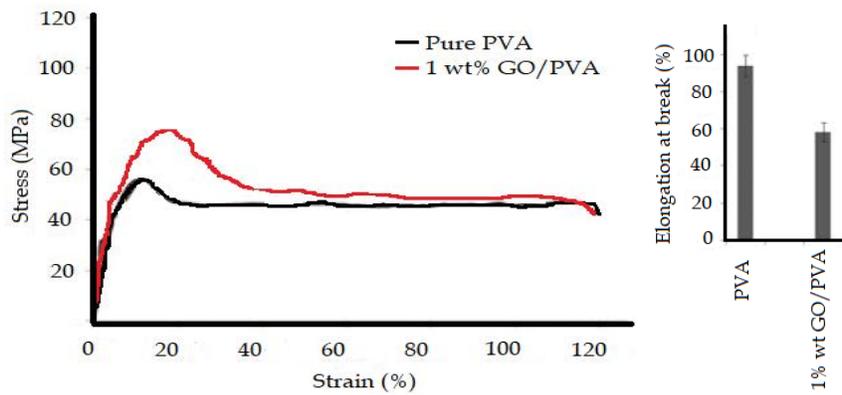


Fig. 7. (a) Stress-Strain curve and (b) Elongation at break of 1 wt% GO/PVA and pure PVA

compared to 55 MPa for pure PVA. Fig. 7(b) demonstrates the elongation at break for pure PVA and 1 wt% GO/PVA. It is observed that a 40

% increase in the elongation at break results for the formation of a dense and stable crosslinking network with improved crystallinity.

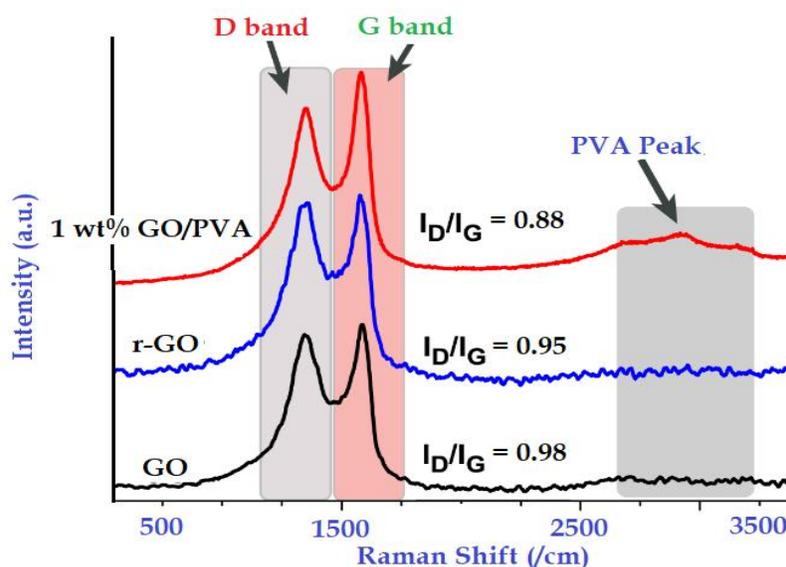


Fig. 8. Raman Spectra of GO, r-GO and 1 wt% GO/PVA

3.2 Raman Analysis

Raman spectra of GO, r-GO and 1 wt% GO/PVA is shown in Fig. 8. For the GO sample, the two absorption peaks at 1344.2 and 1583.6 cm^{-1} correspond to the D and G bands, corresponding to the structure defects and the first-order scattering of the E_{2g} vibration mode respectively. For the r-GO sample, besides the above D and G bands, no obvious absorption peak also appeared. For 1 wt% GO/PVA sample, the band around $2600\text{-}3000$ cm^{-1} corresponds to the absorption peak of PVA molecules, indicating that an abundance of PVA molecular chains are grafted onto GO layers.

The intensity ratio (I_D/I_G) for the GO sample is estimated to be around 0.98, which gradually reduces to 0.95 for the r-GO sample. For the 1 wt% GO/PVA, the (I_D/I_G) value decreased to 0.88, indicating a reduction of GO defect due to the anchoring effect of PVA molecules.

The self-assembled graphene oxide from vacuum filtration is viewed under SEM to compare the structure between the assembled GO and pure GO. Fig. 9. (a,b) illustrates the SEM imaging of self-assembled graphene oxide formed by depositing diluted concentration of GO suspensions on a silicon wafer or carbon tape that reveals a layer-by-layer sheet like an

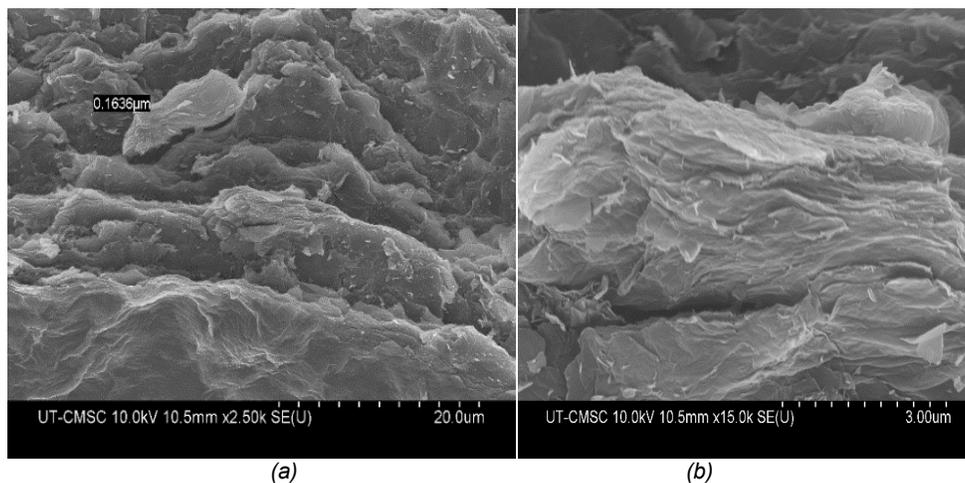


Fig. 9. SEM images of self-assembled GO

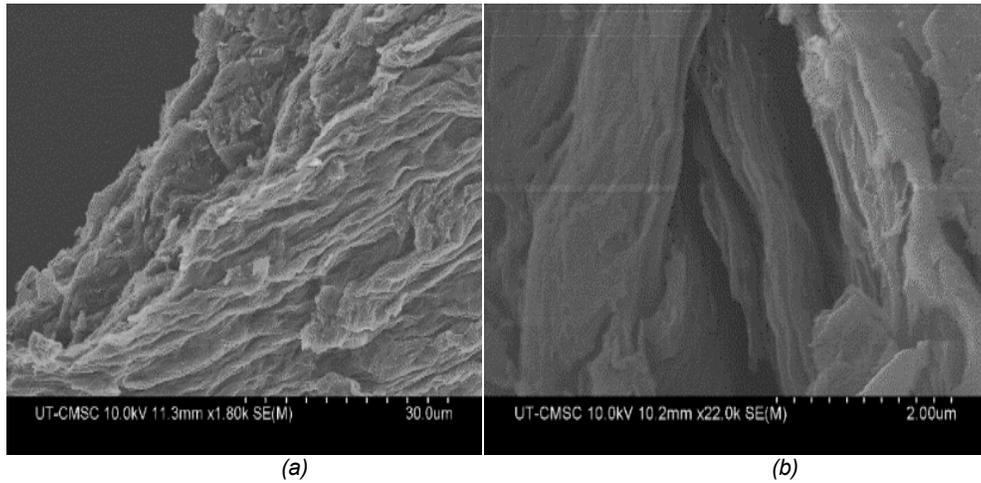


Fig. 10. SEM images of filler

assembly of GO sheets, which is due to interaction between GO flakes due to van der Waals attractions

The formed assembled graphene oxide sheets are made into fine particles known as filler. The following show the SEM images of the filler, where the self-assembled graphene oxide is made in a fine powder. Fig. 10. (a,b) depicts a schematic representation of the self-assembled GO which is made into finer particles and then viewed under SEM. There is no change in the morphology or the structure when viewed was similar to that of the self-assembles film, it was a layer-by-layer orientation. This states that the structure of graphene oxide was not varied when the films and fine powder were compared.

Since the filler should be incorporated into the polymer to obtain the polymer composite, the fibers were initially extruded using a fiber extruder with GO filler mixed in it. Fig. 11(a) shows the chopped nylon fibers that were processed using the single-screw extruder using the pure nylon pellets. These are again extruded using the same equipment to obtain the filaments in such a way that there are no air bubbles (bludge) forming during the extrusion process. Fig. 11(b) depicts the fibers that contain both nylon and graphene oxide where nylon and GO are uniformly dispersed. The nylon pellets were grounded into a fine powder and then mixed well with graphene oxide to attain 1% weight percentage.



Fig. 11. (a) Processed nylon fibers, and (b) Processed graphene-nylon fibers

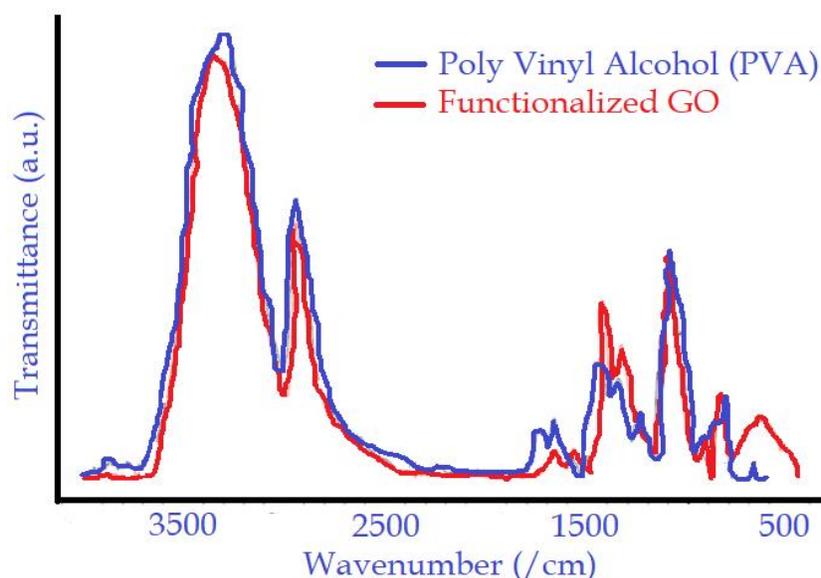


Fig. 12. FTIR of functionalized GO

In order to achieve superior properties, the graphene oxide was functionalized using the esterification process, and infrared spectroscopy was conducted on it. The FTIR spectrum of esterified GO is similar to the neat PVA, though some of the spectra changed in intensity or even disappeared due to the modification (Fig. 12). The development of the band around 1000 cm^{-1} suggests the presence of adsorbed water, which contains a significant contribution from the skeletal vibration of non-oxidized graphitic domains. Indeed, this band was also observed in the esterification reaction of PVA [22].

4. CONCLUSIONS

We developed a rational design to make GO-based self-assembled fillers especially targeted for additive manufacturing based composite applications. This involved the preparation of GO with the modified Hummers method that has both the pre-oxidation and oxidation steps. This graphene oxide was used in the vacuum filtration for obtaining self-assembled sheets, which are further made into fine particles or preferably fine powder. The fine powder is known to act as a filler in manufacturing the composite with nylon as a polymer. The structure and orientation of GO, self-assembled GO were observed under the SEM. Also, infrared spectroscopy was performed on GO and functionalized GO for analyzing the peaks and respective dispersions in the functional groups. The nylon fibers and the graphene-nylon fibers are processed twice using

the fiber extruder. The Raman analysis revealed that an intensity ratio of 0.88 was observed for 1 wt% GO/PVA as compared to a ratio of 0.98 for pure PVA. Similarly, the stress-strain curves reveal a sharp increase in linear characteristic for the 1 wt% GO/PVA and a 40 % increase in the elongation at break due to a strong crystallinity and orientation. The fibers are processed twice to avoid the air bubbles caused by the moisture, which further results in irregular and thinning of the filament. The processed fibers were fabricated using a aon 3D model M printer with 1.75mm nylon filament.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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