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**FUNCTIONALIZED GRAPHENE REINFORCED  
THERMOPLASTIC NANOCOMPOSITES AS STRAIN SENSORS  
IN STRUCTURAL HEALTH MONITORING (Preprint)**

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<b>14. ABSTRACT</b> Functionalized graphene-polyvinylidene fluoride (f-G-PVDF) nanocomposite films were synthesized using simple solvent casting technique. The investigation demonstrates the real time strain response of f-G-PVDF nanocomposite on macro scale under tensile loads and the use of this nanocomposite as 10 strain sensor. This is ascribed to the variation in electrical properties of graphene in the polymer upon mechanical deformation at the nanoscale.							
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ARTICLE TYPE

# Functionalized graphene reinforced thermoplastic nanocomposites as strain sensors in structural health monitoring

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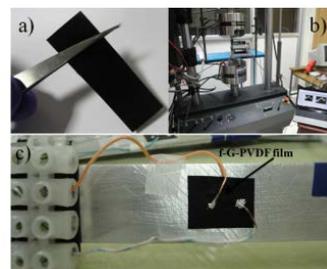
Functionalized graphene-polyvinylidene fluoride (f-G-PVDF) nanocomposite films were synthesized using simple solvent casting technique. The investigation demonstrates the real time strain response of f-G-PVDF nanocomposite on macro scale under tensile loads and the use of this nanocomposite as strain sensor. This is ascribed to the variation in electrical properties of graphene in the polymer upon mechanical deformation at the nanoscale.

A wide range of smart materials have been developed for practical applications such as addressing challenges in advanced aerospace, mechanical, bionics and medical technologies.<sup>1,2</sup> Meanwhile nanotechnology has developed rapidly, permitting manipulation of matter at the level of the atoms and molecules that form the building blocks of smart materials. The combination of these two fields can foster new concepts and realize novel designs that cannot be achieved through conventional approaches thereby offering great opportunities. Graphene has simulated wide interest due to its intriguing properties such as high aspect ratio, high mobility of charge carriers, unique transport performance, high mechanical strength, and high electrical conductivity.<sup>3-5</sup> Their thermal conductivity and mechanical stiffness may rival the remarkable in-plane values for graphite (3,000 W m<sup>-1</sup> K<sup>-1</sup> and 1,060 GPa, respectively); their fracture strength should be comparable to that of carbon nanotubes for similar types of defects.<sup>6</sup> These fascinating properties render graphene suitable for many promising applications such as high strength composite materials,<sup>5</sup> radiation protection etc.<sup>7</sup> There are several possible potential applications using graphene polymer composites especially in automotive, aerospace, electronics, and packaging. The micromechanical cleavage of graphene could produce only minute quantities of graphene and hence it is very difficult to harness its extraordinary properties in polymers in order to utilize graphene in real world applications. With the development of chemical and non chemical techniques for bulk preparation, the scenario of graphene synthesis has changed entirely.<sup>8,9</sup>

Recently there is an increased interest in the arena of strain sensing in structural health monitoring using novel polymer nanocomposites due to the distinct advantages of the polymer and nanofiller. Especially, there are a number of theoretical and experimental reports on strain sensing behavior of 1D carbon nanotubes reinforced polymer nanocomposites. Li et al.<sup>10</sup> reported that SWNT films can be used as strain sensors at macro

scale due to the dependence of the electrical properties of the SWNT films on mechanical deformation at nanoscale. Dharap et al.<sup>11</sup> reported a linear change in voltage when carbon nanotube film is subjected to tensile strain and they proposed that multiple location strain can be measured in the isotropic carbon nanotube film. Hu et al.<sup>12</sup> exclusively studied the strain sensitivity of the carbon nanotube-polymer composites based on statistical resistive network using theoretical and experimental results. The limiting factor of all these hybrid nano composites is the high cost of carbon nanotubes.

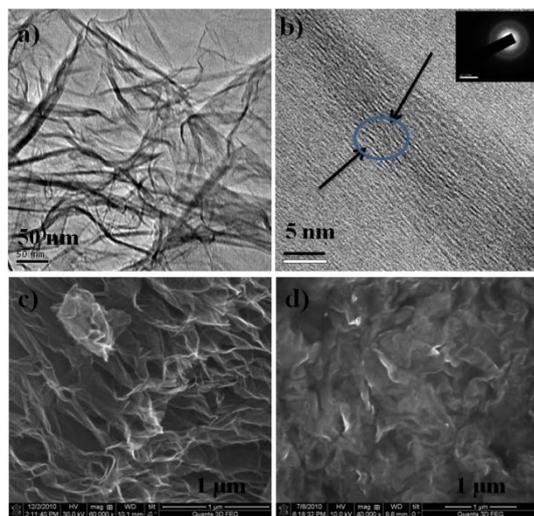
Herein we present a novel nanocomposite for efficient strain sensing, exploiting a combination of functionalized graphene (f-G) and PVDF. Selection of polyvinylidene fluoride (PVDF) was based on its unique properties such as highest chemical resistance,<sup>13</sup> high temperature sustainability and its applications in wide variety of fields such as piezoelectric, pyroelectric etc. The surface of the graphene was modified with hydroxyl and carbonyl groups in order to avoid the aggregation of graphene nanofillers in the polymer and to disperse graphene in the solvent without prolonged sonication, since functionalized graphene sheets in polymer matrices improves the solubility of the f-G in polymers.<sup>14</sup> The aim and scope of the present work is to develop a low cost, light weight and flexible strain sensor with functionalized graphene reinforced PVDF composite.



**Fig. 1:** Optical photographs of a) 2 wt% f-G-PVDF film, b) experimental set up for testing strain sensing response from the nanocomposite films and c) f-G-PVDF composite film attached to the aluminium specimen with two copper leads.

In a typical synthesis process, graphite oxide (GO) was prepared by modified Hummers method.<sup>15</sup> The prepared GO was loaded into a quartz boat and kept in a furnace and hydrogen exfoliated at 200°C for 30 s with a flow of hydrogen gas and resulting graphene in powder form was collected.<sup>16</sup> PVDF with

M.W 1, 00,000 g/mol was purchased from Alfa Aesar. N, N-dimethyl formamide (DMF) in analytical grade was used as solvent. The graphene was functionalized with conc. nitric acid in combination with sulphuric acid in 3:1 ratio for 6 h at 60°C and this solution was washed several times with millipore water to remove the unreacted materials and vacuum filtered through 0.25  $\mu\text{m}$  size micro filter. The final product was dried at 70°C over night in vacuum and labelled as functionalized graphene. For the preparation of PVDF nanocomposites with different weight fractions of f-G, we have employed the following procedure. Initially, fixed amount of f-G nanofillers were dispersed in DMF for 60 min using ultrasonicator. In order to prepare fixed weight fraction of the f-graphene in PVDF matrix, fixed amount of PVDF polymer was dissolved in DMF with the help of magnetic stirrer for 30 min. These two solutions were mixed together using ultrasonicator for one hour. The mixed solution was transferred to a shear mixer and stirred at room temperature for 2 h and at 80°C for 30 min at 4000 rpm. Finally, the composite solution was taken out from the mixer and transferred to a petri dish and kept in the oven at 70°C to evaporate the solvent. Systematic analysis of electrical conductivities of 1 wt%, 2 wt% and 3 wt% graphene reinforced polymer composites have been carried out. The conductivity measurements reveal the insulating nature of 1 wt% composite. 2 wt% f-G-PVDF nanocomposite is conducting in nature due to electrical percolation in conducting filler polymer nanocomposites. On the other hand, the 3 wt% f-G-PVDF nanocomposite shows saturation behavior in electrical conductivity. Hence, it is obvious that percolation is happening with 2 wt% f-G-PVDF nanocomposites.

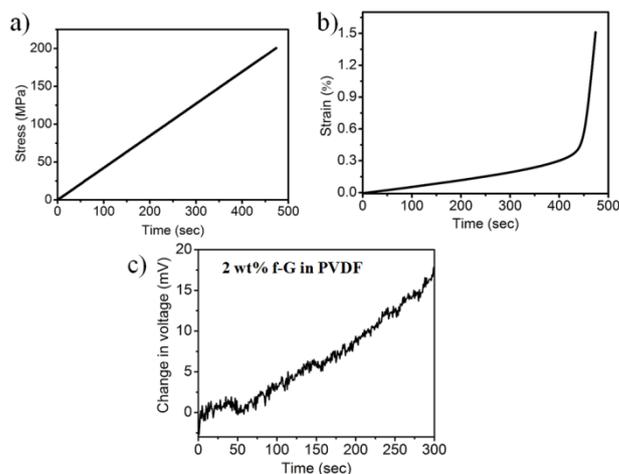


**Fig.2** a) Transmission electron micrograph of the functionalized graphene, b) Lattice imaging of f-G, c) field emission scanning electron micrograph of f-G and d) FESEM image of 2 wt% f-G in PVDF matrix.

Dispersion and distribution of nanofiller in polymer matrices play a major role in determining the improved properties of polymer nanocomposites. Owing to the extraordinary mechanical properties, graphene is considered to be one of the best known and cheap materials for polymer reinforcement. We successfully dispersed the nanofiller (graphene) using homemade shear cum

solvent mixing technique. Figure 2 shows the morphology of graphene and graphene-PVDF composite. Figure 2a exhibits randomly aggregated, wrinkled, thin crumpled sheets of graphene, closely associated with each other thereby forming a disordered solid. Figure 2b shows the lattice imaging of graphene, with thickness  $\sim$ 5-6 nm, indicating a few layered graphene. Figure 2c and 2d show the FESEM images of f-G and 2 wt % f-G-PVDF composite. It is interesting to note that there is a close resemblance between these two figures. The scaffolds in figure 2d suggest that superior conductive network has been formed among graphene flakes in the PVDF matrix.

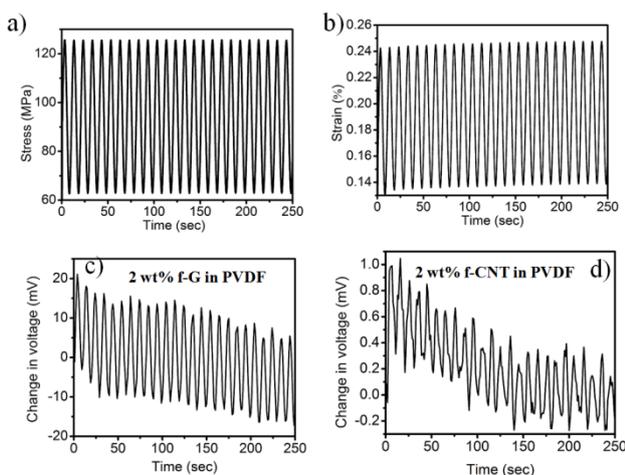
A nanocomposite film of 2 wt % f-G-PVDF was attached to one side of the Aluminium (Al) specimen (Dimensions: 28 cm x 5 cm x 0.3 cm) using high strength epoxy to make perfect bonding between Al and the nanocomposite film and on the other side, (Fig. 1) a conventional metallic strain gauge was adhered using glue. A constant current (Keithley source meter 2400) was passed along the axial direction of the film and the corresponding change in voltage was systematically measured for various strains along the axial direction. Data was continuously acquired using Lab VIEW programme. Al specimen was subjected to ramping loads, tensile and compressive loads on materials testing system (MTS 810) servo hydraulic test machine. The corresponding strain in the composite film was measured by conventional metallic strain gauge.



**Fig. 3** a) Monotonic increment of stress on Aluminium specimen, b) Strain measurement using strain gauge, c) Change in voltage of the 2 wt% f-G-PVDF nanocomposite of Aluminium specimen.

Figure 3a & 3b shows the stress and strain curves with respect to time when the specimen was subjected to continuous increment of loading (2 kN/min). When the load was applied on the aluminium specimen, the composite film bonded through high strength epoxy experiences the same. The change in voltage was observed while the specimen undergoes continuous increment in loading. The corresponding change in voltage of the 2 wt% f-G-PVDF composite while the film was under tension is shown in figure 3c. The change in voltage of the nanocomposite increases continuously with the applied load. As the tensile strain increases, the change in the voltage of the composite also increases. Linear change in voltage was observed with respect to applied strain in 2 wt% f-G-PVDF composite in the elastic region. From figure 3c, it is obvious that, voltage is changing linearly in the elastic region.

For 0.12 % of strain, a voltage change of  $\sim 9$  mV was observed in film and it further increases monotonically up to 0.27 % of strain with a voltage change of 24.6 mV. This leads to nonlinear behavior in voltage change when the specimen goes to inelastic limit. Figure 4 shows the cyclic behaviour of 2 wt % f-G-PVDF composite. It clearly confirms the cyclic response of the graphene composite to the applied strain. The change in voltage also follows the cyclic behavior as depicted in figure 4c. For 0.10% of strain applied, there is a change of  $\sim 20$  mV which is very large value compared with that of carbon nanotubes as shown in figure 4d. This confirms the continuous bending and relaxation of graphene nanofillers in the polymer. The change in voltage of the f-G-PVDF nanocomposite can be mainly attributed to breakage of conductive network or loss of contacts between the nanofiller (graphene) under tensile strain. The second factor is the change in voltage due to the change in distance between the conductive filler particles which promotes the tunnelling effect. Finally, change in the band gap of graphene under tensile strain can also increase the voltage. The present experimental investigation validates the theoretical assumption of changes in the band gap of the graphene when it is strained under tensile and compressive loads.<sup>17</sup>



**Fig.4** Tensile and compressive cyclic test on functionalized graphene-PVDF nanocomposites) applied stress on the specimen, b) induced strain, and the corresponding change in voltages of c) 2 wt% f-G-PVDF and d) 2 wt% f-CNT-PVDF nanocomposites.

2 wt% as well as 3 wt% f-G-PVDF nanocomposites were tested for strain sensing performance. The better strain sensing performance has been obtained with 2 wt% f-G-PVDF nanocomposite. The deterioration in sensing at higher concentration can be attributed to the increased overlap of nanofillers in polymer.

## Conclusions

In conclusion, functionalized graphene-PVDF nanocomposites are synthesized by simple shear cum solvent casting technique. The homogeneous and stable dispersions of graphene in polymer solution have been attained after functionalization. The morphology of the graphene and graphene-PVDF nanocomposites have been characterized by scanning electron

microscope which reveals the 3D interconnecting conducting network of graphene in polymer matrix. The analysis of the change in voltages of different nanocomposite films reveal that 2 wt% f-G-PVDF composite films show higher strain sensing performance compared with its counterparts based on carbon nanotube polymer composites. For higher concentrations of f-G, low strain sensing performance was observed due to the overlap of nanofillers. The rapid changes in contact and tunnelling resistance between optimum concentration of graphene nanofillers in PVDF polymer causes high performance in strain sensing and it can be attributed to the 2D nature and flexibility of the graphene.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: [details of synthesis, Raman spectra, FTIR, are provided in supplementary information].

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