

SiO₂-Ni/Graphene nanocomposite reinforced polymer films with improved mechanical properties and self-heating behavior

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Abstract

In this study, flexible polyvinylidene fluoride (PVDF) nanocomposite films reinforced with SiO₂-Ni/Graphene (NSG) hybrid nanocomposites were successfully fabricated using a simple solution casting method. The NSG nanocomposite was synthesized through a probe sonication-assisted process, and different NSG loadings (100, 200, 300 and 400 mg) were incorporated into the PVDF matrix. The structural and morphological characteristics of the fabricated films were investigated using X-ray diffraction (XRD), Raman Spectroscopy, and Field Emission-Scanning Electron Microscopy (FE-SEM), confirming the successful deposition and uniform dispersion of NSG within the polymer matrix. The electrothermal performance of the films was evaluated using infrared thermography under applied DC voltages ranging from 5 to 20 V. The results demonstrated that increasing NSG content significantly enhanced the Joule heating performance, with the PVDF/NSG-400mg film achieving a maximum surface temperature of 156.5°C at 20 V, compared to 59.8°C for PVDF/NSG-100 mg.

Keywords: Polymer nanocomposites, PVDF, Graphene, SiO₂-Ni nanocomposite, Joule heating, Electrothermal films, Solution casting, Flexible heaters.

Introduction

Polymer nanocomposite films (PNFs) reinforced with inorganic-organic hybrid nanomaterials as electrically conducting additives are gaining increasing interest in the area of development of advanced functional materials for energy and environmental applications¹. Owing to the useful properties such as low mass to volume ratio and high mass to surface area ratio, robust mechanical properties, excellent electrical conductivity and chemical stability². Also, the inorganic-organic hybrid nanomaterials endow easy processability when compared to the metallic and ceramic nanomaterials³. Conductive hybrid nanomaterials of graphene such as silica-graphene⁴ and nickel-graphene⁵ nanocomposites loaded polymer matrices can be responsive to the external stimulus such as heat, pressure, light irradiation, electricity and so on⁶⁻⁸. As a result, these materials have been shown promising performances in different areas including energy production and storage materials/devices⁹, as shielding for Electro Magnetic Interference (EMI)¹⁰, Photothermal energy applications, mechanical sensors, separation and purification materials, waste heat energy utilization devices, surface heaters, joule heating devices, etc.¹¹ as both electrical and thermal conducting nanofillers to various polymers, CNTs and graphene have shown tremendous potential as efficient heating materials^{12,13}. For example, self-segregation induced structures were achieved by Polydimethyl Siloxane-Multi-Wall Carbon NanoTube (PDMS-MWCNT) nanocomposites, that resulted in excellent piezoresistive sensitivity and low percolation threshold by sustaining their mechanical abilities¹⁴. In another study, foam like multifunctional elastomer with strong mechanical and piezoresistive sensitivity, special temperature-sensitivity and EMI shielding properties was successfully fabricated by direct introduction of heat-expandable microspheres (EM) into PDMS-CNT¹⁵.

The multiple interface structure was constructed by PDMS-MWCNT-glass microsphere for reflection and scattering of electromagnetic waves to obtain strong EMI shielding. In another similar study, PDMS-MWCNT composite with highly efficient and tunable microwave shielding were obtained via Liquid Metals (LMs) incorporation¹⁶. When energy (electrical) is delivered to the conductor, it allows certain current to flow through it. The energy (electrical) is dissipated in suppressing the resistance (frictional) between the atoms/molecules of the conductor and electrons. As per the law of conservation of energy, the dissipated electric energy must be changed into some other form of energy (thermal energy) hence, increases the temperature of the material (conductor). This effect is called as Joule heating effect¹⁷.

Recently, owing to Graphene's advantages such as flexibility, high electron conductivity, transparency and mechanical robustness, it has been extensively used in variety of new functional materials especially for the

applications such as defrosters and defoggers, anti-icing, vehicle windows, photothermal materials, interfacial heating devices and so on¹⁸⁻²². Some of the recent reports on graphene based joule heaters explain the heating efficiency of the graphene-polymer system considering the highest temperature reached under specific voltage and input electrical energy²³. It has been suggested that decreasing the resistance of graphene-polymer composites/films is the key factor in enhancing the joule heating efficiency. PVDF due to its properties such as ease of solubility, film forming ability, chemical resistance and thermal stability up to 170°C, it is one of the best polymer matrices to host the graphene sheets through dipole-dipole interactions for the fabrication of flexible self-heating films or composites²⁴⁻²⁶.

Herein, we propose the scalable and facile fabrication of Ni-SiO₂/Graphene (NSG)/PVDF electrical film heaters via solution casting method. The PVDF- NSG film heaters with different concentration of NSG (from 100 mg to 400 mg of NSG mixed separately into the solution prepared of 90 g of solvent N-Methyl-2-pyrrolidone (NMP) and 10 g of PVDF are fabricated. The structural morphological and electrical heating properties of the as fabricated film heaters are improved with increase of their NSG content. In addition, aiming to propose the advantage of these hybrid nano composite film as efficient low power responsive electrical-heating materials, IR thermography was performed under different voltages (5, 10, 15 and 20 V).

Experimental

Materials:

Polyvinylidene fluoride (PVDF) (Kynar®4000HD) polymer was purchased from Arkema Co., Ltd. Nickel nitrate, tetraethyl orthosilicate (TEOS), Ammonia solution, 2-Propanol, Ethanol(99% purity) and N-Methyl-2-pyrrolidone (NMP) was purchased from Sigma-Aldrich. The graphene (few-layered graphene (FLG)) of lateral size less than 10 µm was procured from Angstrom Materials (OH, USA). All these chemicals were utilized as received throughout the experiment without further purification.

Synthesis of Ni-SiO₂/Graphene (NSG) hybrid nanocomposite:

SiO₂-Ni/Graphene hybrid nanocomposite was synthesized by probe sonication mixing at room temperature. Typically, about 0.03 g of FLG was added into 50 ml of ethanol and probe sonicated for about 30 min and designated as solution A. About 0.5 g of Ni(NO₃)₂ was dissolved in 10 ml of water/ethanol (1:1) mixture. The as obtained solution was then poured into 60 ml of 2-propanol solution containing 10 ml of TEOS and 2 ml of aqueous ammonia and designated as Solution-B. Solution B was added dropwise into

solution A with stirring and further probe sonicated for about 1 h under 4 W power and 15 mV amplitude with Pulse on and off interval of 10 min and 2 min respectively. The resultant mixture was filtered, washed with ethanol followed by distilled water and dried in an oven at 100 °C. The dried sample was calcined at 350 °C for 4 h to obtain SiO₂-Ni/Graphene powder. The schematic of synthesis process is shown in Figure 1.

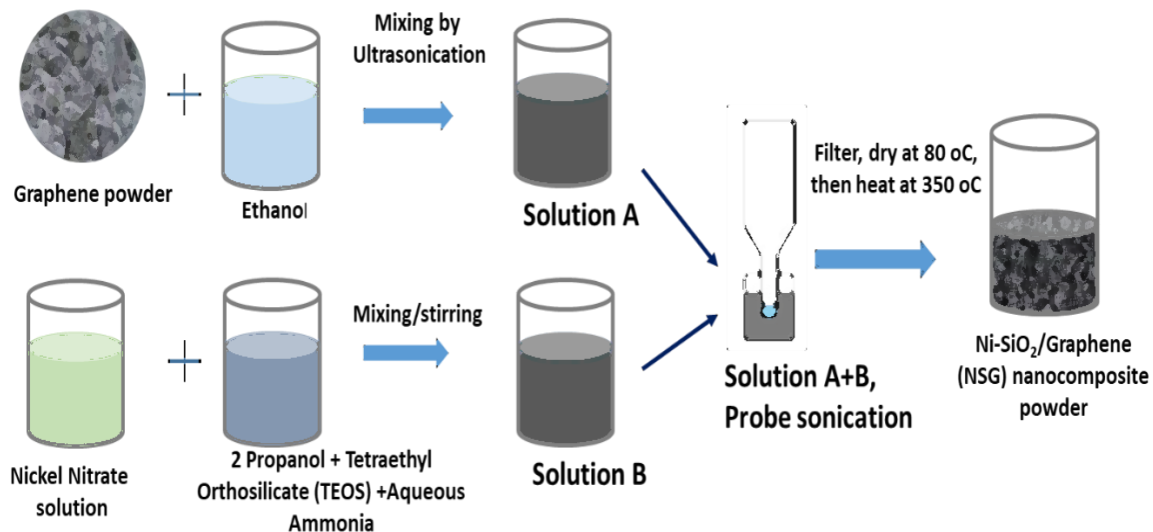


Fig.1: Schematic for the synthesis of SiO₂-Ni/Graphene (NSG) nanocomposite powder.

Fabrication of NSG-PVDF nano composite film heaters:

The NSG-PVDF nanocomposite film heaters were fabricated via facile solution casting method. The well homogenized casting solutions of NSG-PVDF mixtures (10 wt. % PVDF-NMP solution containing NSG of 100, 200, 300 and 400 mg) were separately prepared by stirring at 6000 rpm for 50 minutes using a homogenizer (125 Ultra Turrax), and then probe sonicated for 30 minutes, for removal of trapped air bubbles from the solution. The homogenized solutions were cast on a clean glass substrate by using a casting rod and dried inside a Hot-air oven at temperature of 80 °C. The thickness maintained during solution casting was 0.4 mm. To fabricate neat PVDF composite, PVDF-NMP solution of 10 wt. % was used. After 12 hours of drying, the nanocomposite films were easily peeled off from the glass substrate and placed in an ambient condition of room temperature (25 °C) and humidity of 60 %.

Characterization:

The morphology of NSG powder and NSG-PVDF nanocomposite films were studied by obtaining FE-SEM images (JEOL JSM-6500F, Hitachi Co., Japan). Joule heating property of the NSG-PVDF nanocomposites as a function of increasing DC voltage were investigated by IR thermography by using an IR thermal imager (Fluke, TI450). X-ray diffraction (XRD) analysis was carried out by using Bruker D2 PHASER, Germany.

Infrared spectra were recorded by using Perkin Elmer, USA. Raman spectra were collected by using JASCO NRS-5100.

Results and Discussion

Structural and morphological characterization:

The XRD and Raman spectroscopic analysis were used for structural investigation of the SiO₂-Ni/Graphenenanocomposite. The typical (002) and (004) crystallographic planes of graphene were appeared at 26.50° and 54.79°, respectively as displayed in Figure 2a, bexhibits reduced intensity of those planes in the SiO₂-Ni/Graphenenanocomposite. The graphitic sp² carbon plane (002) in the SiO₂-Ni-Graphene nanocomposite shifted to lower angle (26.50° to 26.22°), and the peak corresponding to amorphous SiO₂ was observed in the 2theta range of 18°–35°. The XRD pattern of the SiO₂-Ni/Graphene presented another minor broad peak in the 2 theta range of 43°–48°, that can be attributed to the (110) plane of Nickel (Ni). The emergence of wider peaks and 2 theta angle shifting of the sp² carbon plane indicated the presence of SiO₂-Ni nanoparticles on the surface of graphene layers.

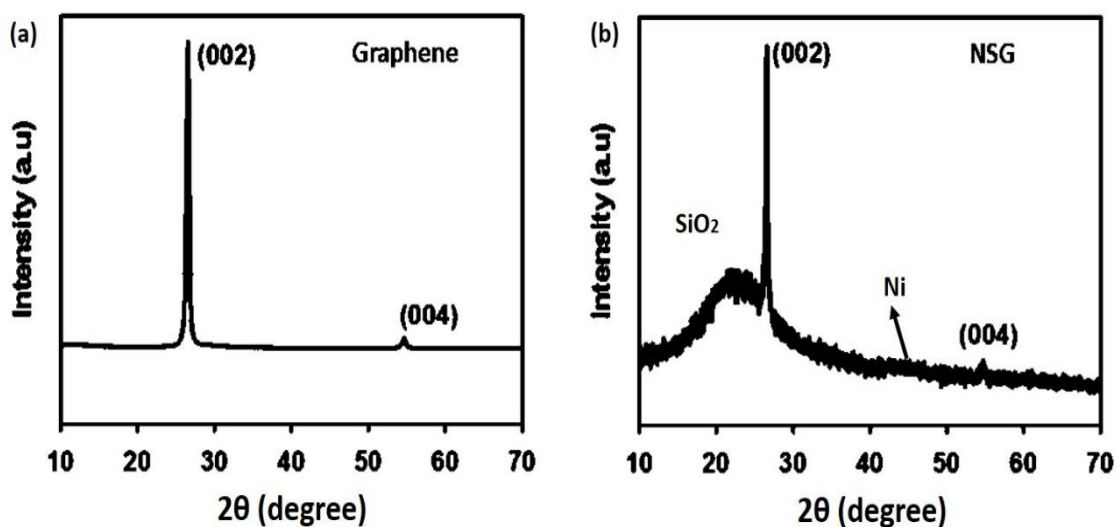


Fig.2: XRD pattern of (a) Graphene and (b) SiO₂-Ni/Graphene (NSG) nanocomposite powder.

The results of SEM analysis also suggested the successful deposition of SiO₂-Ni nanoparticles on the graphene. Figure 3a presents the defective basal and edge planes confirming the graphene sheets exfoliation as a result of probe ultrasonication. Such defective sites permit the coating or chemical modification on the surface. Therefore, SiO₂-Ni nanoparticles were well coated on both the edge and basal planes of graphene as displayed in the Figure 3b. The structural properties of graphene and SiO₂-Ni/Graphene are confirmed by the

Raman spectroscopy as presented in Figure 3c. The clear and prominent peaks at 1577 and 2681 cm^{-1} are ascribed to the G-band and 2D-band of few layered graphene sheets. The significant intensity decreases of these bands in the $\text{SiO}_2\text{-Ni/Graphene}$, confirmed the successful deposition of the $\text{SiO}_2\text{-Ni}$ nanoparticles on the layers of graphene.

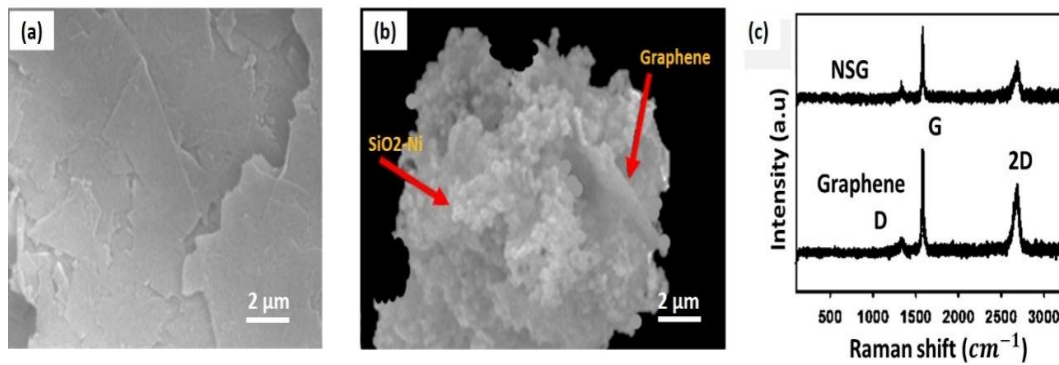


Fig.3: SEM image of (a) Graphene sheets after probe sonication and (b) $\text{SiO}_2\text{-Ni/Graphene}$ (NSG) nanocomposite, (c) Raman spectra of Graphene sheet and $\text{SiO}_2\text{-Ni/Graphene}$ (NSG) nanocomposite.

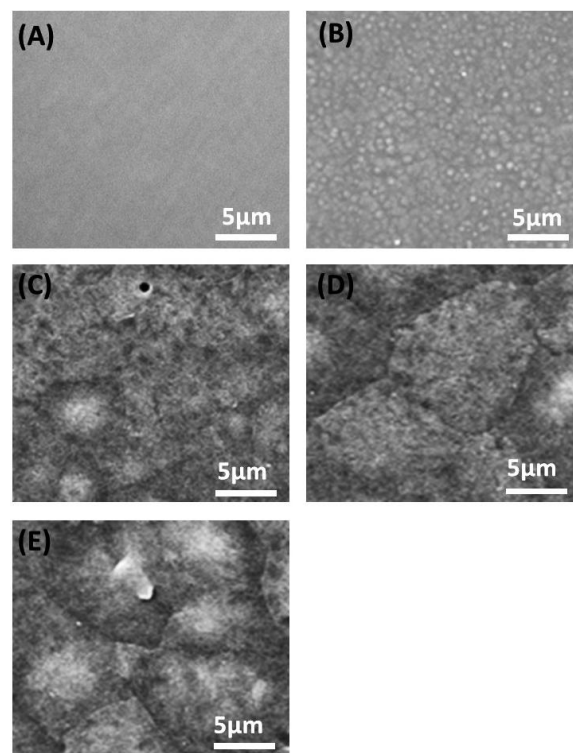


Fig.4: SEM image of (a) PVDF (b) PVDF/NSG-100mg (c) PVDF/NSG-200mg (d) PVDF/NSG-300mg (e) PVDF/NSG-400mg.

The morphological characteristics of the neat PVDF and NSG nanocomposite film heaters were examined by capturing FE-SEM images. The surface of neat PVDF composite Figure 4 (a, b) exhibits smooth and non-porous surface properties. The NSG nanocomposite film heaters (Figure 4 (c-e)) presented dense, rough and non-porous surface with better blending between NSG and PVDF polymer. Interestingly, the increasing content of NSG resulted in increased surface roughness suggesting that the films can provide high surface area for effective heating.

Joule heating performance:

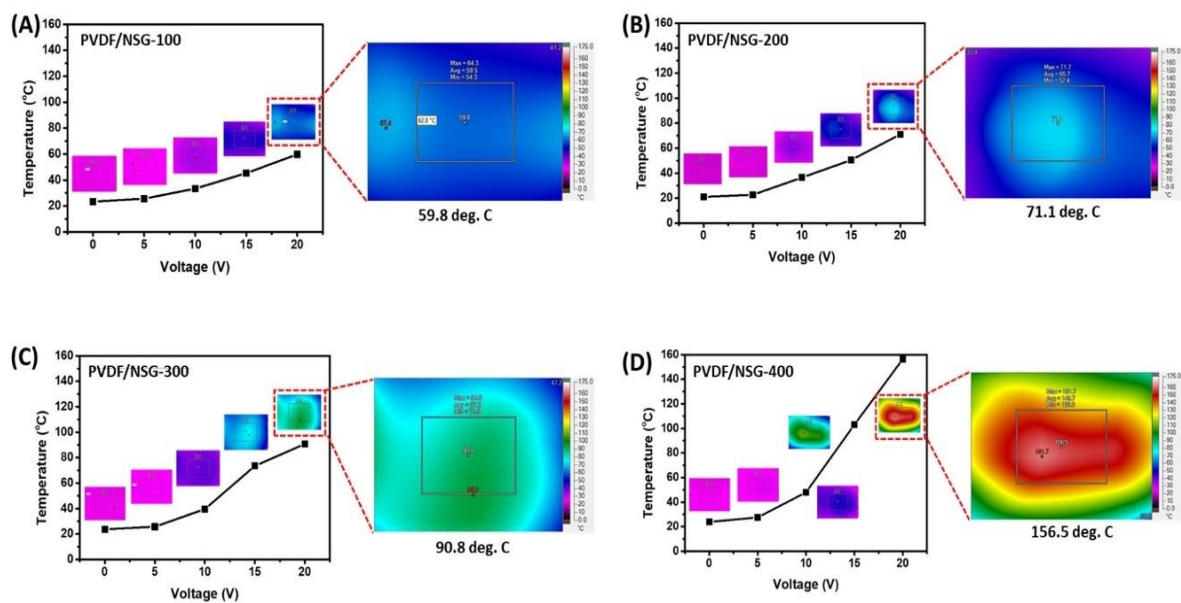


Fig.5:Electrical heating performance of (a) PVDF/NSG-100mg (b) PVDF/NSG-200mg (c) PVDF/NSG-300mg (d) PVDF/NSG-400mg.

With increase of NSG content, the electrothermal heating of the PVDF/NSG nanocomposite films drastically improved, attributing to the efficient electrical and heat properties of NSG (Figure 5). The films samples (size, 3 cm×6 cm) were cut randomly from each sample and connected to power supply using crocodile clip wire, the increase of temperature with increase of voltage within the range of 5 to 20 V was tested by IR thermography. Temperature of (PVDF/NSG-100-PVDF/NSG-400mg) nanocomposite films remarkably enhanced when the DC voltage was increased (Figure 5a-d). The PVDF/NSG-100exhibited the least increase in temperature i.e., from 21°C to 59.8°C, which could be ascribed to lower power to heat transduction due to poor current flow through the nanocomposite film. Little enhance in the temperature is observed to PVDF/NSG-200with high temperature of 71.1°C at 20 V. The temperature of PVDF/NSG-300got increased from 22.2 °C to 90.8°C with rise of voltage. As expected, the highest heating

performance is observed for PVDF/NSG-400 with temperature ranging from 22°C to 156.5°C with rise of voltage from 5 V to 20 V. The electrical heating effect of these films was directly proportional to power supplied to them. This can be ascribed to the increased current through the films leading to increased consumption of electrical energy, with rise of NSG incorporation.

Conclusions

In conclusion, PVDF/NSG films reinforced with SiO₂-Ni/Graphene (NSG) nanocomposite particles were fabricated by the solution casting method. The as fabricated nanocomposite films were characterized by X-Ray Diffraction, and Field Emission-Scanning Electron Microscopy (FE-SEM) and Raman spectroscopy. The IR thermography method was used to study the electrical heating properties of PVDF/NSG films. The infusion of NSG nanocomposite particles of various amounts from 100 mg to 400 mg, exhibited notable increase in temperature from 59.8 °C to 156.5 °C with increase of applied voltage (5 V-20 V). Therefore, Ni-SiO₂/Graphene nanocomposite reinforced polymer films are suitable to be applied in different joule heating areas attributing to the effective heating upon low power delivery.

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