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Fabrication of a cost-effective piezoresistive pressure sensor based on PVC/reduced Graphene Oxide (rGO) composite

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Keywords

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Composite.

Abstract

A cost-effective piezoresistive sensor based on PVC/reduced Graphene Oxide (rGO) was fabricated and its performance was investigated. The weight percent range from 0.1 to 30% of rGO in PVC matrix was studied. Composite parts were prepared by using the solution casting method from Tetra-Hydro-Furane (THF) solvent followed by solvent evaporation. The plot of electrical conduction versus rGO percentage was constructed to obtain the percolation threshold concentration. It was found that the percolation threshold of rGO leading to a continuous stable electrical conductivity in PVC matrix is about 25% beyond which electrical resistance was reduced from about 800 GΩ to lower than 100 KΩ range. The relative changes in electrical resistance of prepared polymer parts as a result of impact (stress), stretch and bending deformation were studied. The results showed that the fabricated composite can be used for sensing and/or monitoring and measurement of any mechanical displacement with high sensitivity, promising reproducibility and satisfactory durability. It must be mentioned that, during impact tests of polymer composites, a small piezoelectric effect was also observed for which further complimentary studies are being planned to be performed in near future in order to better understand this effect and its underlining molecular basis.

1. Introduction

Graphene is a wonderful material in view of the measured extraordinary properties like high thermal conductivity, Young's modulus, electron mobility. There are various methods adopted for the synthesis of graphene. Among the various method of synthesis of graphene, chemical method of synthesis of graphene is widely studied in the literature. The chemical method of graphene synthesis includes, initially the oxidation of graphite followed by reduction using reducing agent [1]. Two protocols are widely popular for the oxidation of graphite via Hummer's method and modified Hummer's method. Graphene is extensively studied in view to obtain polymer nanocomposites for various applications [2]. The functional group presents on graphitic lattice acts as a defect and deteriorates the properties of graphene. Thus, elimination of remaining functional groups of reduced Graphene Oxide (rGO) is an important step to obtain the graphene nanosheets with lower defects. In order to improve the sensitivity of mechanical sensors, it is very important to improve the piezoresistive effect factor. The effect of piezoresistance was discovered by Smith (1945), which further led to the development of the technology of fabricating sensitive sensors and also used as the main technology of mechanical sensing [3]. The fractional change in resistance under applied strain is called as the Gauge Factor (GF). This technology has many practical applications, such as touch force pressure sensors

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and accelerometers [4]. It is also possible to check the efficiency of piezoresistant construction configuration through the carrier mobility of the nature of the piezoresistive material. There are different types of stress sensors, the three main categories of them are ceramic sensors, polymer composites, and natural samples [5]. The category that has been studied in this research is polymer composite. The performance of these composites is based on the piezoresistance effect. The preference of this class of materials over the other counterparts is to improve their thermal, mechanical and electrical properties which have many applications, including production of pressure, biological and energy sensors [6]. The efficiency and functional superiority of composites in terms of the above-mentioned properties depends on the type of polymer material used for composite fabrication [7]. The way the polymer composites operate is by addition of conductive particles. The electrical current can be distributed to all parts of the composite, which changes electrical resistance by causing local stress. This is the basis of the preparation and function of the rGO polymer composites [6,8]. Among the various forms of stress that can be created on the composites (stretching, impact, squeezing, etc.) the stretching of the components increases the electrical resistance. However, squeezing reduces these physical properties. Therefore, the resistance of composite components depends on the concentration of the conductive material on the proper site [9]. Because application of stretching force reduces local concentration of rGO in a given area of the composite, the current also decreases followed by a subsequent increase in the electrical conductivity of the material, while an increase in the compression of the polymer segment results in a reduction in electrical conductivity which arises from increase in local rGO particles concentration. Both piezoresistive and piezoelectric effects are placed in the category of anisotropic properties of materials as a result of changing the numerical value of their parameters due to deformation [6,10]. Anisotropic properties are direction-dependent properties. Piezoelectric polymer materials are known as lead-free organic piezoelectric materials. These materials are classified based on their morphology and dipole moment. The most common piezoelectric polymers investigated are PVDF (PVF_2 or polyvinylidene fluoride or polyvinylidene difluoride) or its PVDF-TrFe copolymer [11]. Polymeric materials have strong polarity, excellent mechanical flexibility, environmental compatibility and low acoustic impedance. Although polymer-based piezoelectric materials have limitations such as high leakage and low thermal stability, but through adding various types of micro and nanofillers such as graphene, metal oxide materials and piezoelectric ceramic materials in order to make piezoelectric composites, their piezoelectric properties and thermal stability have been improved. Because other types of polymer materials can be used to make sensors, actuators and energy harvesting devices [12,13]. Despite what has been said about the advantages of polymer materials and their preference for making piezoelectric components, these materials have low piezoelectric coefficients [14]. The piezoelectric coefficient, expresses the number of changes in the volume of a piezoelectric material due to the application of a field or mechanical stress. The investigation and study of piezoelectric properties was first started with ceramic materials. These materials have large piezoelectric coefficients, but it is easier to make and treat organic materials such as polymers in order to prepare piezoelectric parts [15,16]. In fact, the combination of these two groups of inorganics (ceramic) and organic (polymeric) materials is the best way to make these parts, and these two. They complement each other. Zinc oxide fine wires are incorporated in flexible polystyrene matrix and studied as piezoelectric strain sensor results showed that a GF of about 1250 can be obtained [17]. Graphene itself shows to some excellent piezoresistive effect. A graphene based piezoresistive pressure sensor has been developed using silicon nitride membrane with graphene meander patterns. A GF of 1.6 for graphene and a dynamic range from 0 mbar to 700 mbar was obtained [18]. A wearable pressure sensor based on polymer materials as a substrate and active materials inspired by the properties of human skin was prepared and investigated. In general, it can be realized that the prepared pressure sensors are less restrictive and the sensor responses show a small hysteresis that the origin of which is still unknown. It's better to use elastic polymers as substrate because it causes a smaller surface area and reduces the costs of the preparation process [19]. Recently composites based on Multi-Walled Carbon Nanotube (MWNT) were prepared for pressure measurement. Prepared sensors possess high linearity and sensitivity and also are thermally and mechanically durable performance analyses. The use of different polymers leads to different resistance properties. The best polymer used is polyimide showing rather satisfactory [20]. In another study piezoresistive behavior of semiconducting polymers has been investigated. The piezoresistivity and the relationship between resistance and the applied force are investigated theoretically. Carbon filled polyethylene has been modeled mathematically [21]. The goal of this research is to develop a cost-effective piezoresistive pressure sensor based on PVC/rGO composite.

2. Materials and methods

All chemicals used for the synthesis of Graphene Oxide (GO) and rGO were as bellows: Graphite powder, H_2SO_4 (Sulfuric acid 98%), $NaNO_3$ (Sodium nitrate), H_2O_2

(Hydrogen peroxide 35%), NaHS (Sodium hydrosulfide). All chemicals were provided by Merck and used as received without any further purification. Commercially available PVC polymer (density=1.33 g.cm^{-3}, melting point=145°C, MW=about 185000 from Tabriz Petrochemical Company, Iran) was used. Well known Hummer's method was adopted for the synthesis of GO and rGO [2]. In brief, 240 mL of H_2SO_4 was added to a 1.5 L round bottle flask placed on the top of a magnetic stirrer. An amount of 9 g of graphite powder and 4.5 g of $NaNO_3$ was added to H_2SO_4. The mixture was cooled down to 0°C in an ice bath and 25 g of graphite powder was slowly added. The reaction vessel was maintained for 30 minutes at 35°C temperature. Then water was added to the mixture followed by addition of 420 mL water and 5 mL H_2O_2 (30%) and the reaction vessel was cooled to ambient temperature. The final solution was centrifuged and washed with deionized water several times, then dried at 60°C in an oven to obtain graphite oxide. The obtained graphite oxide was reduced by NaHS (2 g in 100 mL solution).

2.1. Characterization

GO and rGO were characterized using X-Ray Diffraction (XRD) and UV-Vis-NIR spectroscopy methods. For XRD studies, a Bruker D8 Advance (Germany) instrument was employed. It was operated at the incident X-rays with K_α=1.54 nm from the Cu target. XRD patterns were recorded in the scanning range of (2θ) 10 to 70 degrees with a step scan and step size of 0.02°. For UV-Vis-NIR spectroscopy in the wavelength range of 400–4000 cm^{-1} a Hitachi U-2800 spectrophotometer (Japan) was used. Scanning Electron Microscopy (SEM) image of the prepared rGO was recorded on a Mira 3 Tescan SEM instrument (Czech Republic).

2.2. Preparation of polymer sheets by casting method

The casting process is a plastic shaping technique in order to produce polymer films or sheets with a thickness of less than 250 μm by melting or dissolving the desired materials and passing through a flat die between several rollers. The polymer pieces were cut as small as possible (about 2 mm ×2 mm) to better and more evenly dissolve in the solvent. Here, a piece of commercial PVC sheet was used as polymer source. Tetra-Hydro-Furan (THF) was employed to dissolve PVC and obtain the desired solution for casting. Prepared rGO as the conductive material in order to tune the conductivity properties of the polymer was used in this study. First, the PVC pieces were cut as small as possible and transferred into a beaker glass, the solvent was added in the presence of a small amount of (0.1% up to 50 % wt.) rGO in several steps until the complete dissolution of the polymer. Then some rGO powder was added to the solution until a

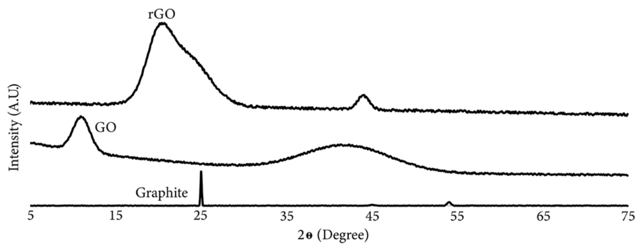

Figure 1. XRD pattern of the graphite powder, prepared GO and prepared rGO.

until a thick solution was obtained. In the last step, the solution was poured into a specific mold and kept at normal ambient temperature for 24 hours. The very thin layer formed due to evaporation of solvent was separated from the mold. Electrical properties were checked and compared with the original PVC sheet.

2.3. Investigating the piezoresistive and piezoelectric properties

The prepared sheets were separated from the mold and their electrical resistance was studied. In this study, choronopotentiometry was used in order to study the piezoresistive properties of the prepared composite i.e., applying a current step and recording the resultant potential changes over time due to stress or tension. A current step of 0 and 100 μA were applied for 20 and 60 s, respectively. The resistance of specimens was easily calculated by Ohm's law, $R = V/I$. In some preliminary experiments with various percentages of rGO in composite, a plot was constructed as variation of resistance versus rGO percentage to determine the percolation threshold of the composites. With the help of the diagram obtained from the Percolation Threshold Theory (PTT), the electrical resistance behavior of nanocomposite can be explained. This theory, which is actually a mathematical theory, expresses the amount of penetration of particles in a surface. The inflection point of the curve shows the maximum amount of rGO present in PVC matrix to achieve a continuous electrical conductivity.

3. Results and discussion

XRD patterns of the graphite powder, GO and rGO were given in Figure 1. As can be seen in Figure 1, the XRD pattern of graphite shows a single sharp peak centered at about 27° which can be attributed to the diffraction peak of (002) plane of the graphite. Also, there is another weak peak at about 55° ascribed to (004) plane of the graphite. The reduction of GO is also confirmed with the help of XRD. Due to the oxidation of graphite, the interlayer distance between GOs is more compared to graphite. Thus, the XRD spectra of the GO shows a peak moved to lower diffraction 2θ angles. The *d*-spacing of the GO is calculated using the well-known Bragg's law, i.e., $\lambda = 2\,\mathrm{d.}\ \sin(\theta)$,

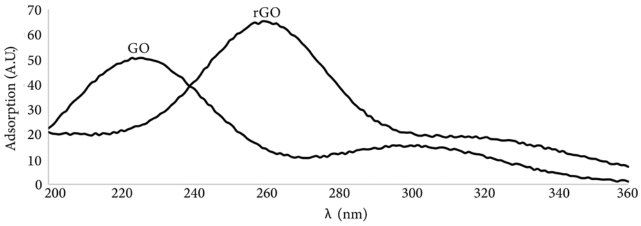

Figure 2. UV-Vis spectra of the prepared GO and rGO.

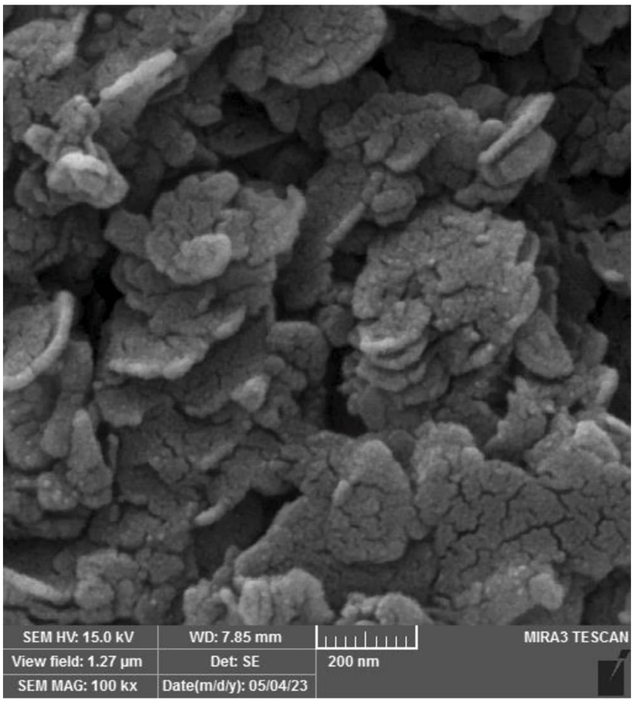

Figure 3. SEM image of prepared rGO.

where λ is the wavelength of X-ray beam (0.154 nm), d is the interplanar spacing, and θ is the diffraction angle. The d-spacing of GO synthesized is about 0.71 nm. As is evident from Figure 1, peak at about 23° approving the successful reduction of GO. The peak at about 23° is due to (002) plane of the rGO and the peak at 43° is an indication of (100) plane of the rGO. The d-spacing of rGO is calculated to be 0.37 nm. Also, the UV–Vis spectra of the prepared samples were measured and recorded. Figure 2 shows the UV–Vis spectra of the GO and rGO. The UV–Vis-NIR spectra, as given in Figure 2, shows a sharp peak at 232 nm wavelength, a characteristic peak of GO as was described before. Upon reduction of GO with NaHS, the peak is shifted rightwards to about 270 nm, approving the successful reduction of GO into rGO. The existence of various functional groups on the surface of rGO deteriorates the electrical properties of rGO. Some researchers have used NaHS as a reducing agent to reduce GO into rGO. In current work, the reduction of GO into rGO with sodium hydrosulfite removes main of the functional groups from the surface as established in literature [22]. Thus, this procedure of reduction of GO is effective for subsequent applications of rGO as a filler in polymer composites/nanocomposites for applications based on electrical properties. Figure 3 shows SEM image of the

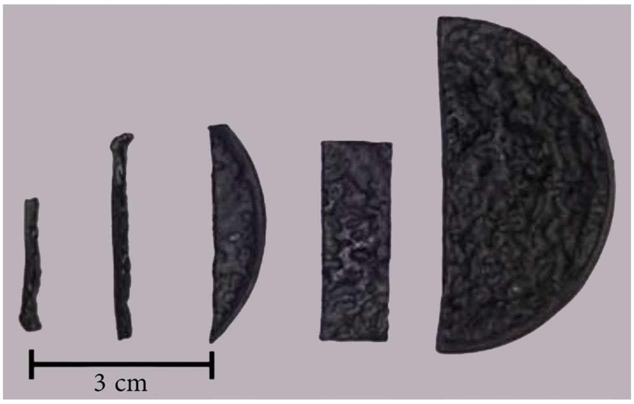

Figure 4. Exemplary samples of prepared PVC/rGO composites.

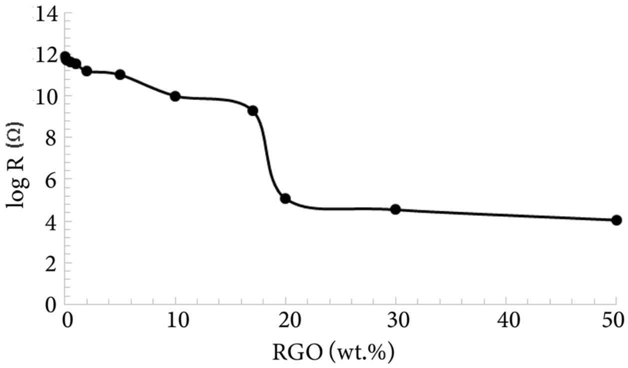

Figure 5. Variation of resistance versus rGO percentage to determine the percolation threshold of the composites.

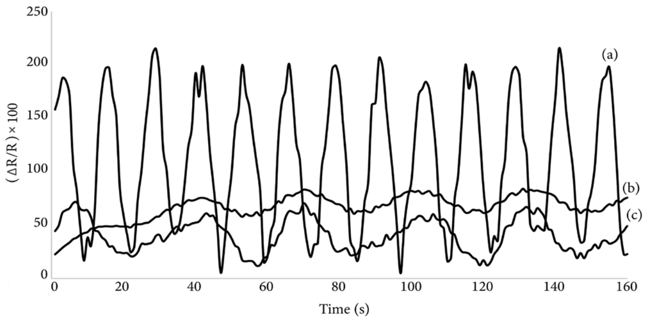

Figure 6. Relative change in electrical resistance (ΔR/R%) versus time for PVC/rGO composite sample during application of: (a) Successive stretching-relaxation; (b) successive bending force and (c) impact on composite plates.

prepared rGO as layered stack like nanostructure. Figure 4 shows exemplary samples of prepared PVC/rGO composites employing cast method. Figure 5 shows the variation of resistance versus rGO percentage to determine the percolation threshold of the composites. From Figure 5 it was found that the percolation threshold of rGO leading to a continuous stable electrical conductivity in PVC matrix is about 25% beyond which electrical resistance was reduced from about 800 GΩ to lower than 100 KΩ range. The results of relative changes in electrical resistance ($\Delta R / R$) for polymer composite for a polymer with 20 mm × 2 mm × 1 mm dimensions during application of cyclic consecutive impact, stretching and bending forces were reported in Figures 6. In these figures, the horizontal axis shows the time during mechanical force

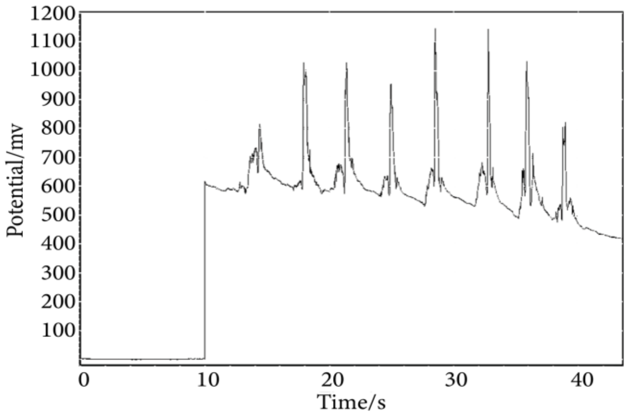

Figure 7. The variation of OCP vs. time while applying multiple impacts with a light 50 g hammer in a 40 s time interval.

application and relaxing cycles. As can be seen from Figure 6, relative change percentage in resistance is about 400% revealing a good piezoresistive effect for this polymer composite. Resistance changes in four consecutive bending cycles exhibit quite desirable and stable piezoresistive effect. Because the time intervals of bending cycles are relatively small, the composite material cannot be recovered after removing the applied tension immediately, so a gradual reduction in baseline resistance can be observed. In order to study the piezoelectric effect, the Open Circuit Potential (OCP) method was used. The variation of OCP versus time while applying multiple impacts with a light 50 g hammer in a 40 s time interval was registered, the plot of which can be seen in Figure 7. From sudden voltage changes that can be seen as very sharp peaks (spikes), it is evident that this polymer exhibits piezoelectric effect to some degree. This piezoelectric effect is actually the result of applying an external force and as a result of stimulating the dipoles of the structure, which creates a momentary electric field and ultimately causes voltage generation. This effect is more important in polymer materials, so the generated voltage can be attributed to the presence of chlorine containing PVC polymer material.

4. Conclusions

In short, the following conclusions can be drawn from this research: A cost-effective composite with satisfactory and reproducible piezoresistive effect up on bending as well as stretching-relaxation of the prepared composite was fabricated. In the process of fabrication of this composite, a simple solution casting method was used without the need for advanced approaches and techniques. Among other advantages of the prepared and studied composite, superiority to conventional ceramic composites in terms of performance, ability to be produced in various shapes and sizes can be emphasized. Also, the produced composites can potentially be used for development and fabrication of biological pressure sensors and tension detectors for health and civil monitoring purposes, respectively. Origin of the observed piezoresistive effect is based on the fact that reduced Graphene Oxide (rGO) has a high electric conductivity acting as local conductive path in PVC matrix as an electrically insulating material. Mechanical displacement changes form and morphology of the percolated paths in the matrix so changing effective electrical resistance. The results showed that in addition to the piezoresistance effect, the prepared composite also shows a weak piezoelectric effect for which more detailed investigation was postponed to some further studies.

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Conflicts of interest
The authors declare no financial or personal conflicts of interest related to this work.

Author Contributions
All authors contributed to the reported work for conceptualization, methodology, validation, writing-review and editing, and supervision.

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