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A Potential Approach to Enhance the Seebeck Coefficient of UHMWPE by Using the Graphene Oxide

Aqsa Irfan¹  Malik Naqash Mehmood²  Malik Sajjad Mehmood*  Arif Aziz³
Mansoor Ahmad Baluch¹  Muhammad Rizwan²  Tariq Yasin⁴
1. Department of Basic Science, University of Engineering and Technology, Taxila, 47050, Pakistan
2. Department of Physics, Air University, 444000, Islamabad, Pakistan
3. Harbin Engineering University, Harbin, Heilingjiang, 150001, China
4. Department of Chemistry, Pakistan Institute of Engineering and Applied Sciences, 45650, Islamabad, Pakistan

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ABSTRACT

Thermoelectric materials have been a competent source for the production of energy in the present decade. The most important and potential parameter required for the material to have better thermoelectric characteristics is the Seebeck coefficient. In this work, ultra high molecular weight polyethylene (UHMWPE) and graphene oxide (GO) nanocomposites were prepared by mechanical mixing by containing 10000ppm, 50000ppm, 70000ppm, 100000ppm, 150000ppm, and 200000ppm loadings of graphene oxide. Due to the intrinsic insulating nature of UHMWPE, the value of Seebeck for pristine UHMWPE and its nanocomposites with 10000ppm & 50000ppm of GO concentration was too low to be detected. However, the Seebeck coefficient for composites with 70000ppm, 100000ppm, 150000ppm, and 200000ppm loadings of GO was found to be 180, 206, 230, and 235 µV/K, respectively. These higher values of Seebeck coefficients were attributed to the superior thermal insulating nature of UHMWPE and the conductive network induced by the GO within the UHMWPE insulating matrix. Although, the values of the figure of merit and power factor were negligibly small due to the lower concentration of charge carriers in UHMWPE/GO nanocomposites but still reported, results are extremely hopeful for considering the composite as the potential candidate for thermoelectric applications.

1. Introduction

Due to the excessive use of natural resources for power generation, i.e. of $4.1 \times 10^{27}$ J, thermoelectric materials are coming to the limelight for the advantage of conversion of heat energy into electrical energy and vice versa. It is based on the thermoelectric effect with Seebeck effect (conversion of heat energy into electrical energy), Peltier effect (conversion of electrical energy to heat energy), and Thomson effect (conductor heating/cooling). These physical phenomenons can be used for the conversion of heat from home, industries, and many other sources into...
useful electricity by means of thermoelectric materials. Thermoelectric generators are basically solid state devices, ideal for small scale power generation with salient features of fixed parts, zero noise, and highly reliable \[^{[1]}\]. The efficiency of thermoelectric material is a function of the figure of merit $ZT = (\sigma S^2/K)T$, where $\sigma$ is the electrical conductivity in units of Siemens per meter, $S$ is the Seebeck coefficient in units of volts per degree, $K$ is the thermal conductivity in units of Watts per degree per meter and the units of $Z$ are the inverse of temperature, so that $ZT$ is dimensionless, where $T$ is the absolute temperature in units of Kelvin. The more efficient thermoelectric materials have high electrical conductivity, low thermal conductivity, and high Seebeck coefficient.

The most commonly used thermoelectric materials were Bismuth telluride (Bi$_2$Te$_3$), Lead telluride (PbTe), Tin Selenide (SnSe), Silicon-Germanium alloys, however; the problem such as the involvement of harmful materials and difficulties in processing were the major constraints. It is therefore, researchers are working to replace the aforementioned materials with conducting polymers \[^{[2]}\].

Among the various conducting polymers, polyaniline (PANI) and poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), Poly(3-hexylthiophene) (P3HT), and their derivatives are promising candidates of thermoelectric (TE) materials. Majority of polymers, other than conductive ones, have low electrical conductivity, which is the major limitation for using polymers as TE materials with reasonable confidence. To overcome this limitation, conductive nanofillers are introduced in polymers to retune their electrical and thermal conductive properties. Among these fillers, graphene based nanofillers i.e. graphene, reduced graphene oxide, graphene oxide (GO) nanoparticles, and graphene nanoplatelets are suitable conductive filler in insulating polymers for required thermoelectric applications because of their excellent electronic, electrical, optical, thermal, and mechanical properties with large surface area \[^{[3]}\].

For the first time, thermoelectric properties of PANI/GNs were reported by Du et al., \[^{[4]}\] using the ratios of 4:1, 3:1, 2:1, and 1:1 of polyaniline and graphene nanosheets, respectively. The values of figure of merit, i.e., ZT for films and pallets were found to change from 0.05 to 1.47 and from 0.64 to 5.60 $\mu$W$m^{-1}K^{-2}$, respectively. Xiang et al., \[^{[5]}\] prepared graphene nanoplatelets (GNP) based polyaniline composites and reported the values of Seebeck coefficient and electric conductivity $\sigma$ 33 $\mu$V/K and 59 S/cm, respectively for the sample containing the 40 wt% of PANI. The major novelty of this work was the in-situ polymerization of aniline monomers for composite preparation. Yoo et al., \[^{[6]}\] were the first to prepare the composites of PEDOT: PSS with 3 wt% of graphene. The following results were obtained in this study:

(1) The value of electrical conductivity for PEDOT:PSS/graphene composites was 637 Scm$^{-1}$ in this study.

(2) The values of electrical conductivity were found 41% higher for the composites compared to pure PEDOT:PSS film.

(3) The highest thermoelectric power factor of 45.7 $\mu$W$^{-1}m^{-1}.K^{-2}$ was obtained, which is 93% higher than that of the primal PEDOT:PSS film.

Using graphene doping and hydrazine treatment Xiong et al., \[^{[7]}\] formulate PEDOT:PSS nanocomposite with the following strange behaviors:

(1) Decreasing behavior of the electrical conductivity was observed with the increase of graphene contents (For 3 wt% graphene decrease in electrical conductivity was from 1298 to 783 S cm$^{-1}$)

(2) A significant increase in thermoelectric power factor was observed, i.e., 53.3 $\mu$W$^{-1}m^{-1}.K^{-2}$, which was two times higher than pure PEDOT:PSS

More recently Gao et al., \[^{[8]}\] prepared acrylonitrile-butadiene-styrene copolymer/reduced graphene ABS/rGO nanocomposites by latex method. Although, electrical conductivity was noted as high as 0.09 S/m but an increase in thermal conductivity was also found with increasing the contents of graphene was increased in ABS.

This study aims to investigate the feasibility of using a unique, gold standard high strength industrial polymer i.e. Ultra High Molecular Weight Polyethylene (UHMWPE) as thermoelectric material. UHMWPE has been the substitute of many organic materials having a long chains of monomers of ethylene (molecular mass ranges between 3.5 to 7.5 million amu), with the properties of having no odor, no taste, nontoxicity, and abrasion resistant. Due to UHMWPE’s high molecular weight, it will not modulus, diffuse, or stream out as a fluid, and can be processed with powder metal technology. The properties of UHMWPE that motivates for analyzing it for the subject matter of interest are its ability to withstand in severe environment, the highest capability of heat insulation/absorption among the family, dissipation of energies from various physical processes like stress, pressure, etc., possibility for inducing the conducting networks within UHMWPE matrix either by incorporating the conductive fillers or by increasing the C=C conjugations and most importantly tuning its electrical conductivity while inducing the free radicals in UHMWPE matrix \[^{[9-11]}\].
2. Experimental

2.1 Materials

UHMWPE resin powder, H₂SO₄, H₃PO₄, KMnO₄, commercial Graphite, HCl, and water were used for the preparation of UHMWPE/GO nanocomposites.

2.2 Preparation of UHMWPE/GO Composite Pellets

Graphene oxide (GO) was synthesized by a modified Hummer’s process in which 1 g of commercial graphite, 8 ml of HCl, and 25 ml of H₂O were stirred under room temperature for 30 min and allowed to settle down. After decantation, washing of the precipitate was performed with distilled water continuously until it achieved pH 7. The precipitates were then left over for 12-16 h at room temperature to obtain expanded graphite having a silverish black color. After obtaining the expanded graphite, a mixture of 1 g of expanded graphite, 40 ml of H₂SO₄, and 3.9 ml of H₃PO₄ was placed in an ice bath (0-5 °C) and continuously stirred for 30 min. After this mixture was slowly removed from the ice bath and 1.8 g of KMnO₄ was added, the admixture was then continuously stirred for 30 min at a temperature below 5 °C. Subsequently, 10-15 ml of H₂O was added to the mixture at room temperature and placed on the magnetic stirrer for 15-20 min stirring again, which turned the color of the mixture to reddish brown. This reddish brown mixture was then sealed and boiled to 100 °C and stirred for the next 2 h which changes its color from reddish-brown to bright yellow. The bright yellow solution was diluted by adding 15 ml of H₂O and 4-5 ml of H₂O₂, stirred at room temperature for 30 min, and the solution is allowed to settle down overnight after that decantation of the upper clear half was performed. The subsequent blend were washed over and over by centrifugation with 10% HCl and deionized water for a few times until it turned to gel-like substance having pH=7. After the process of filtering, drying, centrifuging at 80 °C for 6 h, and sonication for 5 hours in H₂O₂, the graphene oxide (GO) was obtained as a black powder.

To get the UHMWPE/GO pellets, the mixture of UHMWPE and graphene oxide nanoparticles were prepared having 1 wt.%, 5 wt.%, 7 wt.%, 10 wt.%, 15 wt.%, and 20 wt.% of graphene oxide. To obtain the homogenous mixture, the mechanical mixture available at Pakistan Institute of Engineering and Applied Sciences PIEAS was used, and each mixture was mixed mechanically for 120 minutes. Afterward, each mixture was pressed in the shape of pellets having the thickness=4mm, diameter =13mm. The pressing was done with the help of a manual laboratory hydraulic press available at PIEAS. The pressure during the fabrication of pellets was slowly varied from 50 to 200 MPa. The pressure rose gradually from lower to a higher value. At maximum values, a holding time of 20 mints were given to have compact pellets. It is worth mentioning here that the whole compaction process was carried out at room temperature. Subsequent to compaction, the pressure was removed and pellets were placed on the shelf for the next 24 hours to ensure their quality of each formulation compaction.

2.3 Characterization of UHMWPE/GO Composite Pellets by X-ray Diffraction

X-ray diffractometer (Model X’ TRA48, Thermo ARL) was used for X-ray diffraction analysis. The operational voltage of the instrument was 45 kV and a current of 40 mA was applied. Using the famous Bragg’s equation, the inter layer spacing dhkl was calculated

\[ d_{hkl} = \frac{n\lambda}{\sin \theta} \]

Where n, λ and θ are the diffraction level, wavelength, and the Bragg’s angle, respectively while hkl are the lattice planes. The wavelength of the X-ray was 1.541 Å. The data was collected in the reflection mode from 5° to 60° at a scanning rate of 10° min⁻¹. The average crystallite size (D) normal to the lattice plane was acquired by utilizing Scherer’s formula given as:

\[ D = \frac{K\lambda}{\beta \cos \theta} \]

Where β is the full width at half maxima (FWHM) in radians K is crystal factor and is equal to 0.89. The lattice parameter was calculated using the following equation

\[ a = \frac{\lambda}{2\sin \theta} \sqrt{h^2 + k^2 + l^2} \]

The % crystallinity of nanocomposites was calculated while using the following equation

\[ X_c(\%) = \frac{\text{Total area} - \text{Peak amorphous area}}{\text{Total area}} \times 100 \]

2.4 Characterization of Physical Properties

Electrical conductivity of UHMWPE/GO composites is measured by four-point probe method. The voltage data is obtained from the inner two ends while the current data is obtained from the outer 2 ends. It is worked by contacting 4 equally spaced, co-linear copper electrodes coated on the glass substrate with the material. The electrical conductivity of composites along with cross-sectional area A and length l is determined by:
3. Results and Discussion

3.1 Structural Analysis of UHMWPE/GO Composite Pellets

To precede the investigation of the impact of graphene oxide inclusions in the crystalline structure of UHMWPE, X-ray diffraction analysis has been conducted. Figure 1(a) expresses the graphs of virgin UHMWPE, and 1%, 15%, and 20% of GO composites embedded in UHMWPE substrate. Two sharp narrow peaks at the angle of 2θ = 21.5° (110) and 2θ = 24°(200) of each image shows the orthorhombic crystallographic planes of UHMWPE in reference to work reported in the literature [10,12,13]. Figure 1(b) shows the phase analysis of raw UHMWPE with intense sharper peaks with a significant amount of amorphous area. It is evident from results that the addition of graphene oxide results in a decrease in the crystalline peaks of both reflection planes for all samples. The reduction in the intensity peak of the 1% sample is higher than that of other percentages. Further increase in graphene oxide content again caused the recovery of sharpen peaks. Plasticity induced by GO within the matrix of UHMWPE is attributed to the variation in chain breakage that occurs close to the crystalline lamellae.

It is also cleared from the images that it has no characteristic broad peak of graphene oxide at the angle of 25.5°, however, some broadness at 30° (figure 1(b)) predicts the complete dispersion of GO composites in the substrate. Another evidence of complete dispersion of GO was the sudden decrease in intensity of 1% UHMWPE/GO compared to that of virgin UHMWPE. GO cause the loosening and breakage in the links of the mother substrate and lead to less crystalline phase [14]. The parameters for all samples obtained during x-ray analysis are listed in Table 1.

![Table 1. Parameters from the X-ray diffraction analysis](image)
3.2 Thermoelectric Properties of UHMWPE/GO Composite Pellets

Figure 2(a) shows the variation of conductivity vs temperature for 7%, 10%, 15%, and 20% content of graphene oxide. There is an irregular variation of current with an increase of temperature for 7%. For the nonconductors, the electrical conductivity is considered as low as less than $10^{-8}$ S/m and the electrical conductivity range for 7% is between $10^{-9}$ and $10^{-8}$ S/m so apparently, we don’t consider it as conductor. When GO content reaches to 10%, the conductivity slowly increases with the increase in temperature, this is because GO has greater aspect ratio and its small amount causes the breakage in the links of UHMWPE and forms the conductive path. However, in the case of 15% and 20% content, there is stability in conductivity with an increase in temperature as graphene oxide begins to strengthen the substrate after influencing the linkage breaks. Hence, more GO content causes a decrease in resistivity of our polymer.

The relationship between thermal conductivity, thermal diffusivity, and volumetric heat capacity of UHMWPE-GO composites and the corresponding content of GO in UHMWPE substrate is illustrated in figure 2(b). Thermal
conductivity increases with the increase of GO content up to 5% and the curve is linear. For 7% content, there is a small abate in thermal conductivity, and further addition of 10% content causes more drop in thermal conductivity approach to 0.51W/mK and for 15% and 20% content very small declination is observed. This trend shows that if we further increase the GO content, thermal results in the decline of thermal conductivity. In essence, phonons are treated as thermal conductivity carriers. The phonons of GO nanoparticles do not counterpart with the phonons of the UHMWPE, which verdict in a large thermal resistance due to the boundaries of graphene oxide, so the property of thermal conductivity of the UHMWPE/GO composites is restrained. The main reason for the deceased conductivity is that the graphene makes the diffusion of heat slower, as a result vibration and rotation of atoms become dislocated. Thermal diffusivity of our composite showed the same behavior as the thermal conductivity but in lower values. While the trend of volumetric heat capacity is completely in contrast to that of thermal conductivity with much larger values.

Since Seebeck coefficient is totally independent of dimension, so sample geometry doesn’t concern. It is obvious that there is no electrical conductivity observed for pure, 1% and 5% content. As the Seebeck coefficient depends on electrical conductivity, so there is no variation in the voltage output to temperature difference ratio. It is illustrated by figure 3(a), the Seebeck coefficient of 7%, 10%, 15% and 20% nanocomposite material increase with the increase in the amount of GO in UHMWPE ranges from 180 to 235μV/K at room temperature.

The efficiency of thermoelectric material is expressed by the figure of merit. Figure 3(b) gives the reliance of the figure of merit of UHMWPE/GO nanocomposites with the increased fraction of graphene oxide. The figure of merit shows the rapid growth from 7% to 10% content. Although the Seebeck coefficient of 7% content is quite higher, yet its electrical conductivity is much lower, i.e, in 10^8 S/m that causes the lower efficiency of this sample. With the increment of graphene oxide from 10% to 15% and 20%, the figure of merit shows the higher values as their respective electrical conductivities and Seebeck coefficients increase with a little bit of consistency in thermal conductivity. Furthermore, these values of the figure of merit are quite not suitable for common applications, but there may be further ways of improvement.

Parameters upon which the figure of merit depends at 303K are listed in Table 2

| Sample | Electrical conductivity σ (S/m) | Seebeck coefficient S (V/K) | Power factor σS^2 (W/mK^2) | Thermal conductivity κ (W/mK) | Figure of merit ZT |
|--------|---------------------------------|-----------------------------|----------------------------|-------------------------------|-------------------|
| P      | 0                               | 0                           | 0                          | 0.4852                        | 0                 |
| PG_1   | 3.82166E-08                     | 1.80E-04                    | 1.23822E-15                | 0.5168                        | 7.25967E-13       |
| PG_2   | 2.62208E-06                     | 2.06E-04                    | 1.11271E-13                | 0.5142                        | 6.55679E-11       |
| PG_3   | 3.12E-06                        | 2.30E-04                    | 1.65286E-13                | 0.5129                        | 9.76441E-11       |
| PG_4   | 3.03E-06                        | 2.35E-04                    | 1.67056E-13                | 0.5078                        | 9.96807E-11       |

4. Conclusion

Organic thermoelectric materials are coming to the limelight for the advantage of conversion of heat energy into electrical energy and vice versa. They are preferred
over conventional thermoelectric materials due to their higher strength, processability, lower cost, and nontoxic. In the present work, we have done systematic studies on the structural and thermoelectric properties of UHMWPE blended with 1%, 5%, 7%, 10%, 15%, and 20% graphene oxide nanocomposites. Sharp peaks of UHMWPE at 21.5° and 24° with the appearance of graphene at 30° by XRD are obtained. The DC conductivity increases with the increase in the concentration of graphene oxide nanoparticles with the increase in temperature. The thermal conductivity decreases with the increase in graphene oxide content at room temperature. The Seebeck coefficient increases with the increase in graphene oxide concentration. As we measured, the Seebeck coefficient increases with the increase in temperature. Efficiency of UHMWPE/GO nanocomposites is also increased in the scenario of all three parameters.

Although the values of the figure of merit are quite not suitable for common applications yet, there may be further ways of improvement by doping the UHMWPE with higher content of graphene oxide and other highly conductive fillers. All in all, these composites after improved efficiency can be used to supply the energy. It is clearly just a matter of time!

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