New Fabricated UHMWPEO-PVA Hybrid Nanocomposites Reinforced by GO Nanosheets: Structure and DC Electrical Behaviour

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Abstract: Polymer-graphene-based nanocomposites are promising to subject for engineering and industrial. This investigation focused on fabricated new nanocomposites from polyethylene oxide (UHMWPEO) with polyvinyl alcohol (PVA) with various loading ratios. In addition, the influence of graphene oxide nanosheets (GO) contribution was significant enhanced the electrical properties. Three different loading ratios of both polymers were applied with the addition of GO to synthesis new six samples using the solution-sonication-casting method as UHMWPEO: PVA: GO (87:12:1, 74.5:24.5:1, and 63:36:1 wt. %). Range of characterization was applied such as Fourier-transform infrared spectroscopy (FTIR) spectra that presented showed strong interfacial connections formed between the blended polymers in the matrix and GO nanosheets in the nanocomposites and the optical microscopy (OM) images exhibited fine homogeneity of the polymer matrix and excellent dispersal of the GO in the matrix of polymers. The DC electrical conductivity showed notable improvement of (PEO - PVA) blended polymer form (2.34663 * 10⁻¹⁷) (Ω·cm)¹ up to (3.00327*10⁻¹⁰) of nanocomposites. The findings are promising that could grow various applications such as sensors, solar cells, IR, electrical and microwave absorption panels.

Keywords: UHMWPEO, PVA, GO, electrical properties, nanocomposites, reinforcement.

1. Introduction
Nanocomposites are an important subject in the development and production of materials, particularly polymer-nanomaterials [1]. It is well recognized that the most significant factors resulting from the interaction of filler nanoparticles with polymer are nanocomposites that improve nanocomposites’ properties in nuclei [2,3]. The addition of a small number of nanoparticles may vastly boost a number of properties while sacrificing none of the polymer's lightweight matrices [4] and overcome several polymer weaknesses [5,6]. Graphene oxide nanosheets have unique characteristics that could bring notable improvement to nanocomposites[7]. Mostly, it is easily functional in wide and various spintronics, electronics, and photoelectronic, applications, etc [8,9]. UHMWPEO is water-soluble and commonly used in several different applications as functional additives, such as flocculation methods, wastewater treatment, mining, food processing, cosmetics, and coagulation [10]. Poly (vinyl alcohol) (PVA)
is a commercial polymer modifier with high grades of hydrolysis [11]. It is used from other polymers for good properties such as wear resistance, strength, thermal stability, and quality [12]. Several studies [13–17] have listed some very interesting findings when PEO and PVA polymers, whereas, the Ultra-high molecular weight PEO (UHMWPEO) that was used in this study does not address it before to the best of our knowledge, or with PVA or GO nanosheets. Abdul kadhim, M. et al. 2020 [18] reported the significant influence of electrical properties after the contribution of GO of the PMMA-PVA blended polymers. They reported the new method to synthesis New PMMA-PVA/GO nanocomposite using DMF as a solvent with several ratios of polymers and GO. Rang of characterized was used such as optical microscope (OM), FTIR, electrical conductivity. The electrical properties of nanocomposites showing an improvement in most of the electrical properties up to 50%, 96.3 % and 96.7 % of dielectric constant, conductivity and dielectric loss with increasing the GO ratio up to by 0.09, 0.18 and 0.27 wt. %, respectively. Kashyap et. al. in (2016) [14] reported the influence of adding various percentages of graphene oxide (GO) on the electrical and mechanical properties of polyvinyl alcohol (PVA). PVA was dissolved and GO was dispersed using distilled water (DW) as the solvent using the casting process. The samples were characterized using various instruments such as XRD, SEM and electrical conductivity. The results of the study showed increases in electrical conductivity from -30 to -35. Rachna Mishra and K.J. Rao (1998) [19] studied the electrical conductivity of PEO-PVA blended polymers that were carried out over a wide frequency range, covering the complete composition range. The conductivity variation was studied using the modified formulation of Almond-West for various compositions, which was established to fit the conductivity data at any temperature. The constant of complex dielectric, complex impedance as well as complex electric modulus of the samples was used to analyze the dielectric data. Pure PEO and PVA have separated the peaks of relaxation in the section of imaginary of the moduli, although dielectric relaxation spectroscopic tests do not disclose the relaxation simultaneously. In any of the blends, both peaks are present.

Many investigations reported PEO with other polymer and nanofillers, but, the PEO with ultra-high molecular weight (5 000 000 g mol⁻¹) have not been studied or mixed with other polymer or nanomaterials. Therefore, this study reported the new UHMW-PEO: PVA blended polymer, which was firstly mixed using different ratios of polymers, then supported with graphene oxide nanosheets using the advanced acoustic mixing method. Various characterization was applied such as FTIR, OM, and electrical conductivity, these nanocomposites characterized the effect of GO on the structure and electrical behaviour.

2. Experimental Part:

2.1 Materials

Materials used in this study are summarized in Table (1).

| Materials             | Details                                      | Suppliers                        |
|-----------------------|----------------------------------------------|----------------------------------|
| PEO                   | Ultra-High Molecular Weight (5 000 000 g mol⁻¹) | Sigma-Aldrich, UK                |
| Graphite Powder       | Size (≤ 39µm)                                |                                  |
| Sodium Nitrate        | (NaNO₃), (35%)                                |                                  |
| Hydrochloric Acid     | H₂SO₄ (99.5% analytical grade), H₂O₂ (KMnO₄) | Media Labs Pvt. Dindori, Nashik, India |
| Sulfuric Acid         |                                              |                                  |
| Hydrogen Peroxide     | Molecular Weight (160,000) gm⁻¹.              |                                  |
| Potassium Permanganate|                                              |                                  |
| PVA                   |                                              |                                  |
2.2 Method

2.2.1 Purification of Graphene Oxide

Our group synthesized GO that was fully characterized in our previous publications. [20, 21].

2.2.2 Purification of the nanocomposites

The polymers PEO and PVA were dissolved separately using distilled water with the assist of a magnetic stirrer under 50 °C. Then, several ratios of UHMWPEO: PVA were applied to dissolve these polymers together, which were (87.5:12.5, 75:25, and 62.5:37.5 wt. %). All sample was mixed for 20 hours without heating. GO was added to the blended polymer mixture with a low loading ratio (1 wt. %) for the samples to fabricate the new nanocomposites. The GO was dispersed in distilled water using the sonication and magnetic stirrer before mixed with polymer. The nanocomposite samples were mixing for 72 hours a using magnetic stirrer with the assist of sonication for 15 minutes every 2 hours for the first 24 hours. Finally, the homogeneous mixtures were cast in the Petri dish to dry for 168 hours under air.

2.2.3 Characterizations

The used characterizations in this study are summarized in Table (2).

| Device                  | Details                                                                 | Company  | Country |
|-------------------------|-------------------------------------------------------------------------|----------|---------|
| Fourier transform infrared (FTIR) spectra | Vertex 701. in the region between (4000 – 400) cm⁻¹ | Bruker Company | Germany |
| Optical Microscope (OM)  | (Nikon - 73346) magnification 40 X                                    | Olympus  | Japan   |
| DC electrical conductivity | The temperatures was between 30 to 80 °C, and the electrical resistance was recorded after six minutes | Keithley 2400 | USA     |

3. Theoretical Part

The DC electrical conductivity was considered using equation (1) [22].

\[
\sigma_{dc} = \frac{L}{RS}
\]  

(1)

Where the normal body with length (L), (R) electrical resistance and (S) constant area, whereas the dielectric constant of the sample (\(\varepsilon\)) was calculated using equation (2).

\[
\varepsilon = \frac{C_p}{\varepsilon_0}
\]  

(2)

Where (Cp) and (Co) mean the parallel capacitance and the vacuum capacitor, which is determined by equation (3).

\[
C_0 = \frac{\varepsilon_0 M t}{\varepsilon}
\]  

(3)

(\(\varepsilon_0\)), means the void permittivity and (M) means the capacitive plate area, whereas (t) means the distance between two plates, respectively. Equation (4) was applied to estimate the dielectric loss and the dispersion factor (D).

\[
\varepsilon'' = \varepsilon' D
\]  

(4)

The equation of Arrhenius (5) was applied to determine the electrical conductivity that varies exponentially with temperature (T) [23].

\[
\sigma_{dc} = \sigma_0 \exp \left(\frac{-E_a}{KT}\right)
\]  

(5)

Where (K) refers to the constant of Boltzmann and (Ea) means the activation energy.
4. Results and Discussion

Figure 1 shows the FTIR spectrum of (UHMWPEO-PVA) blended polymers and (UHMWPEO-PVA/GO) nanocomposites with various mixing ratios of polymers. It was registered in the range (4000-500) cm\(^{-1}\) wavenumber. The (PEO-PVA) spectrum, where (O-H, C-H, C=O, O-H and C-H, and C-H\(_2\)) exhibited at the peaks 3284, 2882, 1716, 1340, 1278, and 959 cm\(^{-1}\), respectively. These peaks display strong interaction between polymers and in agreement with the other finding in the literature [16,21]. The addition of GO exhibited notable strong interfacial integration assist to shift in the ost peaks positions, for instance, C-H\(_2\), C-H and C=O, as existing in Figure 1. This could be related to the fabricated of the hydrogen bonding between these polymers and the GO functional group as reported by other investigations [24–26].

![Figure 1. FTIR spectra of (UHMWPEO-PVA) blended polymers and (UHMWPEO-PVA/GO) nanocomposites](image-url)
In Figure (2), the optical microscopy images (OM) presented the change, homogeneity and dispersion of the UHMWPEO-PVA films after the addition of GO in the UHMWPEO-PVA/GO nanocomposites. The samples were clearly showing fine homogeneous of the blended polymers matric and good dispersion of GO in the nanocomposites without aggregations or affecting on the optical transparency of the prepared films [27,28]. The strong evidence of the successful fabrication of these blended polymers and nanocomposites.

Figure (2). The images of the optical microscopy (OM) with (100X) magnification of (UHMWPEO-PVA) films and (UHMWPEO-PVA/GO) nanocomposites.

Figure (3) displays the DC electrical conductivity of the surface of the sample as a function of the various concentration of polymers in the matrix at a range of temperatures (30, 50, 60, 70 and 80 °C). The results indicate, which the electrical conductivity increased with rising in the ratio of PVA in the blended polymer matrix, whereas there is a significant increase in the results after the rise of the temperature gradually from 30 to 80 °C. For instance, the value of the conductivity of the mixture (PEO-PVA) was (2.34663 * 10^{-17}) (Ω.cm)^{-1} of P1, it was observed an enhancement in the conductivity with an increase in the concentration of PVA in the mixture (PEO-PVA) of P3 up to (1.15808*10^{-15}) (Ω.cm)^{-1}. Another important finding was the addition of GO to the mixture that was a significant improvement in electrical conductivity, and this improvement of NC3 up to (3.00327*10^{-10}) (Ω.cm)^{-1}. The results indicate that the electrical conductivity significantly increased after the contribution of graphene oxide GO in agreement with the literature [29].
Figure (3). DC Electrical Conductivity of PEO-PVA blended polymers and (PEO-PVA/GO) Nanocomposite at various temperatures.

Figure (4) displays the electrical conductivity of PEO-PVA and (PEO-PVA/GO) nanoparticles with increasing the temperature for each sample. From this figure, it was observed that the bulk electrical conductivity improved with increasing the temperature with the rise in the PVA concentration of the (PEO-PVA) blended polymers films. The contribution of graphene oxide assisted to notable enhancement in the conductivity of the (PEO-PVA/GO) nanocomposite. In addition, the increase in the PVA ratio also important that improved the electrical conductivity. Where P3 and NC3 showed the best results. That means that these samples had resistance to the negative thermal modulus and the resistance decreases with increasing the temperature. This is because the polymer chains with graphene oxide nanostructures (GO) can act as traps aimed at the moving charge carriers through the jumping process. Additionally, increasing the temperature assist to increases the mobility of the chains of the polymer. Thus, the trapped charge carriers are released and the conductivity of the (PEO-PVA/GO) nanocomposite improved as a result of the increase in charge carriers and the transport of these charges [30].

Figure (4). The DC electrical conductivity with increasing the temperature for (PEO-PVA) blended polymer and (PEO-PVA/GO) Nanocomposites.

Figure (5) shows the association between Ln with the reverse absolute temperature of the nanocomposite (PEO-PVA / GO). Figure (5) represented the relationship between Lnσdc and the inverse absolute temperature of blended polymers and nanocomposites. The results revealed a
significant increase of the results during the absolute temperature, where the increasing of PVA ratio with the addition of GO nanosheets presented a significant influence on the results. The activation energy was calculated in equation (5). These calculations exhibited improving activation energy ranged from (2.26) eV to (1.4) eV of (PEO-PVA) blended polymer to (PEO-PVA/GO) nanocomposites as exposed in Table (3). The presence of high values of activation energy in the blended polymer state. Increasing in the PVA concentration in the PEO-PVA mixture with the addition of graphene oxide (GO) nanostructures, the activation energy of (PEO-PVA/GO) nanocomposites decreased by the influence of space charges. The GO forms local energy levels in the sealed energy gap. This interacts as traps for the charge carriers that move with the movement between these levels. The activation energy decreased as a result of the increased PVA concentration, as shown in Figures (6) of the (PEO-PVA/GO) nanocomposite. This is due to the formation of a continuous network of graphene oxide nanoparticles that contain pathways within the nanocomposite and allow the passage of charge carriers. This led to a notable reduction in the activation energy in agreement with another finding [18].

| Samples | $E_a$(eV) |
|---------|-----------|
| P1      | 2.25      |
| P2      | 2.09      |
| P3      | 1.88      |
| NC1     | 1.64      |
| NC2     | 1.52      |
| NC3     | 1.4       |

**Figure (5).** The variation of $\ln$ the DC electrical conductivity with the inverse absolute temperature of blended polymer (PEO-PVA) and (PEO-PVA/GO) nanocomposites.
5. Conclusions
The New nanocomposites were successfully synthesized from UHMWPEO with PVA with various ratios of both polymers. These blended polymers were reinforced using GO nanosheets. The FTIR spectra showed a significant interfacial interaction between polymers and GO. These nanocomposites presented fully homogeneous with a fine dispersion of GO nanosheets as exposed using OM. The electrical properties indicated outstanding improvement of the results especially after increasing the ratio of PVA. For instance, the value of the conductivity of the (PEO - PVA) blended polymer improved form $(2.3463 * 10^{-17})$ $(\Omega \cdot cm)^{-1}$ of P1 up to $(1.15808*10^{-15})$ $(\Omega \cdot cm)^{-1}$ of P3, then the contribution of GO add notable improvement up to $(3.00327*10^{-10})$ of NC3. The results exhibited enhancement in electrical properties could lead to potentially contribute to a wide range of applications of these nanocomposites.

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Figure (6). The variation activation energy of the D.C electrical conductivity with PVA concentration in the (PEO-PVA) blended polymers and (PEO-PVA/GO) nanocomposites.
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