Preparation Characterization and Electrical Study of New Polymeric Mixture (Consist of Three Polymers) Nanocomposites

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ABSTRACT. By using hummers’ method, graphene oxide (GO) was synthesized and by reducing it gave reduced graphene oxide (RGO). The polymeric blend contains three polymers; Poly Aniline (PANI), Poly Vinyl Acetate (PVAc), and Pecten (Pc) which have been prepared at studied amount. The composites for above polymers with various concentrations of, graphene oxide (GO) and with reduced graphene oxide (RGO)were prepared, and then pour into films (chips). The dielectric constant properties of chips were measured, which its point the electrical conductivity values for the prepared chips increase with increasing of frequency. As well, the electrical conductivity is research in terms of the Arrhenius plot, it is plotted against the reverse temperature for the prepared films at different applied frequencies.

1. Introduction
The interesting of Polymer nanocomposites are increased due they collect the merits of polymers with little amounts of nanoparticle materials [1]. The polymer structure is so important to define , the polarity of polymer and this effective on electrical and dielectric properties [2] Conducting polymers offer optical and electrical characteristic of the metal and keep the engaging mechanical properties of polymers leading to extensive range of uses [3]. Using of PANI as matrix materials for more research, because it is much stable in several solvent and air, as well it is shows dramatic changes in its physical properties and electronic structure [4]. In our study, it prepared polymeric mixture consist of three polymers; Poly Aniline( PANI) Poly Vinyl Acetate(PVAc), and Pecten (Pc) and it composite with different concentrations of, graphene oxide (GO) and with reduced graphene oxide (RGO or G). and effect this addition on the electrical properties of the polymeric mixture.

2. Experimental

2.1. Synthesis of Nanoparticles
All materials used in this research from Sigma Aldrich, and it used without any purification. graphene oxide nanosheets (GO) was prepared by Hummer’s method [5] by oxidation of graphite with concentrated H$_2$SO$_4$, NaNO$_3$, KMnO$_4$. graphene nanosheets (G) were prepared by reduction GO with hydrazine hydride [6].

2.2. Preparation of Composite
Polyvinyl acetate (PVA), (commercial/ German), poly aniline(PANI) and Pecten (Pc), (commercial). Mixture Composite was prepared in the previous paper [7]. Then polymeric mixture nanocomposites were prepared by following: Four 40 ml beakers were prepared with
25 percentages of PANI (5 g in 100 ml distilled water) Pecten, (12.5 g in 100 ml distilled water) PVAc, (0.8070 g) of Ammonium persulphate and (0.367 g) of Aniline chloride) and blended totally under mechanical stirring for 120 minutes at normal temperature. Every composite was blended ultrasonically for 20 minutes with various (GO) composites weights (0.000, 0.0065, 0.015 and 0.029 g). By solution casting, the films were prepared, then they let dry at (60°C) for 130 hour. From measured $\sigma$ (electrical conductivity) to the above films, it found that the highest value of $\sigma$ was the film which include 4% Percentage of (GO), that is cause this ratio elected for our research. then repeated this procedure with (G) nanosheets.

2.3. Dielectric Constant Measurement

The dielectric parameter (for prepared films) as a function of frequency is obtained by the complex permittivity.

$$\varepsilon^* (\omega) = \varepsilon' (\omega) - \varepsilon'' (\omega)$$  \hspace{1cm} (1)

where the $\varepsilon'$ (the dielectric constant) and $\varepsilon''$ (dielectric loss) are the components for the energy storage and energy loss, respectively, in each cycle of the applied electric field. To calculate $\varepsilon'$ from measured capacitance $C$ by using following equation:

$$\varepsilon' = \frac{Cd}{A\varepsilon_0}$$ \hspace{1cm} (2)

$A$ is the area of the electrodes, $d$ is the thickness between the two electrodes, $\varepsilon_0$ is the permittivity of the free space, and $\omega$ is the angular frequency ($\omega = 2\pi f$), $f$ is applied frequency. ($\varepsilon'' (\omega)$) is described with equation (3), where $\tan \theta (\omega)$

$$\varepsilon'' (\omega) = \varepsilon' (\omega) \cdot \tan \theta (\omega)$$ \hspace{1cm} (3)

Electrical conductivity $\sigma$ of fabricated chips was determined by expression (4).

$$\sigma = \varepsilon' \times \varepsilon_0$$ \hspace{1cm} (4)

3. Results and Discussion

3.1. FTIR Characterization

3.1.1 FTIR of Nanomaterials

Figure 1 shows the FTIR spectrum of GO and G nanosheets, respectively. In (1a), a broad peak at (3431 cm$^{-1}$) attributed to the stretching vibration of (OH) group, the two peaks at (1618 cm$^{-1}$ and 1720 cm$^{-1}$) can be referred to the stretching vibration of (C=C) groups and (C=O) groups of carboxylic acid and carbonyl groups present at the edges of GO. The absorption peaks at (1360 cm$^{-1}$ and 1227 cm$^{-1}$) can be attributed to the stretching vibration of (C=O) group of carboxylic acid and (C-OH) group of alcohol, respectively. In (1b), as we see absence of stretching vibration of (C=O) group [9].

3.1.2 FTIR of Composites

Proof of polymeric mixture composite, polymeric mixture GO nanocomposite and polymeric mixture G nanocomposite was studied by FT-IR spectroscopy, as appear in the Figure1. From figure (2a), the special absorption peak at (1402 cm$^{-1}$) for (C-N) group in PANI [10], the peak at (1188 cm$^{-1}$) due to (C-N$^+$) group [11], which gave electrical conductive of polymeric mixture. The peaks at (3321 cm$^{-1}$ and 3131 cm$^{-1}$) for aromatic(C-H) and (O-H) at acetate group, respectively. The band at (1111 cm$^{-1}$) to (C-O-C) group in Pecten [12]. In (2b), there is a clear increase in the peak at (3136 cm$^{-1}$), which indicates the (OH) group in GO nanosheets Figure (2c) Shows a decrease in the bands at (1111, 1400 cm$^{-1}$), which indicates of (C-O) group and (C=C) group, another decrease in the peaks at (3410, 32281 cm$^{-1}$) indicating the weakness of hydroxyl group, which appeared in GO spectrum.
Figure 1. FT-IR spectrum of (a) GO nanosheets and (b) G nanosheets.
3.2. XRD Analysis

Figure 3 shows the XRD analysis of GO and G nanosheets, the peak at (10.77°) corresponding to GO nanosheets was disappeared in G nanosheets, while the two major peaks are observed at about (25.07, 44.47°) [6,13].

Figure (4) shows the X-ray diffraction pattern (XRD) of polymeric mixture composite, polymeric mixture GO nanocomposite and polymeric mixture G nanocomposite. In (4a), where the more peaks of diffraction have appeared at (14.01, 19.88 and 25.12), while in (4b), the X-ray diffraction peaks at (12.14, 18.03, 23.22, 26.12, 35.13) [14]. In (4c) a pattern of diffraction showed the spread of G nanosheets within polymeric mixture, the distinctive peaks of G appear at (20.01, 29.47) [15].
Figure 4. The X-ray diffraction pattern (XRD) of (a) polymeric mixture composite (b) polymeric mixture GO nanocomposit and (c) polymeric mixture G nanocomposite

4. AFM Analysis of Nanomaterials
The synthesized nanomatials GO and G nanosheets, were investigated by (AFM), the results were almost identical as in 'figures 5' and with nanoparticles size about (25.7 nm). 'Figure 6' shows AFM of polymeric mixture composite. 'Figure 7' shows AFM of polymeric mixture G nanocomposite, which are distributed within the polymeric mixture and are encapsulated in the polymer mixture particles. The size changed from nanoscale to about (371 nm).

Figure 5. AFM pictures of G nanosheets (a):2-D topographic and (b):3-D topographic
Figure 6. AFM pictures of polymeric mixture composite (a): 2-D topographic and (b): 3-D topographic

Figure 7. AFM pictures of polymeric mixture G nanocomposite (a): 2-D topographic and (b): 3-D topographic

5. SEM Analysis

'Figure 8' show the surface morphology of GO and G nanosheets, from this figure it appeared the d-spacing of sheets of G is smaller than GO.

Figure 8. SEM pictures of (a) GO nanosheets and (b) G nanosheets

'Figure 9' shows SEM pictures of polymeric mixture composite, while 'figure 10' of polymeric mixture G nanocomposite which are distributed within the polymeric mixture and encapsulated in the polymer mixture particles.
Figure 9. SEM pictures of polymeric mixture composite.

Figure (10). SEM pictures of polymeric mixture G nanocomposite.

6. Electrical properties measurements

The difference in electrical conductivity of the chips prepared from the polymeric mixture composites, polymeric mixture GO nanocomposites, and polymeric mixture G nanocomposites, is shown in Figure (11) and there is a steady increase in the conductivity values by increasing the frequency. The conductivity of the polymeric mixture without the addition of a nanomaterials gave a value of conductivity of (0.514 s/m), which is the conductivity of PANI, which is the only conductive polymer in the polymeric mixture, and the other are non-conductive polymers.

Chips prepared from polymeric compositions with 4% of nanomaterials. The results showed that the electrical conductivity values increased with increasing frequency, with a gradual and stable increase at (100-4000 Hz). The conductivity is clearly and strongly increased at (100000 Hz), as shown in Figure (11) showing the difference in the conductivity values of the composites. The highest conductivity at the frequency (100000 Hz) of the polymeric mixture G nanocomposites is shown. This indicates the effect of the conductivity G nanosheets conductivity on the polymeric mixture as the highest conductivity of GO, which is an electrical insulating material. The conductivity has very little start and oscillates until it becomes zero at the frequency (100000 Hz). This is an indication of the effect of GO sheets scattered within the polymeric mixture on the conductivity on the composites. It is clear that the doping processes effects on the conductivity of the chips prepared from polymeric mixture, that the conductive nanomaterials increase the carriers of the charge (electrons or gaps) and thus increase the conductivity of composites.
Figures (12) and (13) were pictorial the variance of real part ($\varepsilon'$) and imaginary part ($\varepsilon''$) of dielectric permittivity with frequency for chips prepared from polymeric compositions with 4% of nanomaterials, respectively, at room temperature. In both cases, permittivity arrived higher values at low frequencies, which decreased quickly with increasing of frequency. This is because at low frequency region the alternation of the field is slow, those give more time to induced and permanent dipoles to align themselves to the applied field, leading to enhanced polarization. Enhanced values of ($\varepsilon'$) particularly at low frequencies can be referred to interfacial polarization, and/or electrode polarization. Electrode polarization is associated to the buildup of space charges at the specimen-electrode interfaces and is describing by very highly values of real part (dielectric constant) and imaginary part (dielectric loss) of permittivity, these chips have a high ability to store electric energy more than a composite of other chips and is suitable for many applications from capacitors for battery manufacturing but the chips prepared from the triple composite with (GO), which is non-conductive material to the value of the electrical conductivity approach to zero and did not get the electric plug as [16-18].
Figure 12. Real permittivity against log frequency for prepared composites.

Figure 13. Imaginary permittivity against log frequency for prepared composites.

7. Activation Energy of the Nanoparticles

The study of conductivity, which is the inverse of resistance as a function of temperature, is the best criterion for determining the behavior of conductivity in the chips and membranes by determining the energy values needed for the conduction of the electrical conduction. This energy is an energizing energy which can be determined by drawing the relationship between the logarithm of electrical conductivity and absolute temperature, according to Arrhenius equation [19], which shown in 'figures 14', (15) and (16), respectively and the results of the activation energy for the polymeric mixture composites, polymeric mixture GO nanocomposites, and polymeric mixture G nanocomposites, in tables 1, 2 and 3, Respectively.
Figure 14. The logarithm of electrical conductivity versus absolute temperatures of polymeric mixture composite.

Table (1): The activation energy values for the polymeric mixture composites.

| F     | high $\theta$ (65 c') | Slop  | $E_a$(ev)/molecule |
|-------|------------------------|--------|-------------------|
| 100   | 0.052334               | -0.263 | 5.219E-05         |
| 400   | 0.054512               | -0.336 | 6.668E-05         |
| 1000  | 0.06557                | -0.581 | 0.0001153         |
| 4000  | 0.070125               | -0.536 | 0.0001064         |
| 10000 | 0.13111                | -0.257 | 5.1E-05           |
| 40000 | 0.492982               | -0.714 | 0.0001417         |
| 100000| 0.794212               | -0.322 | 6.39E-05          |

Figure 15. The logarithm of electrical conductivity versus absolute temperatures of polymeric mixture GO nanocomposites.
Table (2): The activation energy values for the polymeric mixture GO nanocomposites.

| F    | high $\sigma$ (55 c°) | Slop   | Ea(eV)  |
|------|------------------------|--------|---------|
| 100  | 0.055406               | -1.0216| 0.00002027 |
| 400  | 0.06756                | -0.758 | 0.0001504  |
| 1000  | 0.068124               | -0.653 | 0.0001296  |
| 4000  | 0.20364                | -0.552 | 0.0001095  |
| 10000 | 0.360655               | -0.525 | 0.0001042  |
| 40000 | 0.51021                | -0.436 | 8.652E-05  |
| 100000| 0.95849                | -0.334 | 6.628E-05  |

Figure 16. The logarithm of electrical conductivity versus absolute temperatures of polymeric mixture G nanocomposite.

Table (3): The activation energy values for the polymeric mixture G nanocomposite.

| F    | high $\sigma$ (55 c°) | Slop   | Ea(eV)  |
|------|------------------------|--------|---------|
| 100  | 0.12787                | -0.747 | 0.0001482 |
| 400  | 0.184641               | -1.152 | 0.0002286 |
| 1000  | 0.436808               | -1.537 | 0.000305 |
| 4000  | 1.456147               | -2.426 | 0.0004814 |
| 10000 | 1.563647               | -1.936 | 0.0003842 |
| 40000 | 1.622633               | -0.925 | 0.0001836 |
| 100000| 2.057813               | -0.53  | 0.0001052 |

8. Conclusion
In this work, the dielectric behavior of the polymeric mixture (contain three polymers; Poly Aniline( PANI), Poly Vinyl Acetate(PVAc), and Pecten(Pe) which have been prepared at
studied amount). with various concentrations of, graphene oxide (GO) and with reduced graphene oxide (RGO) nanocomposite films has been investigated. The results show that the electrical conductivity values for the prepared chips increase with increasing of frequency. As well, the electrical conductivity of above films is research in terms of the Arrhenius plot.

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