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Graphene Effect on the Mechanical Properties of Poly (Ethylene Oxide)/ Graphene Oxide Nanocomposites Using Ultrasound Technique

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Abstract. Graphene is one of the most important materials that have attracted the attention of scientists and engineers because of its unique properties. Graphene oxide was used with different concentrations (0.5, 1, 1.5 and 2 wt%) that were mixed with high molecular weight polymer to prepare several models of PEO-GO nanocomposites using solution casting methods. Some of the properties of the samples, including the density, viscosity and ultrasonic velocity were measured using different technologies such as the ultrasound (US). The results showed a change and significant enhancements in these properties with the increase of graphene oxide concentrations in the matrix. Where, the viscosity increased up to 112.5 %, meanwhile the mechanical properties enhanced by 86.2 % and 719 % of ultrasonic velocity and bulk modules, respectively. Most of the mechanical properties were increased exponentially with the increase of GO concentrations. The results found that the best concentration of (GO) was (1.5 wt%) that greatly enhanced the mechanical properties in this study. SEM images presented a clear change in the fracture surface that showed a smooth surface and homogeneous dispersion of the GO nanosheets into the PEO matrix.

1. Introduction

Poly (ethylene oxide) (PEO) is a polar semi-crystalline polymer, liquid or solid and highly hydrophilic nature, meanwhile, it is lubrication properties and water retention (1,2). Both organic and aqueous are considered good solubilize of PEO that presents hydration and high flexibility. Additionally, PEO performs to be not toxicity or antigenicity as well as immunogenicity. The properties of PEO make it a significant polymer of a range of applications, for instance, polymer electrolyte (3), biomedical (4) and pharmaceutical. Furthermore, Other applications, such as batteries, fuel cell applications (5,6), supercapacitor and polymer-drug conjugates (1) use PEO as a commercial polymer. Meanwhile, the main disadvantage of PEO presents a low ionic conductivity of the solid polymer electrolytes. That is related to the relatively weak interfacial interaction as also presented weak mechanical properties. The nanoscale filler corporation could improve the polymer properties, which are mechanical, thermal, electrical and magnetic, in the matrix without losing optical transparency (7).

The unique properties of graphene, such as physical, electrical, chemical and mechanical properties etc. (8). Meanwhile, the excellent optical transmittance of graphene is about 97.7% (9) with nearly 1 TPa of high Young's modulus and 130 GPa of ultimate tensile strength (10). Additionally, graphene has an unusual honeycomb structure. The GO nanosheets with unique properties were used to improve the properties of

nanocomposite material (11), such as supercapacitor, thermal storage and mechanical etc. GO was used enhanced the heat storage density and for the solid/liquid phase change process of PEG-shape-stabilized nanoparticles (12) as well as their thermal energy storage (13). Ethylene glycol is used by researchers for the supercapacitor application applying the reduction the GO/ polypyrrole nanocomposite (14).

The ether oxygen of the PEO was involved through the hydrogen bonding mechanism that along with isolated surface hydroxyls of the PEO molecule (15). Whereas, the dispersion degree of nanofiller in the polymer matrix impacts through the interfacial interactions (16), including, van der Waals attractions, hydrogen bonding and electrostatic interaction between the nano-fillers and polymer in the matrix. The stress transfer may determine through the interfacial interaction between the components of the matrix (17). In the nanocomposites, the interfacial interaction of the polymer is important and forms a significant volume fraction with fillers. Achieve this objective need to understand the nature of interfacial interaction and the nanocomposites unique structure between the polymers and nanoparticles because of it governs the property of the nanocomposite and considered of paramount importance (7,18).

Therefore, in this study, semi-crystalline polymer (PEO) was applied as polymer model to examine the GO effect on some physical and mechanical properties of PEO compared to the bulk PEO. Firstly, GO was prepared from graphite and mixed with the PEO at various concentrations. The PEO-GO nanocomposites properties were examined with a range of characterization such as, viscosity meter, ultrasound, atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2. Experimental section and calculations

2.1. Materials
poly(ethylene oxide) with high molecular weights (Mw) of $2*10^{\wedge 6}$, graphite powder (≤ 20 μm), sulfuric acid (H_2SO_4) (analytical grade, 99.8%), potassium permanganate ($KMnO_4$), sodium nitrate ($NaNO_3$), hydrogen peroxide and hydrochloric acid (HCl, 35%) were purchased from Sigma-Aldrich Company, UK.

2.2. Methods

2.3. Graphene Oxide Synthesis
Modified Hummer's method (19) was applied to synthesized graphite oxide from graphite powder. After getting graphite oxide nanosheets. Firstly, it was washed several times with distilled water and HCl at a ratio of 4:1, respectively to remove remind metal ions (20). Secondly, the washings procedures were continues but with distilled water only until the pH reached 5. Fine dispersion graphite oxide in distilled water was obtained using a magnetic stirrer. Graphite oxide was sonicated in a sonication bath (Fisherbrand, 230 V, 50 Hz for 30 minutes) to exfoliate graphene oxide into single nanosheets. The resulting GO suspension was lyophilized in a Labconco FreeZone benchtop freeze dryer and stored in powder form in a desiccator before use.

2.4. Syntheses the nanocomposites
PEO was dissolved in distilled water, first. Meanwhile, the GO was exfoliated for 30 minutes after dispersed in distilled water. Where PEO was mixing with GO at the room temperature for an hour to prepare the nanocomposites, another sonication for 30 minutes was done for the mixture. The mixture was mixed again for 2 h then was sonicated for 30 minutes also. After that, it was mixed for 72 h before casting in the petri dish and dried for 72 h at 40 °C in the vacuum. The same methods were applied to prepare all the nanocomposites and were kept in a desiccator under the vacuum, as shown in Table 1. Codes were created to help identify the samples. Letters P, G and number in the codes of refer to PEO, GO and sample number to recognize the increase in the concentration of GO in the nanomaterials of PEG/GO as shown in Table 1.

Table 1. The preparation methods and sample denotations of PEO-GO nanocomposites.

Sample ID	GO consternation wt%	Mixing time	Vacuum Oven
PEO	0		
PG 1	0.5		
PG 2	1		
PG 3	1.5	72 h	72 h at 40 ℃
PG 4	2		

2.5. Characterization

Density was measured using a bottle with a capacity density (25 ml) and the sensitive balance of the factory was made by a meter Switzerland Company with sensitivity (0.0001). Viscometer type (NDJ-8S) was used to measure the viscosity. Mechanical properties were measured using ultrasonic (SV-DH-7A/SVX-7 velocity of the sound instrument) with a pulse technique of sender-receiver type with frequency (35 kHz). Inspect F, scanning electron microscopy (SEM) was made by FEI Company that applied to test all the samples at voltage 5 kV. Atomic force microscopy (AFM) images were engaged through atomic force microscope (a Veeco Dimension 3100) with an Olympus AC160TS probe with tapping mode at 0.5 Hz.

2.6. Calculation

Relaxation is a phenomenon that occurrence of any sudden change in the system and leads to the walk to the case of a new budget process. This process occurs during a given time defines a time to relax and to be given to the relationship (21,22):

$$t = \frac{4\eta_s}{3\rho V^2} \tag{1}$$

were, t means relaxation time, η viscosity, p density and V ultrasound wave velocity. Whereas, carrying capacity (D) depends on the wave energy and decreased with the increase of relaxation frequency (f) that is given to the relationship:

$$D = \alpha / f^2 \tag{2}$$

were, α means the absorption coefficient. Impedance audio quality (z) was calculated using the relationship the following:

$$z = \rho V \tag{3}$$

Compressibility (B) was calculated using the Laplace equation:

$$B = (\rho V^2)^{-1} \tag{4}$$

Modulus of elasticity (k) is inverted of the compressibility that is given the following relationship:

$$k = B^{-1} = \rho V^2 \tag{5}$$

3. Results and Discussion

Figure 1 shows the density of the PEO and nanocomposites. The results showed gradually increasing of the density with increase of GO concentrations. It increased up to 137 % with the

increasing of GO ratio to 2 wt% compared to PEO results. That related to increasing the swelling of the polymer, the mass of GO and interaction between the polymer and GO functional group that presented complex network during the humongous and good dispersions. Where the hydrogen bond between the PEO and GO are considered the main interaction between these materials, where the functional groups of GO contact with ether group of PEO (23,24).
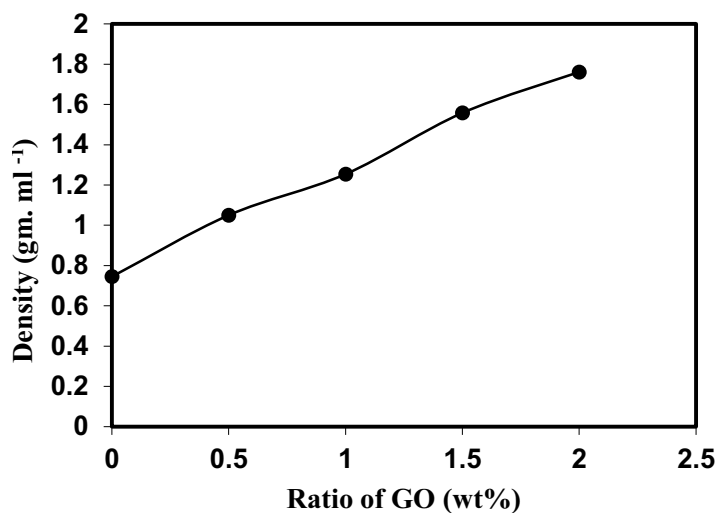

Figure 1. The density of PEO and nanocomposites.

Figure 2 shows the change in viscosity with concentration. The viscosity values increase with the increase in the concentration of graphene oxide (GO). This is in respect of its transformation into a complex form, which led to the formation of polymeric chains with large molecules due to the increased concentration of graphene oxide in the solution, thus increased the rotational and transition friction forces between the polymer and solvent molecules and between the graphene nanosheets from the other side. This is on account of the increased formation of hydrogen bonds between the disintegrating polymer and the solvent (24), as well as their association with the paraffin-oxide nanoparticles that form net structures and enhance the structure of the overlay (23).
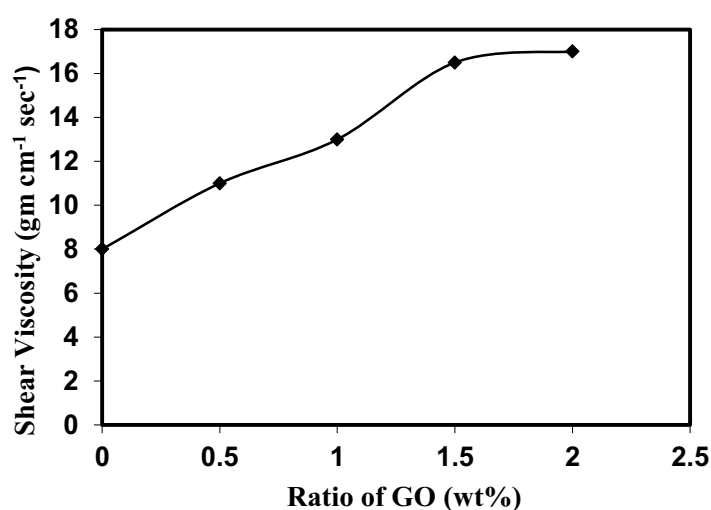

Figure 2. The shear viscosity of PEO and nanocomposites.

The velocity of the ultrasound was calculated by dividing the distance travelled of the wave within samples to the delay time. Figure 3 shows the relationship between ultrasound velocity and nanocomposites with increasing GO concentrations. The ultrasound velocity increased with the concentration of the GO in the matrix. This is because of the increase of the interlinkage as the interfacial interaction led to the combination of two types of polymer particles and GO nanosheets, which led to the formation of macromolecular molecules inside the membrane. Where, the ether groups in polyethylene oxide bonded with the carbonyl and carboxyl groups to form hydrogen bonds that enhanced the mechanical properties of the nanoparticle (24). The stacking is better with the GO, which transports the mechanical waves from the source of the disturbance through the strong interfacial interaction (11). But the increased concentration of GO to 0.2 wt% led to a reduction in the properties of nanocomposites. This could be related to the overlap of some of the sheets of GO with each other as a result of increasing concentrations. This aggregate led to weakness of mechanical properties and disturbed the transferring of the ultrasound wave. Additionally, the aggregate GO nanosheets bonded by weak Vander Wals force, but that reduced the mechanical properties on the 2 wt % concentration. However, all the nanocomposites presented an enhancing in the ultrasound velocity compared with PEO after adding the GO (25).
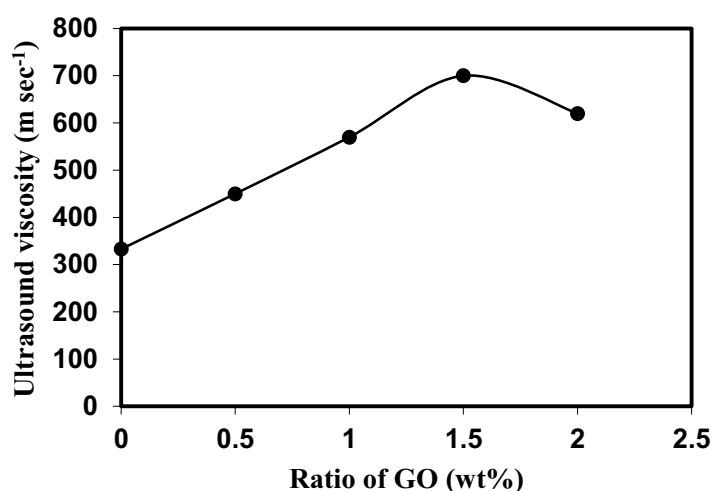

Figure 3. The ultrasound viscosity of PEO and nanocomposites.

Ultrasonic absorption coefficient values were calculated at different concentrations of graphene oxide (GO) from the difference in value between sender and receiver ultrasound waves. Figure 4 shows the increase of the absorption coefficient with increasing concentration of GO in samples. The absorption coefficient is responsible for increasing the absorption of ultrasound waves by the samples. Therefore, any increase in viscosity led to an increase in the absorption coefficient. The absorption coefficient is highly dependent on the concentration in the solution and the strong interfacial interactions. The hydrogen bond between PEO and GO is considered the main factor of the strong interfacial interaction (25). The increase in the absorption factor after the addition of the nanoscale (GO) is on account of the fact that the ultrasound waves falling on the membrane that are mechanical waves and their transmission as compression and inactivation. In addition, the volume of the polymer chains increases, thus increasing the absorption of the falling mechanical energy to respond to the pressure and the membrane. Because of the garaged GO led to slipping of nanosheets of GO that caused defects in the samples and reduced the mechanical properties.
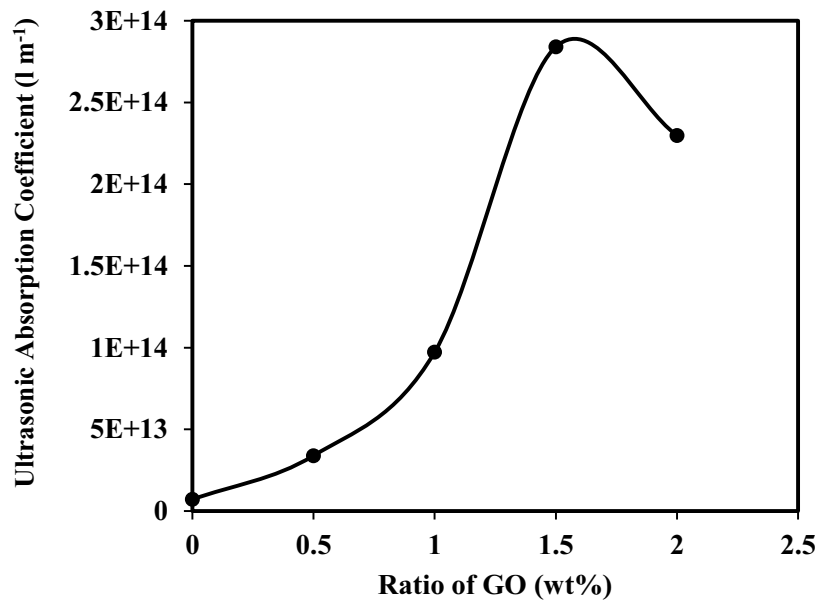
Figure 4. The ultrasonic absorption coefficient of PEO and nanocomposites.

The relaxation time values were calculated by relationship (1). Figure 5 shows the relationship between relaxation time and increased concentration of GO, the results show reducing of relaxation time with an increase in GO concentration in the matrix. The decrease in the relaxation time in general with increased concentration is explained by increasing the volume of the polymer chains, which led to increased internal friction between the layers of liquid resulting from compressing and deactivation as a result of ultrasound effect and the strength of interfacial interaction with the GO nanosheets (1), which restricted the movement of the polymer molecules. This results in decreasing the time needed to restore the excited molecule back to its original state (24).
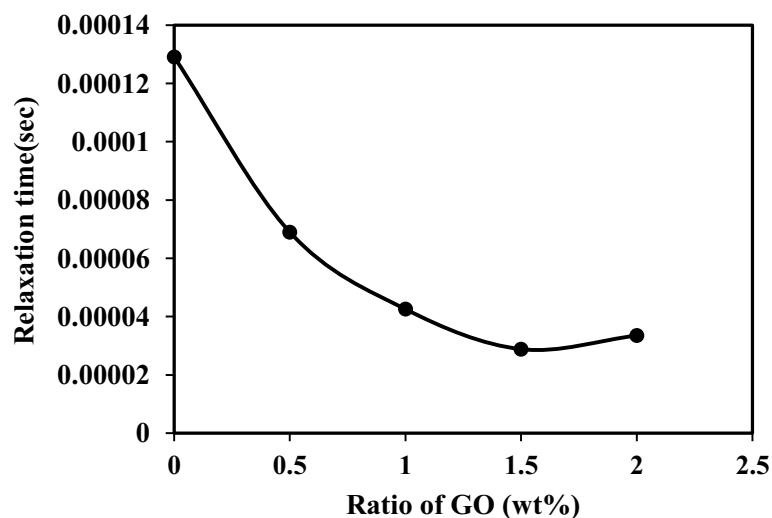

Figure 5. The ultrasound viscosity of PEO and nanocomposites.

Their values were calculated by the amount of the equation (2) and Figure 6 shows the relationship between the relaxation amplitude and increasing the concentration of GO in the nanoparticles. The results showed that the relaxation amplitude increased with the increase of the GO concentrations, where that because of the increased of the distance travelled by the molecule during the excitation process. Moreover, the determination of the inertia of the large molecule is significant due to its interrelationships with the GO nanosheets (26). In addition, the relaxation amplitude is directly proportional to the absorption coefficient as shown in the equations. When the frequency is constant for both cases, the relaxation amplitude of the solvent molecules is expected to increase when the absorption coefficient is increased. Where the nanoparticles of GO are associated with relatively weak bonds (Vander Waals) during the aggregation at a concentration of 2 wt%, which led to a decrease in mechanical properties (24).
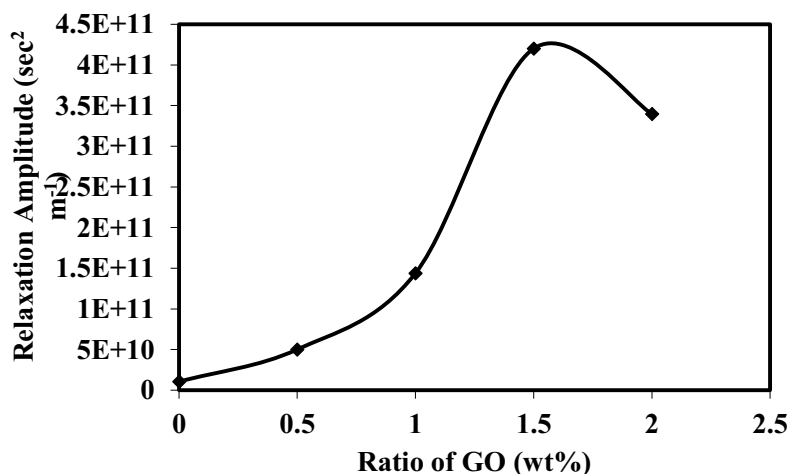

Figure 6. The relaxation amplitude of PEO and nanocomposites.

Compression values were shown in Figure 7, which were obtained from the equation (4). Where, the compression is inversely proportional to the speed square, so increasing the speed with density leads to a decrease the compressibility. Figure 7 illustrates the change in compression values with increasing of GO concentrations. The results showed a decrease in compressive values with increasing of GO concentration in the nanocomposites. This is a reason for the fusion of two types of molecules, which in turn led to the clustering of polymeric chains converging with each other due to their interaction with the GO nanosheets.
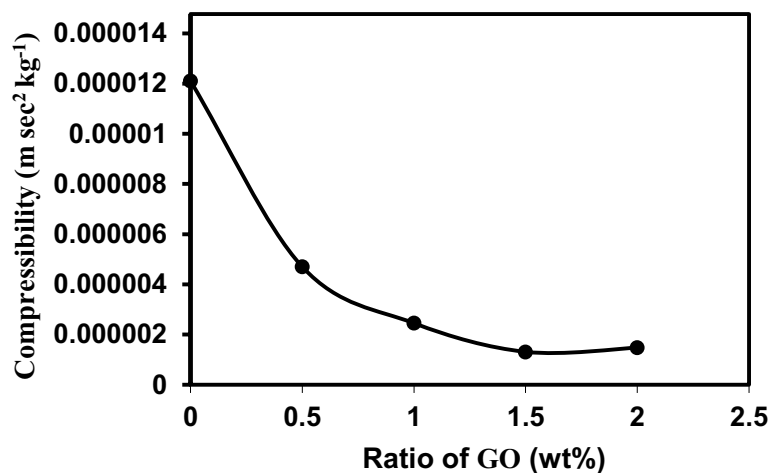

Figure 7. The compressibility of PEO and nanocomposites.

The values of the specific acoustic impedance and modulus of elasticity were calculated using the equations 3 and 5, respectively. Table 2 summarized the results and demonstrated an increase in both of the mechanical properties, where the values enhanced after the addition of GO with different concentrations. Because of the increase in the number of molecules in the solution, which increases the density of the carrier medium and increase the speed of ultrasound that caused the speed increases significantly with increased concentration of GO nanosheets (26).

Table 2. The specific acoustic impedance and modulus of elasticity of PEO and PEO-GO nanocomposites.

Sample ID	The ratio of GO wt%	Modulus of Elasticity $(kg/m.sec^2)$	Specific Acoustic Impedance (kg.sec/m2)
PEO	0	82612.305	248.085
PG 1	0.5	212625	472.5
PG 2	1	407424.6	714.78
PG 3	1.5	763420	1090.6
PG 4	2	676928.4	1091.82

FTIR trace of GO shown a significant change in the basil plan compared with graphite, as shown in Figure 8. Where the oxidation the h strong acid using hummer method's (19) illustrated various functional group on the GO surface, such as O-H at 3219 cm^{-1}, C=C at the 1720 cm^{-1}, C-O at the 1260 cm^{-1}, C-H at 1360 cm^{-1} and COO at the 1040 cm^{-1} in agreement with many literature (24,27). These FTIR result proved the successful synthesizes of GO and provide the GO specific unique characterization.
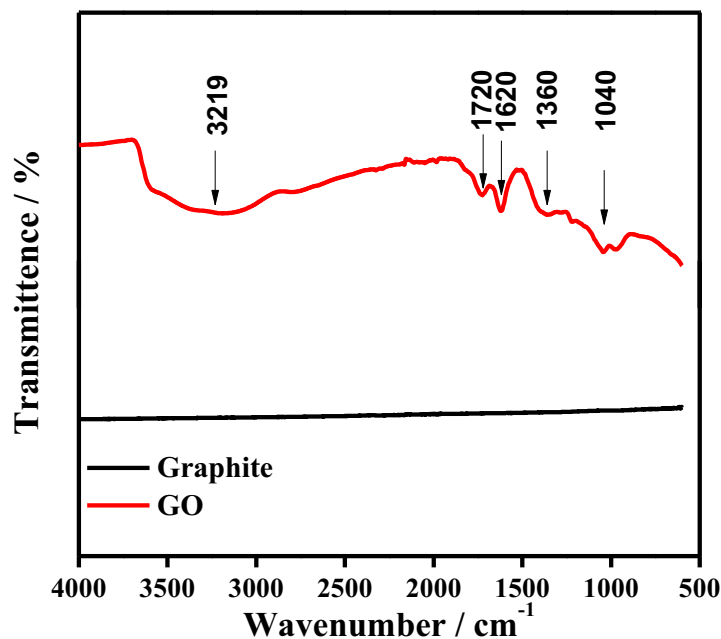

Figure 8. FT-IR trace of the graphite and GO.

A 3D AFM image presented roughness surface of GO, where the characterization of the morphology and 0.72 nm thickness as an average thickness of the GO single sheets, whereas showed different shape of GO nanosheets was presented using the AFM as well as size, which illustrated between 2000 nm to less than 50 nm, as shown in Figure 9.
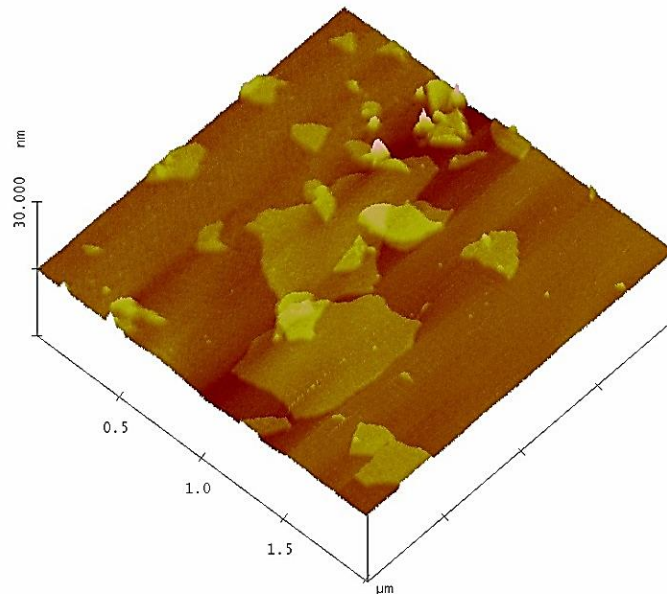

Figure 9. The compressibility of PEO and nanocomposites.

The fracture surface of GO, PEO and nanocomposites were demonstrated using the SEM images, as shown in Figure 10. In Figure 10 (A), the SEM image of PEO that presented with crazies or chain rupture the concentrations but samples was a without defects, for instance surface pores and air bubbles. Where the semi-crystalline PEO present stacks of crystalline lamellae, solid inclusions and cavities in the agreement with the literature (28). Whereas, Figure 10 (B) clearly showed the surface of GO, which looked a flaky morphology behaviour. In Figure 10 (C), the fracture surface of PG 3 had few crazies, but with a smooth surface, moreover, the GO nanosheets overlap by PEO, fine dispersion and the small feature of multiple GO nanosheets that attract each other with increasing the GO concentrations in the matrix. This behaviour of nanosheets was clearly increased and presented as aggregated of GO nanosheets in sample PG 4 as shown in Figure 10 (D). PG 4 presented textures, whereas some of aggregated GO were displayed on the surface. The SEM images agreed on the finding and presented as another significant confirm. However, the GO corporation providing a significant role in the improvement of the interlocking and reduction of cracks on the PEO surface and matrix that presented very a clear with some cavities.
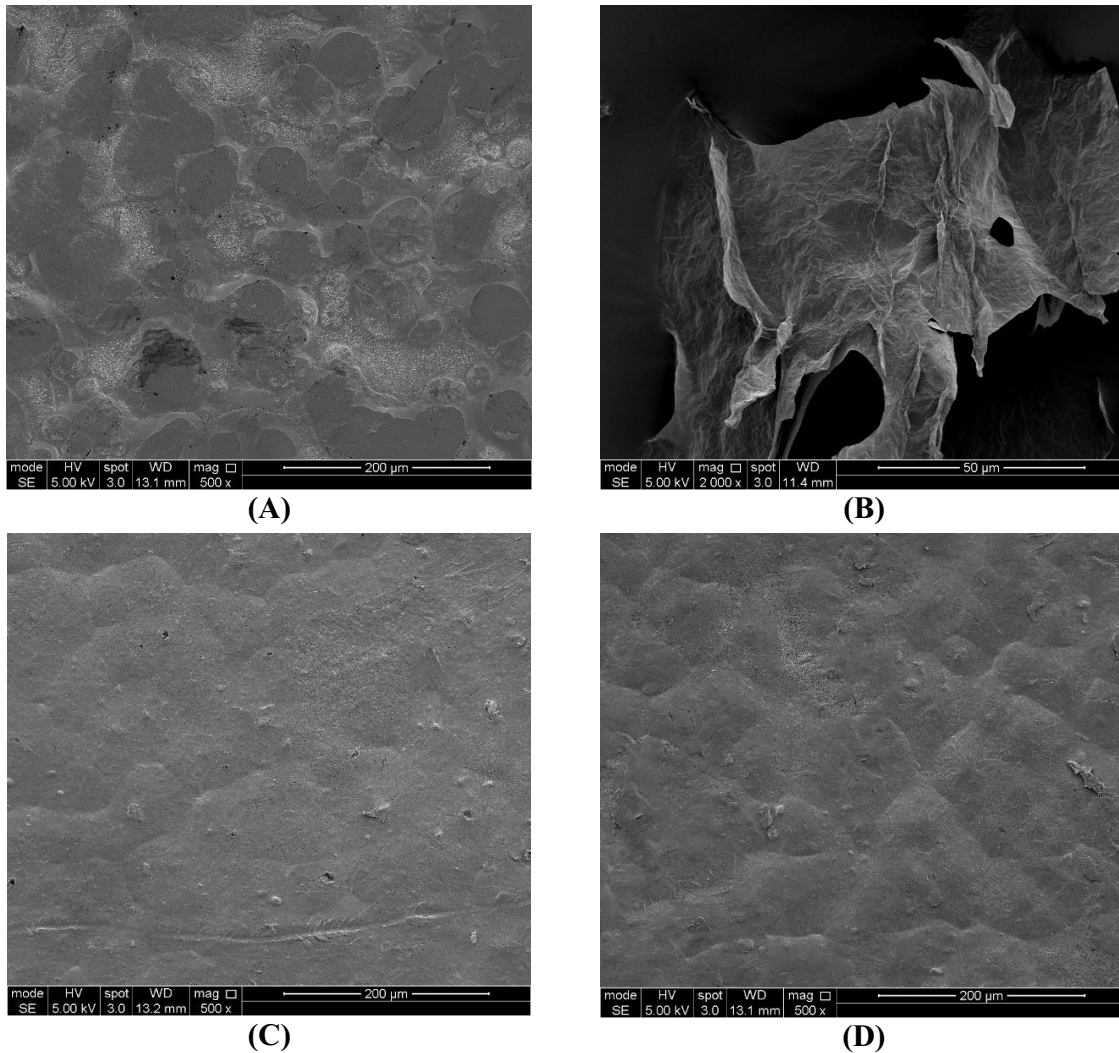
(A)

(B)

(C)

(D)

Figure 10**.** SEM image of the (A) PEO, (B) GO, (C) PG 3 and (D) PG 4.

4. Conclusions:

The results that obtained show that most of the physical properties affected by the increase in the concentration of GO. Most of the results have improved and presented the values of higher than normal with the addition of GO. Where, the addition of graphene oxide (GO) nanosheets increased the ultrasound velocity and the ultrasonic absorption coefficient of the polymer-based GO nanoparticle and also increased the density, viscosity and ultrasonic absorption coefficient. In addition, GO nanosheets led to a decrease in compressive values of the recorded membrane and thus became more tolerable to environmental conditions and can be used in the external environment, so it can be used in various industrial applications. The viscosity increased up to 112.5 %. Additionally, It was found that the best concentration of (GO) is (1.5 wt%) in this study, which showed the best mechanical results. The mechanical properties enhanced by 86.2 %, 719 % of ultrasonic velocity and bulk modules, respectively. Whereas GO concentration of 2.0% resulted in a decrease in mechanical properties.

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