

## STUDY THE EFFECT OF GRAPHENE ON POLYMER (PAPA) COMPONENT

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### ABSTRACT

In this study graphene was prepared from the reaction of the graphene oxide by hummer methods. The prepared nanoparticles were characterized by infrared spectra, X-ray diffraction (XRD), atomic force microscope (AFM), and scanning electronic microscope (SEM). Two types of polymers were prepared (PAPA), were diagnosed by FT-IR. The polymeric chips were mixed with vinyl alcohol polymer (PVA) (its physical and chemical properties were known). The physical and electronic properties of these polymers were studied after deflection with nanoparticles. Electrophysiological measurements showed that the PAPA with graphene nanoparticles has shown a higher conductivity than the (PAPA) polymers and the real dielectric moment constant of (PAPA + Graphene). Whereas the electrostatic moment constant showed a significant in PAPA. The study showed that these latter particles have a higher electric capacity of store energy than the polymer and are suitable for many applications ranging from the manufacture capacity to batteries.

**Key word: Graphene, nanoparticles, polymer PAPA, conductivity, Dielectric constant, Nanocomposites.**

### INTRODUCTION

Materials that are added to nanoparticles, during the synthesis of these materials, nanoparticles will significantly improve of material properties for example; the addition of carbon nanotubes to material changes the electric and thermal of this material. And the addition of other types of nanoparticles may improve the optical properties (such as strength and hardness). The volume percentage of added nanoparticles should be very low (within 0.5 - 5%), because the ratio between interface area and size of nanoparticles should be high. The paper reports the synthesis and characterization of nanoparticles containing nanographene and polymer and study the electric properties of these compounds before and after adding nanographene, and investigate their effect on properties [Vicki Bolam et al., 2008]. The modern society is observing an increase in renewable energy productions, such as the sun, wind, water...Etc. Hence, interest has been generated in the development of electrical vehicles and hybrid vehicles with low CO<sub>2</sub> emissions. Energy storage systems are starting to play a major role in modern lives since many limitations mainly related to reliability and sustainability for these renewable energy productions [Yan Wang, et al., 2009].

Therefore, many studies have focused on the development of new electrical energy storage system to meet higher demands for future systems, ranging from portable electronics to hybrid electric vehicles and large industrial equipment [Yan Wang, et al., 2009, Ibrahim, 2008]. Electrochemical supercapacitors, with nano particles are one of the new technologies currently under

development for advanced energy storage systems.

Composite materials are compound of two or more distinct materials and are expected to display extensive features emerging from the combination of properties of each component. The property of composite is superior to those of individual components. They have high specific modulus and high strength comparing to individual traditional materials and these properties can be tailored for specific application [Ahmad Varvani-Farhani 2010].

Compared to conventional composites, nanocomposites are defined as multi-phase solid materials where one of the phases is a nanomaterial whose size is between 1-100nm and in at least one dimension [Bandy Opadhyay]. Due to the nanometer size of the materials, nanocomposites possess unique size dependent properties, which are not typically shared by their conventional micro composite counterparts. Nanocomposites with their outstanding properties are finding applications in numerous fields. It has been estimated that there is a great increase in the trend of global consumption of composites in the next few years [Ajayan and Schadler 2003].

### 2. MATERIALS AND METHODS

**2.1. chemical materials:** Graphite, Potassium Permanganate, Sodium nitrite, Sodium hydroxide, Methanol, Sulphuric acid, Poly (vinylalcohol) (PVA), Terephthaloylchlorid, N, N-Dimethylformamide (DMF), Pentaerythritol, Pyridine, Ethanol, 4-hydroxybenzaldehyde, Dichloroethane

**2.2. Properties of graphene:** To get the graphene, graphene oxide should be prepared from the

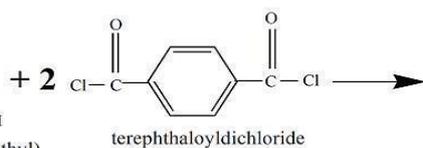
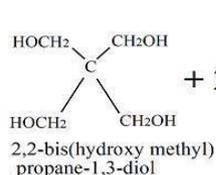
graphite by hammer method, which is reduced to graphene as in the following steps:

**Step one:** The preparation of graphene oxide by hummer method [William and Richard, 1958]

A 23ml of the con.  $H_2SO_4$  was put an Acebath 0.5 g of  $NaNO_3$  was added Slowly and add of  $NaNO_3$  0.5g to a 23ml of con.  $H_2SO_4$  on Ace bath with stirring at 0 °C for 15min, and 0.2g of graphite powder was added slowly to the mixture for 10 min. This is followed by the slow addition of  $KMnO_4$  3 g for 15min. The mixture was left at Acebath for 5min and left to stirrer for only 1.0 hr. After, that add 46ml of distill water; very slowly drop by drop. The addition lasts for more than 20 min and raise the temperature to 98 °C for 20 min. Then add 140ml of distilled water and the mixture was left to stir for 10 min and add 9ml of  $H_2O_2$  30% with stirring for 30min. The mixture was cooled at room temperature and filtered off by special filter paper. The pot. was washed several times with distilled water and dried in oven at 60-70°C for 4hr.

**Step two:** Reduction of graphene oxide.

A 50ml of distilled water was added to 0.1g of graphene oxide in round flask 250ml with stirring, and a suspension of graphene oxide and water was

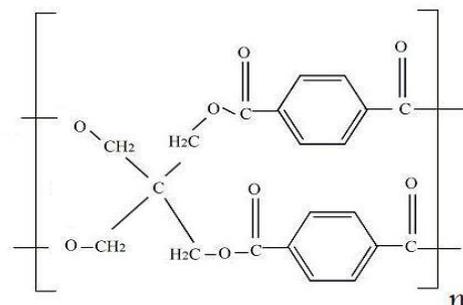
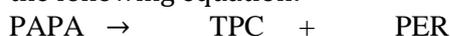


formed. The mixture was taken to ultrasound and left to become clear solution, and 1.0 ml of hydri-sine hydrate was added and heated to 100°C for 24hr.

The solid ppt. was filtered off, washed with distilled water (approximately 5 times \*100ml) followed by Etoh (approximately 5 times \* 100 ml) and dried in oven.

### 2.3. Preparation of polymers:

1. poly [2,2bis ((4-acety benzoyl oxy) methyl)] propane - 1,3-diylbis (4-acetyl benzoate) PAPA: A solution containing( 1.36 g , 10 m mole) of pentaerythritol (PER) in pyridine 5ml and DMF 2ml and cooled at - 5°C and added to it a Terephthaloylchlorid TPC (4.06g, 20m mol) in pyridine 7ml under an inter atmosphere of nitrogen gas with stirring, The mixture was stirred at room temperature for 24 min. The polymer was receipted by adding the reaction mixture to three times its volume of Methanol ( $CH_3OH$ ). The ppt. was filtered off and washed with distilled water and Methanol ( $CH_3OH$ ), and dried in oven under vacuum at (60°C) as in the following equation:



Poly[2,2-bis((4-acetylbenzoyloxy)methyl)propan-1,3-diyl bis(4-acetylbenzoate)]

### 2.4. Methods of preparing the polymeric sheets (or Films):

The polymeric films were prepared with different concentrations in order to get the best sample that could be considered as standard to prepare the polymeric Films containing nanoparticles in preparation. We tested many weights to prepare the polymeric films from the mixture PVA with 40% of any polymers prepared (PAPA). The best combination through the strong, transparent and reliable homogeneous films can be obtained in the preparation of nanoparticles.

**2.5. The preparation of composite polymer films:** Graphene Films was prepared with PAPA to obtain good films so that they are thin, strong and homogeneous to do the electric measurements. It should be of **one type: PVA 60% + polymer PAPA 40%**.

The different concentrations of nanoscale films were prepared as shown in table 1. The nanoparticles were used with two types of composite polymer Films as shown in table 1.

**Table 1:** PAPA concentration, graphene weight and (%) of nanoparticles.

No.	Wt. Graphene	Polymer	Nanoparticles %
1.	Zero	0.333	0%
2	0.0016	0.333	0.6%
3	0.0033	0.333	1.3%
4	0.005	0.333	2%
5	0.007	0.333	2.8%
6	0.0083	0.333	3.3%

## 3. RESULTS AND DISCUSSION

**3.1. Characterization of nanoparticles:** The Graphene and Graphene oxide was characterized by using (FT\_IR). The IR spectra of Graphene

oxide (fig. 1) and Graphene (fig. 2) shows that the  $\nu$  (OH) was stretching at  $(3200-3400) \text{ cm}^{-1}$ , and  $\nu(\text{C=O})$  at  $1726 \text{ cm}^{-1}$  where-as the  $\nu(\text{C=C})$  appeared at  $1627 \text{ cm}^{-1}$ , and hetero cycle for the epoxy group (OH) at  $(1396_1425) \text{ cm}^{-1}$  and  $\nu(\text{C-OH})$  at  $1032 \text{ cm}^{-1}$ .

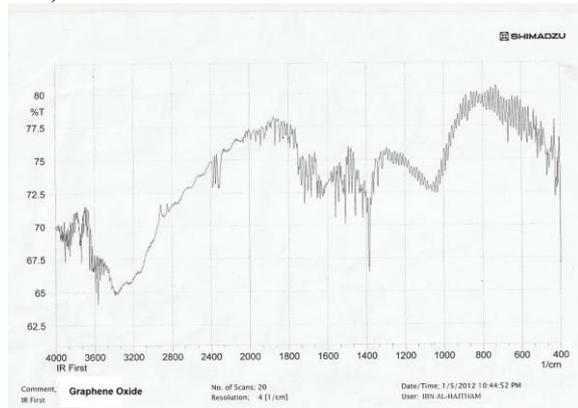


Fig 1: FT\_IR spectrum of graphene oxide.

After the reaction the  $\nu$  (C=O) group disappeared, and  $\nu$  (C=C) was shown at  $1577 \text{ cm}^{-1}$ , where-as, the band was at  $1060 \text{ cm}^{-1}$  in spectra of graphene and graphene oxide due to the  $\nu$  (C-C) group, which was the stand and bond in the structure of the graphene and graphene oxide.

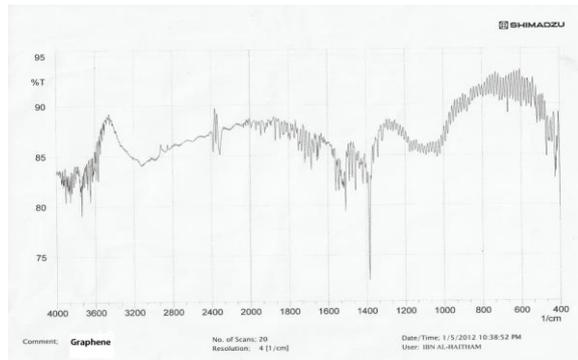


Fig. 2: FT\_IR spectrum of the nanographene Films.

The forms show clearly that the reaction results have formed a bond of type ( $\text{sp}^2$ ) in carbon structures. Based on these results, it can be concluded that the graphene Films are formed (see fig.3).

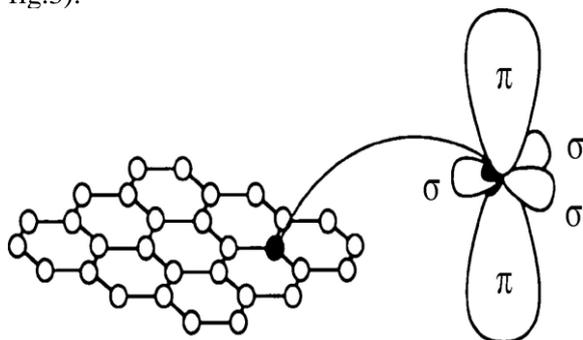


Fig.3: Hybridization of carbon orbitals for  $\text{sp}^2$  bond.

These results were supported by the XRD tests for graphene and graphene oxide (figs. 4 and 5)

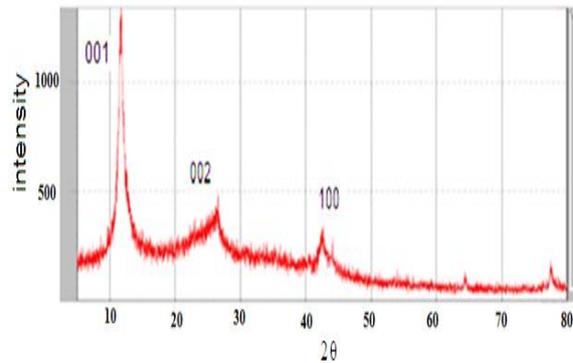


Fig.4: XRD of nanographene oxide particles.

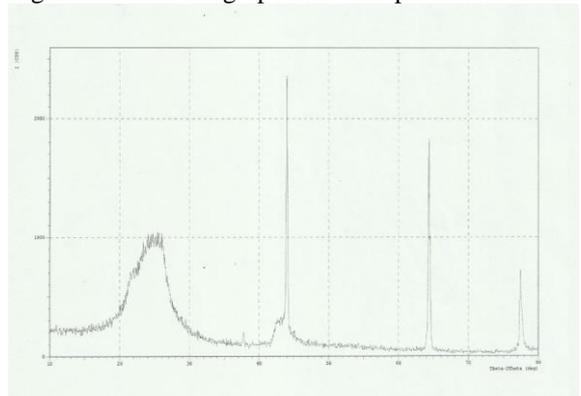


Fig.5: XRD of nanographene pellets.

These results correspond to references [Sun-gjin Park et al., 2011, Nethravathi et al., 2010]. In fig. 4, a strong peak at  $2\theta = 11.7$  represents the internal distance, and equals  $7.6 \text{ \AA}$  while in fig 5, a broad peak in the XRD spectrum of graphene, at  $(2\theta = 22.3, 25.68, 26.83)$ , and due to the interstitial intervals between the nanoparticles were equal to  $(\text{\AA} 4.91, 3.72, 3.39)$  respectively. These results resulted from the exfoliation, reduction process of graphene oxide, and removing the water molecules between the nanoplates that were associated with hydrogen bonding between the oxygen atoms of oxide groups (see fig.6)

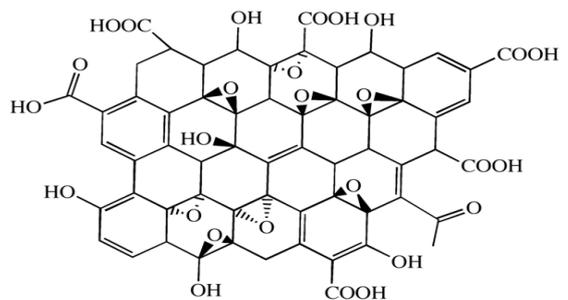


Fig. 6: Suggested structure of graphene oxide Films.

The results of AFM (Atomic force microscope) show that the preparation of graphene by chemical method, which depending on hydrothermal method clearly shows that the Films will be over-



if  $k = 1.57 \cdot 10^{-4}$ ,  $a = 0.79$

using the (mark-hunk) equation [Shen, 1971], the M.w is equal to 45687.

**3.3- Electric properties of graphene pure.**

**3.3.1-A.C Electric conductivity:** The electric measuring of graphene was studied by using HPL-CR apparatus. It was observed that the electric measuring of the nanoparticles at the frequency (100-4000Hz. sec) is low to stable at low frequency, and beings to rise slightly to (1000Hz.sec) After that it will be clearly and forcefully high (see fig. 11).

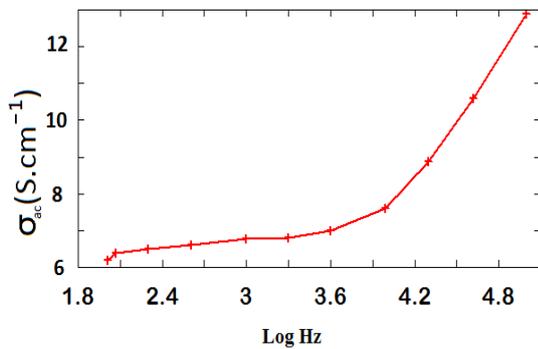


Fig 11: AC electric conductivity with Change of pure graphene frequency.

**3.3.2- Dielectric constant:** The measurement of real and imaginary constant ( $\epsilon''$ ,  $\epsilon'$ ) respectively, are shown in fig 12. The values increased in the low frequency zone at (100\_200 Hz.sec). On the other hand, it began to decrease and became stable at (200\_100.000 Hz. sec) frequencies zone.

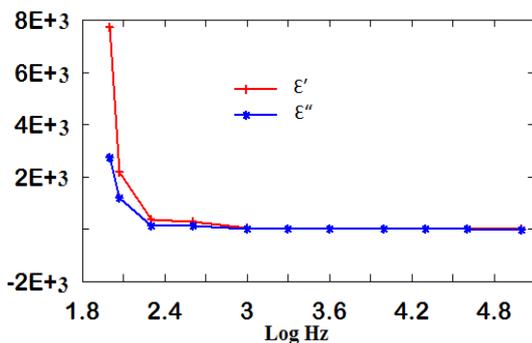


Fig. 12: change of dielectric constant with the change of pure graphene frequency.

The factor of the real and imaginary dielectric constant is  $M'$  and  $M''$  respectively. We show a clear atrophy of its values in the low frequency zone (about 100\_200 Hz), The values are noticed to raise at the high frequency zone (2000\_4000 Hz), which is unexpected after 4000Hz. After that, they started to fall again. The frequency value of the peak is the relaxation time frequency at (40000Hz) (see fig.13)

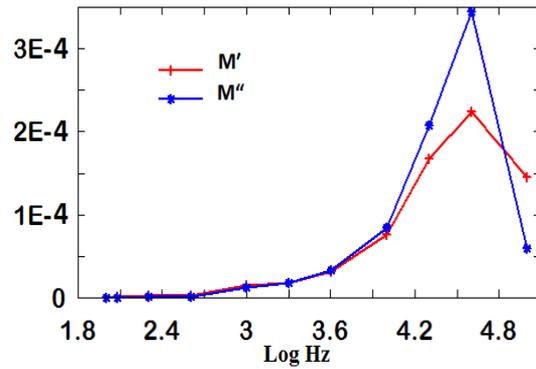


Fig.13: change of the values of factor of real and imaginary dielectric constant with the frequency change of graphene pure.

**3.4. Electric properties of pure PAPA polymer: Poly[2,2-bis-((4-acetylbenzoyloxy) methyl)-propane-1, 3-diylbis-(4- acetylbenzoate)]( PAPA).**

**3.4.1\_Ac electric conductivity:** The present study of conductivity values of pure PAPA polymer in alternative current by using different frequencies showed that the conductivity values in low frequency zone are (limit 100\_120Hz) between (2.9 E-6 \_ 3.7 E\_6) (S.cm<sup>-1</sup>), but with the increase of frequency to (200\_2000Hz.sec), the conductivity becomes at the lowest value. After that, there is a sudden increase in conductivity values after (40000Hz.sec) see (fig. 14).

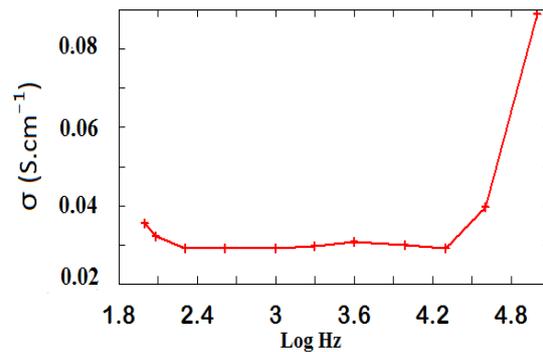


Fig.14: Ac electric conductivity values with change of pure PAPA polymer frequency.

**3.4.2 Dielectric constant:** Fig. 15 shows that the values of real and imaginary dielectric constant ( $\epsilon'$ ,  $\epsilon''$ ) increase in low frequency region, especially at (2000Hz.sec), and later significantly increase to the frequency (100Hz.sec). But the real and imaginary dielectric constant values are stabilized after (2000Hz.sec) frequency.

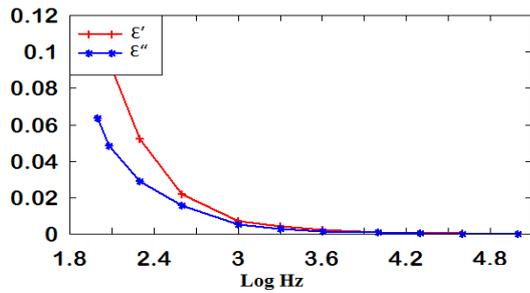


Fig. 15: change of real and imaginary dielectric constant values in pure PAPA polymer.

The factor values of real and imaginary dielectric constant ( $M'$ ,  $M''$ ) respectively (fig. 16) are stabilized at 100\_200Hz.sec frequencies and start to increase at 4000Hz.sec to its highest peak with the increase of frequency at (100.000Hz.sec).

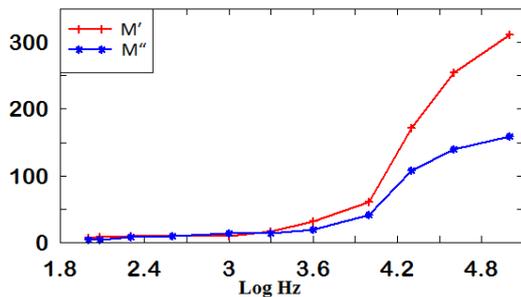


Fig 16: values of real and imaginary dielectric constant of pure PAPA polymer.

### 3.5. Electric properties (graphene + PAPA polymer)

**3.5.1. Actual electric conductivity:** The electric conductivity values of polymeric nanoparticles were studied with the change in the graphene concentration and percentage in Ac with different frequencies (see fig. 17)

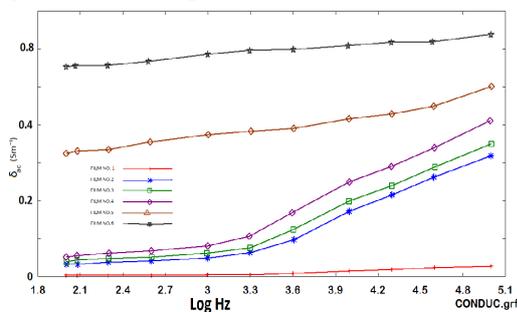


Fig. 17: Ac electric conductivity values with the change of frequency of composite (Graphene + polymer PAPA).

The film 1 does not have a clear effect at low frequency (100\_4000Hz.sec), but a slight change is observed after frequency 10000\_100000 Hz. sec. While the films containing low concentration

of graphene, which can be seen in table 1 (in experimental section) (film 2\_4) are equal to or less than (0.15%) and have very low electric conductivity values especially at (100\_2000 Hz. sec). They start to increase with the frequency increase to be more than (2000\_100.000Hz.sec).

The electric conductivity of film (5) (concentration equal to 0.20, fig. 21) shows a specific value of electric conductivity between (0.015\_0.02 S.m<sup>-1</sup>). It behaves differently from other concentrations. particularly, in low frequencies because as conductor materials (semiconductor materials). As for the concentration (0.25%) we see that this-films has a good electric conductivity.

It is noticeable that the graphene concentrations have an important role in the composite conductivity. Note that when the increase of concentration of graphene, especially at low frequencies which are less than (2000Hz.sec), a sudden rise in electric conductance nature is seen, and the transformation of the composite from insulation materials to semi conductance materials and to conductance materials this is called accompanying to beginning of the nomination [Yu Chao Li et al., 2010], can explain the change in the electric conductivity depend on the graphene amount in the composite. As for the concentration (0.2%) in film 5 (see fig 17), these amounts of graphene will form, may interfaces between the nanoparticles and the polymer. This will increase the number of nanoparticles and ( $\pi$ ) orbitals of graphene. The polarization between the interfaces will be regulated and the electrons in the present the electric current will be rearranged. Furthermore, increasing the conductivity will increase graphene concentration. This is called accompanying the beginning of the nomination, and in this case the real dielectric constant will be decreased (see fig. 18).

**3.5.2. Dielectric constant:** Figure 18 shows that the real dielectric constant values ( $\epsilon'$ ) are changed with composite frequencies in 24°C. Hence, the composite which has high ( $\epsilon'$ ) values will be decreased with the rise of frequencies; especially at (1000\_2000Hz.sec).

This result can be explained when the low frequency range is less than (1000 Hz.sec). The alternative current is low, which gives sufficient time for the fixed and induced for the dipole constant to arrange the particles and direct with electric current, except the composite (1), that has a low ( $\epsilon'$ ) value at (400\_100.000 Hz.sec) range.

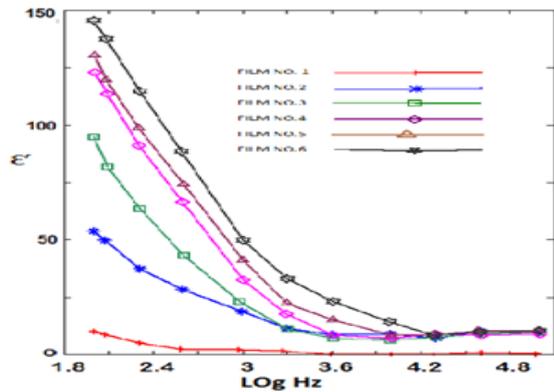


Fig. 18: change of  $\epsilon'$  values with the change of (graphene + polymer PAPA) frequency.

In the composite (2-6), the increase in dielectric constant value can be explained by the increase of polarization, which makes the value of ( $\epsilon'$ ) the highest at low frequencies, and due to the presence of the interfaces between the nanoparticles and the polymer, in addition to polarity of the poles and this depends on the properties and composition of the samples [Tsangaris et al., 1998, Gatos et al., 2007, Psarras et al., 2007].

It is observed in fig. 17 that there is a constant increase in the electric conductivity with the increase of graphene concentrations. This is reflected in the values of ( $\epsilon'$ ), so that the increase of  $\epsilon'$  is a homogeneous increase with the concentration. This indicates that the polar value and the stored energy are proportional with graphene concentration.

Fig. 19 shows that the  $\epsilon''$  values decrease with increased frequency values; especially at (1000 Hz.sec). The clear difference between  $\epsilon'$  and  $\epsilon''$  means that these composites have excellent power in the manufacture of the electric capacities or electric loses [Psarras et al., 2007].

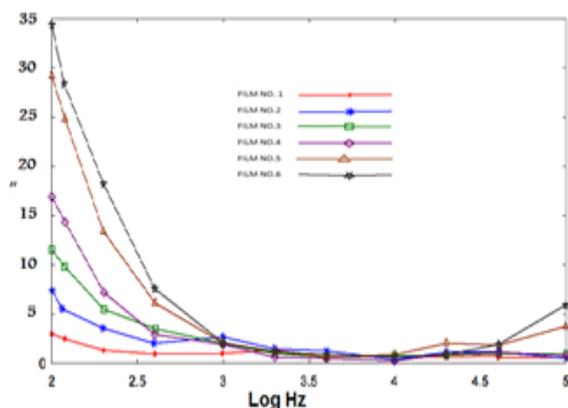


Fig. 19: change of  $\epsilon''$  values with the change of frequency of (Graphene + polymer PAPA).

Fig.20 and 21 show the change of  $M'$  and  $M''$  values with the change of nanoparticles.

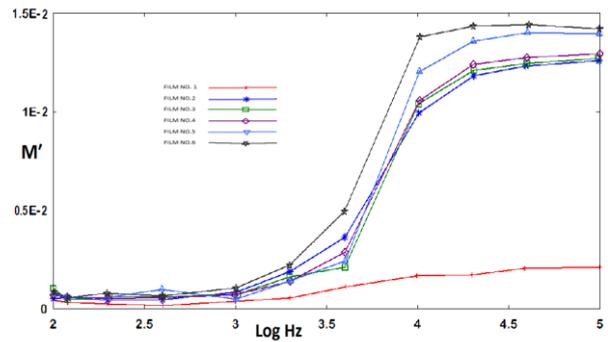


Fig. 20: change of  $M'$  values with the change of (graphene + polymer PAPA) frequency.

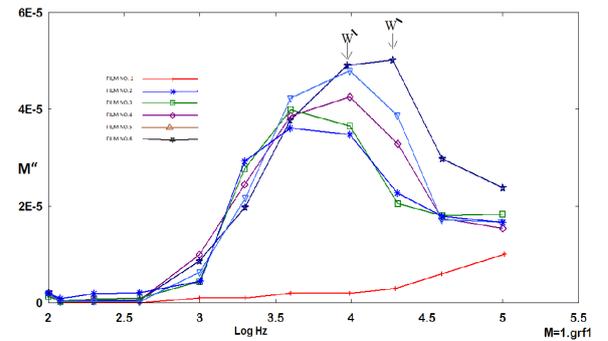


Fig. 21: change of  $M''$  values with the change of (Graphene + Polymer PAPA) frequency.

The  $M'$  value suddenly increase at (4000Hz. sec), while  $M''$  value increase is proportional to the concentration of nanoparticles, and the peaks are shown in fig. 25i.e the  $W'$  value is the relaxation time for each sample.

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