The Effect of Nano Graphene Additive on the A.C Electrical Properties for Epoxy-Copper Composites

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Abstract: ***Composites of Epoxy/Copper have been prepared with different weight percentages (5,10,15,20,25,50%), and the other adding Graphene nanoparticle to Epoxy resin to prepared nanocomposites with different weight percentages (1,3,5,7,9%). Hybrid composites have been prepared with specificweight percentages. The A.C electrical properties were studied to the composites with different weight percents, their contents have been characterized. The A.C electrical properties show that the dielectric constant and dielectric loss of the composites and nanocomposites decrease with increasing of the frequency applied electrical field with range (10KHz-10MHz), and temperature with range (293-373K) The A.C electrical conductivity increases with increasing ofthe frequency and the concentration of Copper and Graphene.The change of A.C conductivity with the amplified electric field frequency is follow to the relationship ($\sigma\alpha\omega^s$), where s values were found from this relation. The activation energy decreases for all samples with increasing the concentration of additive Copper and Graphene.***

Keywords: Epoxy, Graphene, Copper, A.C conductivity, dielectric constant, dielectric loss

1. Introduction

Polymer adhesives as epoxy, however, are inherently electrically insulating materials. By adding electrically conductive filler materials, they can be made to conduct electricity [1]. The addition of a conductor to an insulator affects the electrical properties of the composite according to the degree of filling and proximity of conductive particles to other conductive particles. Particle size ratios and particle shape are the main factors controlling the properties of the polymer/metal system [2].The two dimensional graphene sheets has emerged as a subject of enormous scientific interest due to its exceptional electron transport, mechanical properties, and high surface area [3]. Graphene and polymer composites show excellent properties in many applications due to their high flexibility, thermal and electrical conductivity [4]. Electrical connection is provided by the continuous network of conductive particles. The discontinuous electrical property change of the composite is normally explained in terms of the metal filler concentrations by percolation theory [5]. When a sufficient amount of conductive filler is loaded into an insulating polymer matrix the composite transforms from an insulator to a conductor, the result of continuous linkages of filler particles. This point where the electrical resistivity decreases dramatically, called the percolation threshold, has been attributed to the formation of a network of chains of conductive particles that span the composite [6]. Usually decreasing filler size leads to a decreased percolation threshold, because inter particle contacts increase with a rise in the amount of the particles [7]. If a very large amount of filler is required for conduction, the polymer material's strength and elasticity may be degraded. It is therefore important to use the minimum quantity of conductive filler to achieve the required degree of electrical performance [8].

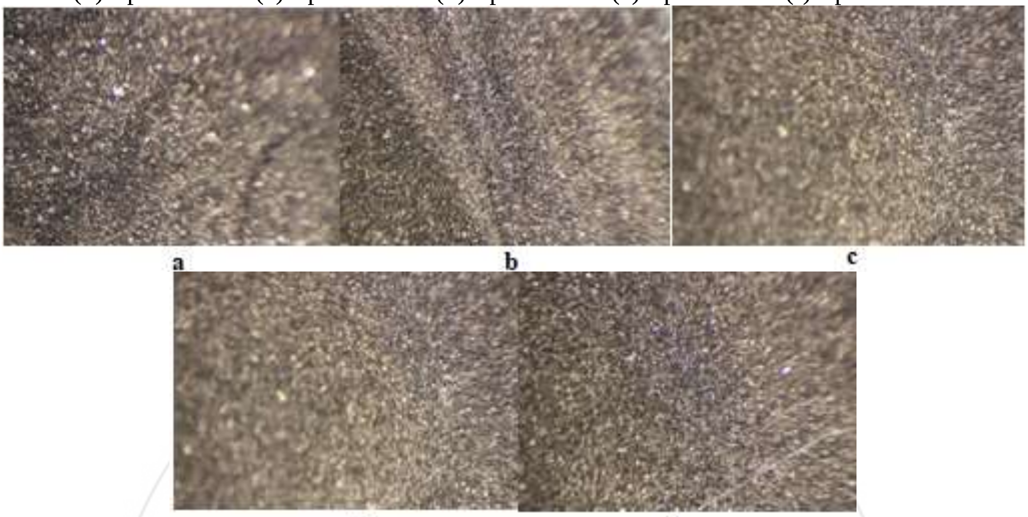
2. Experimental Work

The materials used in the paper is epoxy resin as polymer matrix type EP10 and hardener type HY-956 in ratio 3:1 for curing, copper powder supplied by BHD Chemical Ltd Poole(England),and graphene nano powder with particle size 6-8 nm, supplied by Sky Spring Nanomaterials, (USA), The electronic balanced of accuracy 10-4 have been used to obtain a weight amount of tin powder and polymer powder. The weight percentages of copper are (0, 5,10,15,20,25 and 50) wt.%. and of graphene (1,3,5,7and9) wt.%. These mixed by Hand Lay-up and the Microscopic Examination used to obtain homogenized mixture as shown in **Figures1**,**2**,**3**. Glass plates of 0.3 cm thickness,10cm length, and 5cm width, were used to configure rectangle mold. Solutions of Epoxy composites , hardener, and different percent of copper and graphene were poured into the mold.. For electrical measurements, circular samples of 2.5 cm were cutted from the original rectangular shape. For better connection with electrodes, the circular samples where cured with liquid silver base of 0.6 cm diameter. Samples of epoxy/copper/graphene hybridcomposites had been prepared with selection of highest percent of graphene (9%) to be added to lowest present (5%) and highest present (50%) of epoxy/ copper composites . Also identify the effect of addition of lowest percent of graphene (1%) to lowest percent (5%) and highest percent (50%) of epoxy/ copper composites.

a b c

d e f

Figure 1: Photomicrographs of Epoxy/copper wt.% composites (a) Ep.+5%Cu (b) Ep.+10% Cu (c) Ep.+15% Cu (d) Ep.+20%Cu (e) Ep.+25%Cu (f) Ep.+50%Cu



a b c

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Figure 2: Photomicrographs of epoxy/graphene nanocomposites (a) Ep.+1%Gr. (b)Ep.+3%Gr. (c) Ep.+5%Gr. (d) Ep.+7%Gr. (e) Ep.+9%Gr.

a b c

Figure 3: Photomicrographs of epoxy/copper/graphene hybrid (a) Ep.+5%Cu+1%Gr. (b) Ep.+5% Cu+9%Gr. (c) Ep.+50%Cu+1%Gr

A.C electrical measurement

The measurements have been done using a computerized sensitive impedance analyzer (LCR Meter)The range of the frequencies that of concern in this work was 10^4 – 10^6Hz,at different temperatures of range 293 – 373 °K by using the oven.

During A.C conductivity, frequency of the electric field will be variable. The empirical relation for the frequency dependence of a.c conductivity is given by [9] :

$$\sigma a.c\ (\omega) = Á\ \omega^s \quad \ldots\ldots\ldots(1)$$

where:

Á is proportional factor, **ω** is the angular frequency ,and**s**is the exponent factor and is determined from the slope of a plot Ln σa.c(ω)versus Ln **ω**, The total conductivity was calculated from the equation [10]:

$$\sigma\ total\ (\omega) = (d/A)G \quad \ldots\ldots\ldots\ldots (2)$$

Where **d** is the thickness of the measured sample, **G** is the sample conductance, and **A** is the cross sectional area.

The real and imaginary parts of the complex dielectric permittivity **ε* = ε' - j ε"** were obtained with the assumption that studied cell is equivalent to a circuit consisting of an ideal capacitance Cp. The capacitance of a parallel-plate capacitor is, for the real case, when the losses are present [11].

$$C = \varepsilon^* C_o = \varepsilon_o (\varepsilon' - j\,\varepsilon'')\, A / d \quad \ldots\ldots\ldots (3)$$

where ε_o is the absolute permittivity of the vacuum (8.854×10^{-14}F/cm), **ε'** is the dielectric permittivity (the real part of the complex dielectric constant), ε" is the imaginary part of the complexpermittivity, d is the distance between the plates, **A** is the area of a plate and C_o is the capacitance of the empty cell

$$C_o = \varepsilon_o A / d \ \ldots\ldots\ldots\ldots(4)$$

The dielectric constant **ε** was calculated from the equation:-

$$\varepsilon' = C/Co \quad \ldots\ldots\ldots\ldots (5)$$

The dielectric loss **έ** was calculated from the equation:-

$$\varepsilon'' = G/\omega\, C_o \quad \ldots\ldots\ldots\ldots (6)$$

The value of **tanδ** can be calculated from the equation:-

$$\tan\delta = \varepsilon''/\varepsilon' \quad \ldots\ldots\ldots\ldots(7)$$

International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

3. Result and Discussion

The variation $\sigma_{a.c}(\omega)$as a function of frequency for epoxy composites samples of different copper weight concentration at 393K is given in **Figure 4**. The figure shows that the $\sigma_{a.c}$ increases with increasing of the frequency. This behavior is in the agreement with equation 1. The increase in conductivity by increasing the frequency and temperature is a common response for polymeric and semiconductor samples. The reason for this increase in AC conductivity, $\sigma_{ac}(\omega)$, is tremendous increase of the mobility of charge carriers in the polymer composite [12].The figure also indicates that $\sigma_{a.c}(\omega)$ is increasing with increasing Cu wt.% content, a result which supports the suggestion of hopping of charge carrier conduction mechanisms. Relation $\sigma_{a.c}(\omega)\ \alpha\omega^{s}$, has been used to find the exponential factor (s).Values of exponential factor were calculated for all the composites from the plotting of $Ln\sigma_{a.c}(\omega)$ verses $Ln\omega$. The obtained values of **s** ranged 0.9102-0.8118 unit that indicate the correlated barrier hopping (CBH). According to the model $\sigma_{a.c}(\omega)$ can be explained in terms of hopping of electrons between parries of localized states at the fermi levels [13]. It is the dominant conduction mechanism, and have a tendency to decrease with increase of frequency and construction as indicated in **Table 1**.

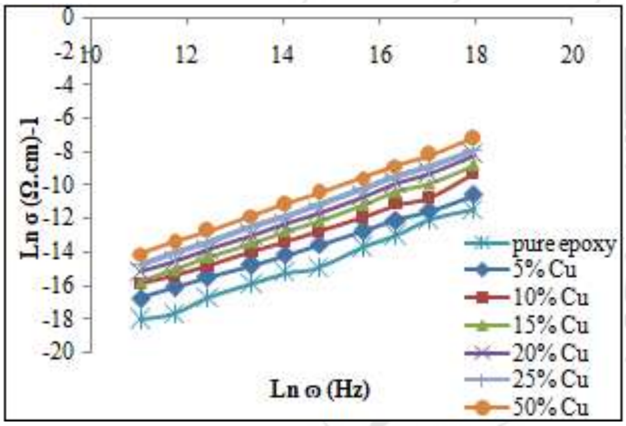

Figure 4: A.C conductivity as a function of angular frequency for different additive concentration of epoxy/copper composites

Figure 5 indicate the variation of A.C conductivity as a function of temperture for different concentrations prepared epoxy/copper composites samples at 100KHz.The figure shows that for all samples the conductivity is increaseing exponentially with increasing temperature, this behavior is according to Arrhenius equation. The effect of temperture on$\sigma_{ac}(\omega)$ for epoxy/copper composite are increased slightly indicating a semiconductor-type behvior [14]. The observed increase in ac conductivity,$\sigma_{ac}(\omega)$,with temperature is due to the mobility of the charge carriers which is responsible for hopping. As the temperature increases the mobility of hopping ions also increases thereby increasing the conductivity. The electrons which are involved in hopping are responsible for electronic polarization in these composites [15].

Table 1: list of exponent factor (S) for epoxy/copper composite samples

wt.% copper	S
0 wt.%	0.9102
5% Cu	0.8863
10% Cu	0.8802
15% Cu	0.8721
20% Cu	0.8647
25% Cu	0.8596
50% Cu	0.8118

Dielectric constant ε' of epoxy/copper composites variation with different concentrations as function of frequency at 293K in **Figure 6**. The dielectric constant decreased with an increase the frequency. It can be attributed to the fact at high frequency the dipole cannot rotate sufficient rapidly, so that their oscillations lag behind those of field. As the frequency is further raised the dipole will be completely unable to follow the field and the orientation polarization ceases [16].The high value of ε at low frequency range can be attributed to the structural changes that occurred in the material which convert its behavior from dielectric to semi conductive behavior [14]. Temperature dependence of the dielectric constant ε at fixed frequency 10KHz. The variation of the dielectric loss, ε", of epoxy/copper composites as function of frequency at 293K is shown in **Figure 8**. At 10KHz-1MHz, ε" decreases exponentially with increasing frequency up to a certain value then start to increases to reach a maximum. The εi value for epoxy/copper composites have been increases to indicate semiconductor-type behavior [14].This oscillatory behavior of ε" may be due to some combined relaxation processes which usually occurred in heterogeneous system. There is a relaxation peak at frequency 4MHz . The decreasing of ε" in the low frequency is due to interfacial polarization at the matrix-filler interface. The increasing of ε" at high frequency is due to on setting of ohmic conductivity of the charge carrier. This argument is adopted by some researchers .

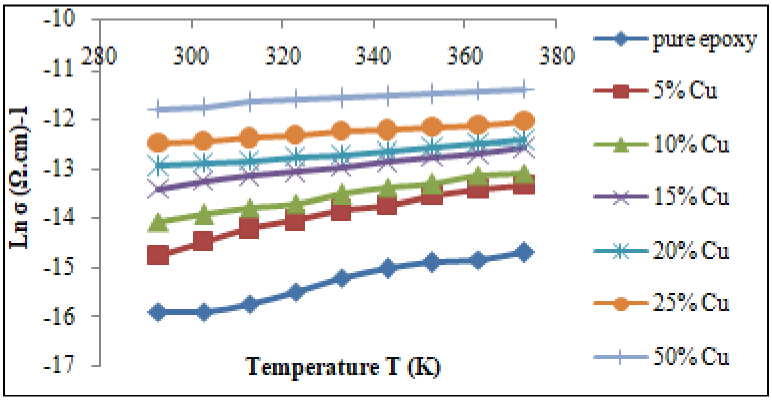

Figure 5: Variation A.C conductivity with temperature for different concentration of Cu at 100 KHz

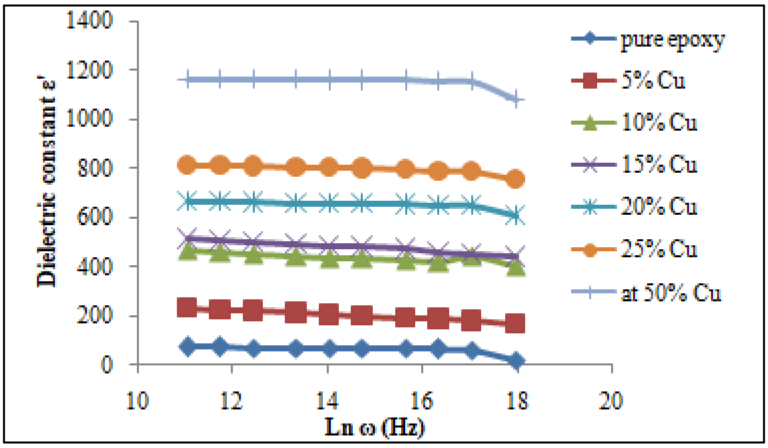

Figure 6 The variation of the dielectric constant ε as a function of frequency at 293 K for epoxy/cooper composites

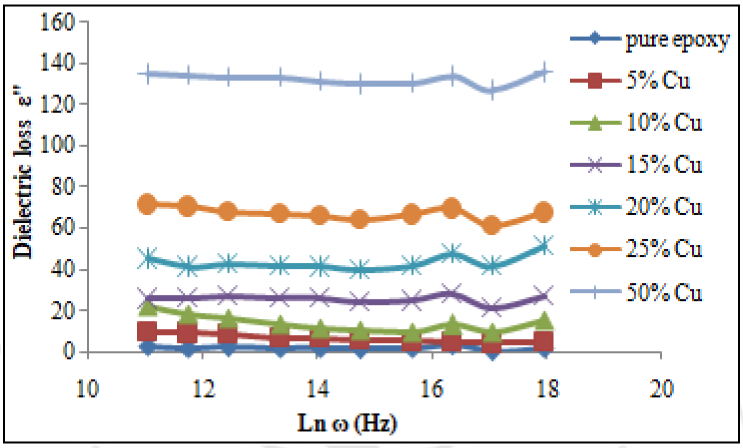

Figure 7 The variation of dielectric loss for epoxy/copper composites below high concentration value as function of frequency at 293K

A.C Electrical Properties for Epoxy/Graphene nanocomposites

The variation $\sigma_{a.c}(\omega)$ with frequency for the epoxy nanocomposites samples having graphene nano filler with different weight concentration at 393K are given in **Figure 8**. The figure shows that the $\sigma_{a.c}$ increases with increasing of the frequency. This behavior is in the agreement with equation1. The increasing of the conductivity with frequencies attributed to the charge carriers which travel by hopping process [17]. The figure also indicates that $\sigma_{a.c}(\omega)$ is increasing with increasing Gr wt.% content, a result which supports the suggestion of forms a continuous network inside the nanocomposites[18]. The relation $\sigma_{a.c}(\omega)\ \alpha\omega^{s}$, has been used to find the exponential factor (s) from the plotting of $Ln\sigma_{a.c}(\omega)$ verses $Ln\omega$. The exponent S for epoxy/graphene nanocomposite samples have been found to be equal to0.8763-0.7442 at 393K. **Table 2**shows that s is decreasing with increasing the Gr. wt.% concentration, this kind of explanation has been the agreement with other research [19].

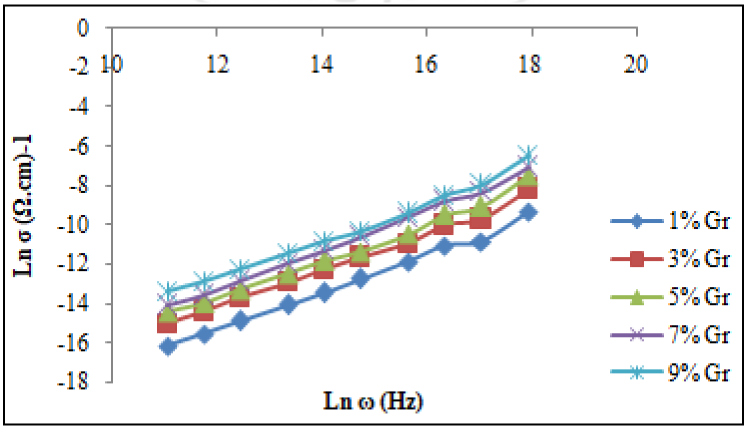

Figure 8 variation of A.C conductivity as a function of angular frequency for different additive concentration of epoxy/graphene nanocomposites

International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Table 2: list of exponent factor (S) for epoxy/graphene nanocomposite samples

Graphene wt.%	S
1% Gr	0.8763
3% Gr	0.8599
5% Gr	0.8142
7% Gr	0.7732
9% Gr	0.7442

The variation of $\sigma_{ac}(\omega)$ with increase temperature for pure epoxy and epoxy/copper composites heated at temperatures 293-373K for fixed frequency 100KHz plotted in **Figure 9**. The conductivity is increasing exponentially with increasing temperature, this behavior is according to Arrhenius equation.

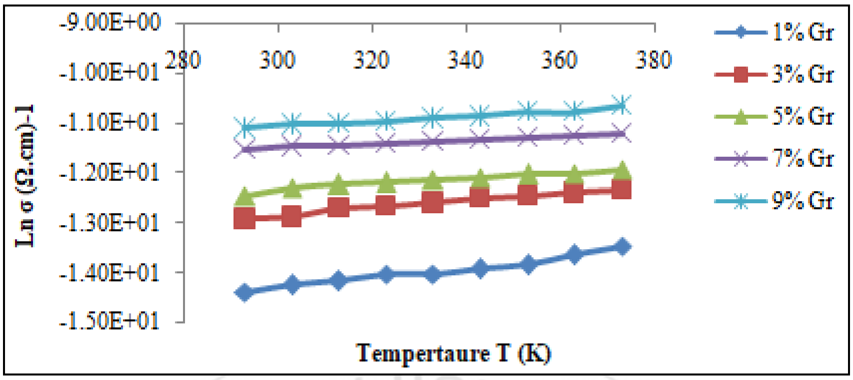

Figure 9: variation A.C conductivity with temperature for epoxy/graphene nanocomposites samples at 100 KHz

The variation of dielectric constant ε'with respect to frequency for epoxy/graphene nanocomposites with different concentrations at 293K is shown in **Figure 10**. The dielectric constant decreases with increasing the frequency. This is because of the nanocomposite will have several dipolar groups which are not interacting with the nanoparticles and so they would be free to orient with the applied electric field. That the interaction zone surrounding the nanoparticles is having a profound effect on the dielectric behavior of the nanocomposite. The nanoparticles appear to restrict end-chain or side-chain movement of the epoxy molecules [20] . The addition of filler to the polymer increases the dielectric constant of the prepared nanocomposite as the filler content increases. For 7% and 9% concentration the values of ε' are very high and also decreases slightly That could be caused by relaxation process between the filler particles and the polymer matrix [21].

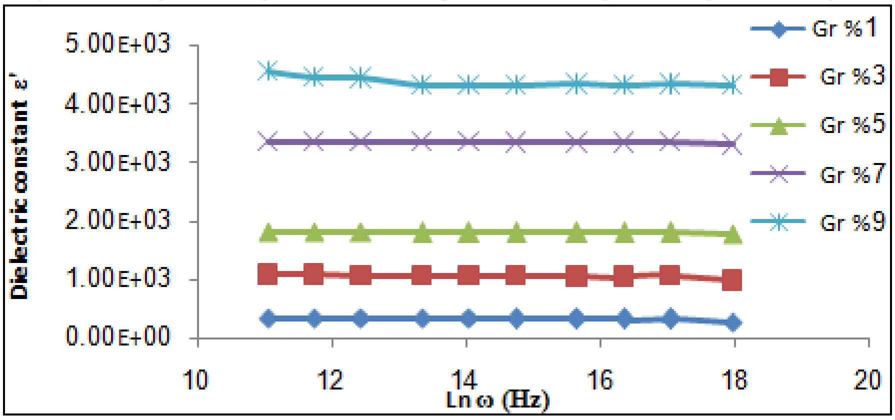

Figure 10 variation of the dielectric constant ε as a function of frequency at 293 K for epoxy/graphene nanocomposites

The variation of the dielectric loss, ε", of epoxy/graphene nanocomposites as function of frequency at 293K is shown in **Figure 11**. At 10KHz-1MHz, ε" decreases exponentially with increasing frequency up to a certain value then start to increases to reach a maximum. This attributed to interfacial relaxation process. In fact, epoxy resin networks present a lacunar structure with micro spherical voids produced during mixing process when air liberation is restricted due to the system viscosity [22].

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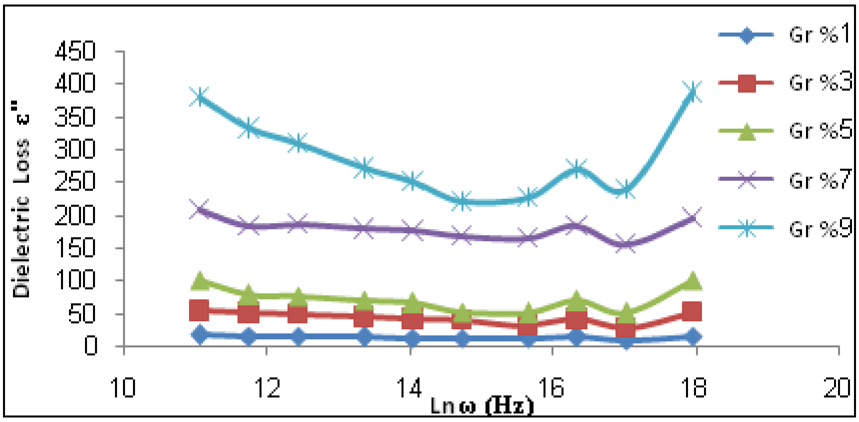

Figure 11 The variation of dielectric loss for epoxy/graphene nanocomposites as function of frequency

A.C Electrical Propertiesfor Epoxy/Copper/Graphene Hybrid Composites

AC electrical conductivity $\sigma_{a.c}(\omega)$ of epoxy/copper/graphene hybrid composites samples with different concentration were studied as a function of frequency at 293K, as shown in **Figure12**. The increase of $\sigma_{a.c}(\omega)$ with frequency as seen in this figure is in agreement with equation1.The A.C conductivity response to the applied field frequency is flat . The flat response of $\sigma_{a.c}(\omega)$ at these frequency ranges can be attributed to the fact that electrons will not have trouble traveling over large distances within these infinite clusters before it just hop to other clusters. At high filler content, the a mount of the interconnecting networks is increase ,the contact resistance is decreased, and hence a good electron conduction is achieved resulting in transformation of the polymer insulator to a conductive polymer [23]. The relation $\sigma_{a.c}(\omega)\alpha\omega^{s}$, has been used to find the exponential factor (s) from the plotting of $\mathrm{Ln}\sigma_{a.c}(\omega)$ verses Lnω. The exponent S for epoxy/copper/graphene hybrid samples have been clear up in **Table 3**.

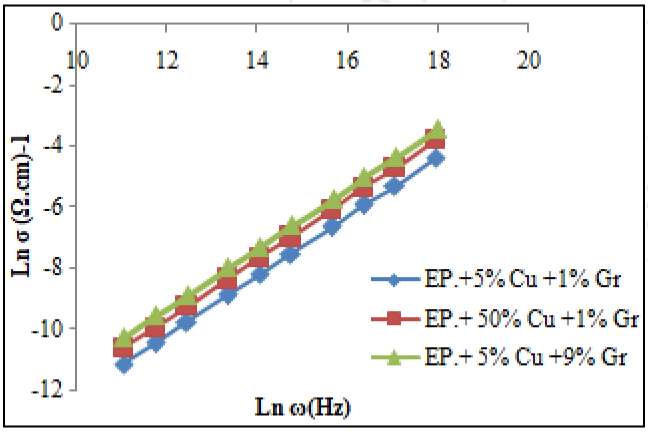

Figure 12: Variation of A.C conductivity as a function of angular frequency for different additive concentration of epoxy/copper/graphene hybrid

Table 3: A list of exponent factor (S) for epoxy/copper/graphene hybrid samples

Hybrid wt.%	S
EP.+5% Cu+1% Gr	0.9775
Ep.+50% Cu+1% Gr	1.0061
EP.+5%Cu+9% Gr	0.982

The variation of $\sigma_{ac}(\omega)$ with increase temperature for epoxy/cooper/graphene hybrid samples, heated at temperatures 293-373K for fixed frequency 100KHz plotted in **Figure 13**. The figure shows that the conductivity decreasing exponentially with increasing temperature, this behavior indicates metallic-type behavior [14].

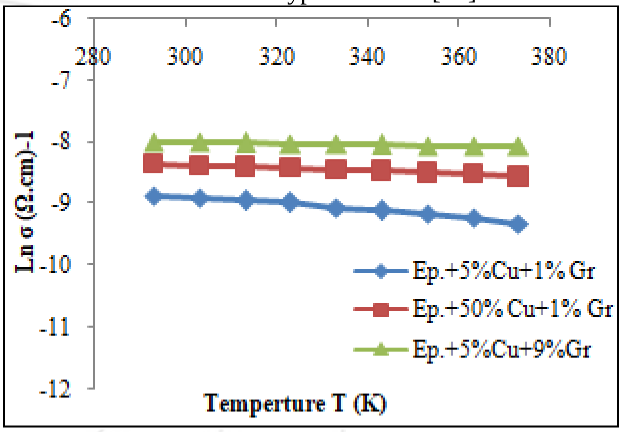

Figure 13: Variation A.C conductivity with temperature for epoxy/copper/graphene hybrid at 100 KHz

The variation of dielectric constant ε' of epoxy/copper/graphene hybrid with different concentrations as function of frequency at 293K is shown in **Figure 14**.The dielectric constant decreased with an increase the frequency. As the electric field frequency increases, the bigger dipolar groups find it difficult to orient at the same pace as the alternating field, so the contributions of these dipolar groups to the dielectric constant goes on reducing resulting in a continuously decreasing dielectric constant of the epoxy system at higher frequencies [24].

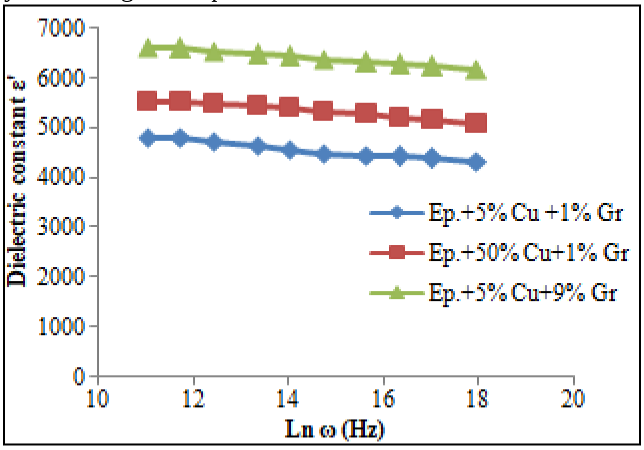

Figure 14: The variation of dielectric constant for epoxy/copper/graphene hybrid composites as function of frequency

The variation of the dielectric loss, ε", of epoxy/copper/graphene composites as function of frequency at 293K is shown in **Figure 15**. At 10KHz-1MHz, ε" decreases exponentially with increasing frequency up to a certain value then start to increases to reach a maximum. The relaxation peak has been masks by the high conductivity that the specimen acquired due to the formation of conductive network (cluster) at this amount of filler content. The composite material become conductive and the samples exhibit carrier dominated behaviors **.**

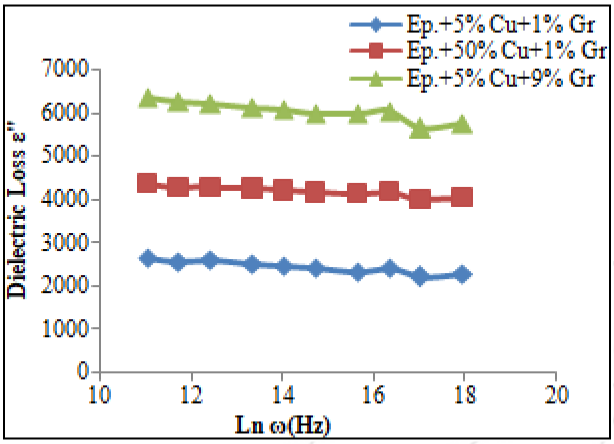

Figure 15: Variation of dielectric loss for epoxy/copper /graphene hybrid with different concentration as function of frequency at 293K

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